

STUDIES ON
MAGNETIC AND STRUCTURAL PROPERTIES OF SOME HEXAGONAL FERRITES

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BY
RISHAN KUMAR LAROLA, M.Sc.,
NATIONAL CHEMICAL LABORATORY, POONA-8.

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CHAPTER I

INTRODUCTION

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GENERAL INTRODUCTION

The ferrites of magnetoplumbite structure find extensive applications as permanent magnet materials. Their high coercivity imparts them special advantages and they are preferred over the traditional permanent magnets for many applications. The ease of their formation and the fact that they do not contain any nickel or cobalt, in contrast to most other permanent magnet materials, are of great economic importance as these two metals are expensive and at present difficult to obtain.

Although the first compound ($\text{PbO} \cdot 6\text{Fe}_2\text{O}_3$) of this series was reported by Aminoff in 1925, the real interest in these developed in the years following 1952 when Gorter and his collaborators in Holland and almost simultaneously Fahlenbrach and Heister in Germany reported the interesting magnetic properties of barium ferrite.

Attempts have since been made to find better materials, to improve the properties of known materials through substitutions and additions and to explain their magnetic properties. In spite of all these attempts very few compounds of this structure have so far been reported, out of which many are not even ferromagnetic, and only a few of the additions or substitutions reported are effective in improving their magnetic properties. The present investigations were, therefore, undertaken to synthesize new materials of this class, to optimise the conditions of their formation and to understand the physical aspects of the phenomenon involved.

Historical Introduction

Survey of the Crystal Structure of Magnetoplumbite:

In this section we shall give a brief description of the crystal structure of magnetoplumbite. (The mineral magnetoplumbite was first described by Aminoff¹ (1925), but its complete structure was determined by Adelskold² (1938) who found that the correct chemical formula of this compound was $\text{PbFe}_{12}\text{O}_{19}(\text{Pb}0.6\text{Fe}_2\text{O}_3)$ and not $3\text{Pb}0.5\text{Fe}_2\text{O}_3$ as suggested by Westgren³ (1937) or $\text{Pb}0.5\text{Fe}_2\text{O}_3$ as suggested by Blix⁴ (1937). A number of compounds are now known to be isomorphous with magnetoplumbite. The most important of these are $\text{BaFe}_{12}\text{O}_{19}$ and $\text{SrFe}_{12}\text{O}_{19}$. The unit cell is hexagonal with $c \approx 23 \text{ \AA}$ and $a \approx 5.8 \text{ \AA}$. The space group is $D_{6h}^4 [P6_3/mmc]$ and there are two molecules of $\text{AB}_{12}\text{O}_{19}$ in the unit cell, where A is Ba^{2+} , Sr^{2+} , Pb^{2+} , etc. and B is Fe^{3+} and Al^{3+}).

The 2A ions are located in (d) $1/3 \ 2/3 \ 3/4$;
 $2/3 \ 1/3 \ 1/4$

$2B_I$ in (a) 000 ; $00\frac{1}{2}$

$2B_{II}$ in (b) $00\frac{1}{4}$; $00\frac{3}{4}$

$4B_{III}$ in (f) $1/3 \ 2/3 \ z$; $2/3 \ 1/3 \ \bar{z}$; $2/3 \ 1/3$
 $1/2 + z$; $1/3 \ 2/3 \ 1/2 - z$; with
 $z_{B_{III}} = 0.028$ when $A = \text{Pb}^{2+}$

$4B_{IV}$ in (f) $z_{B_{IV}} = 0.189$

$12B_V$ in (k) $x \ 2x \ z$; $2\bar{x} \ \bar{x} \ z$; $x \ \bar{x} \ z$; $\bar{x} \ 2\bar{x} \ \frac{1}{2}+z$;
 $2x \ x \ \frac{1}{2}+z$; $\bar{x} \ x \ \frac{1}{2}+z$; $x \ 2\bar{x} \ \bar{z}$;
 $2x \ x \ \bar{z}$; $\bar{x} \ x \ \bar{z}$; $x \ 2x \ \frac{1}{2}-z$;
 $2\bar{x} \ \bar{x} \ \frac{1}{2}-z$; $x \ \bar{x} \ \frac{1}{2}-z$ with $x_{B_{IV}} = 0.167$
and $z_{B_V} = -0.108$

... 3.

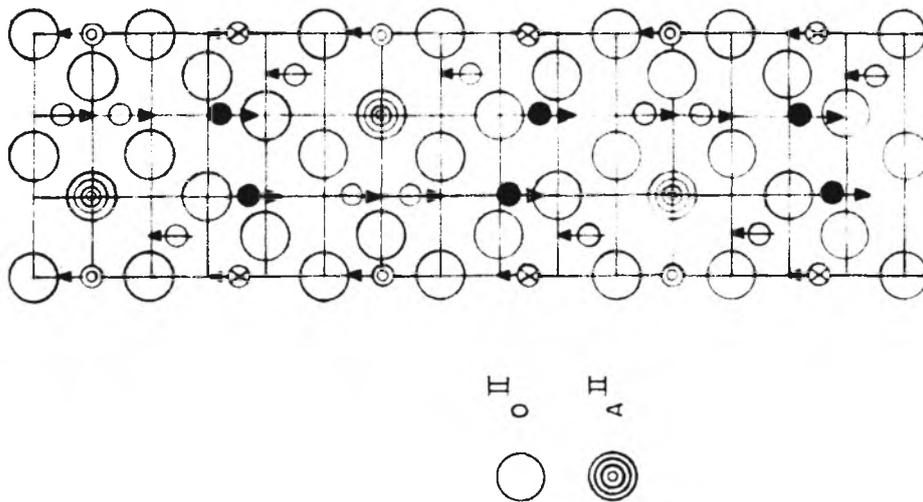


FIG. I (A) CROSS SECTION OF THE MAGNETOPLUMBITE STRUCTURE WITH THE C AXIS VERTICAL. THE ARROWS INDICATE THE SPIN ORIENTATIONS.

- OCTAHEDRAL
- ⊙ TRIGONAL BIPYRAMID } Fe^{3+}
- TETRAHEDRAL

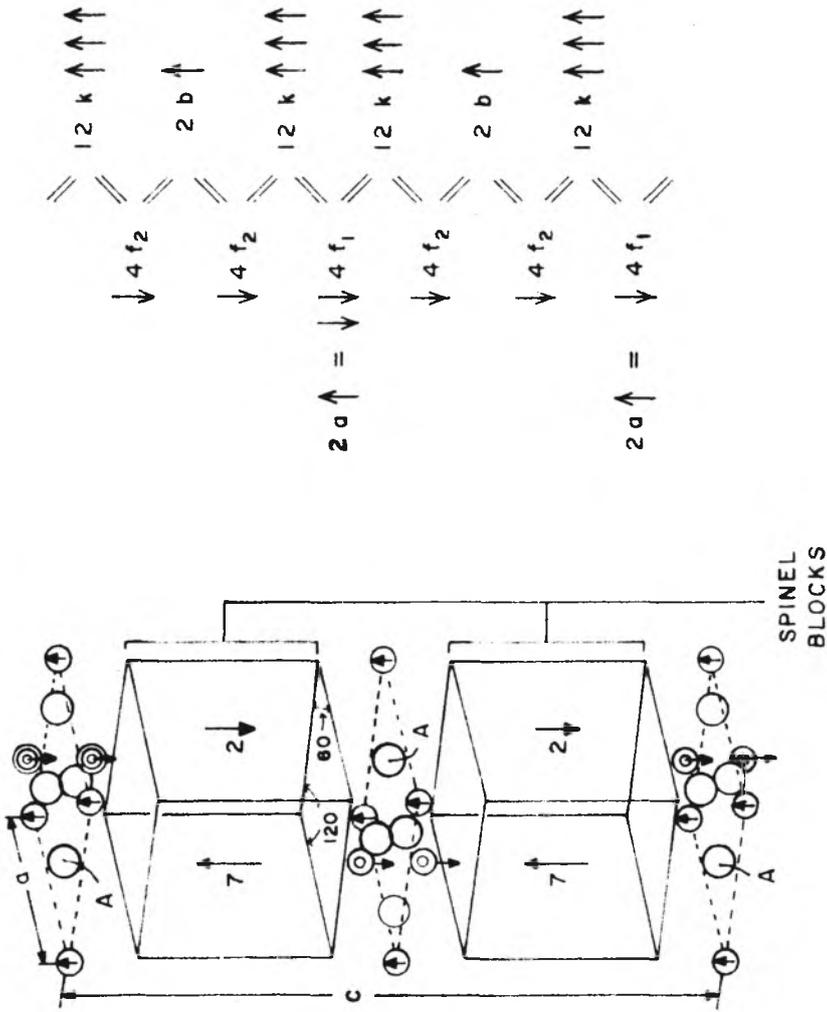


FIG. I (B) LARGE CIRCLES INDICATE OXYGEN IONS OR 'A' IONS AND THE SMALL CIRCLES REPRESENT Fe^{3+} IONS. THE POSITIONS OF THE IONS INSIDE THE SPINEL BLOCKS ARE NOT SHOWN.

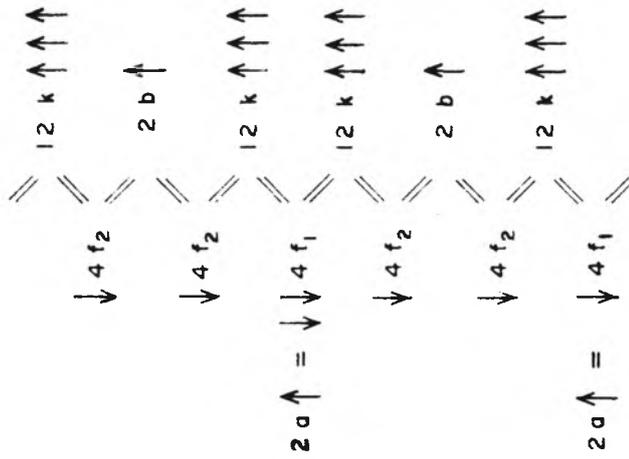


FIG. I (C) SUPEREXCHANGE INTERACTION CHAIN. THE SPIN DIRECTIONS AT VARIOUS SITES ARE SHOWN BY ARROWS.

40_{I} in (e) $00z$; $00\bar{z}$; $00\frac{1}{2}+z$; $00\frac{1}{2}-z$
 with $z_{0_{\text{I}}} = 0.150$

40_{II} in (f) with $z_{0_{\text{II}}} = -0.050$

60_{III} in (h) x $2x$ $\frac{1}{4}$; $2\bar{x}$ \bar{x} $\frac{1}{4}$; x \bar{x} $\frac{1}{4}$; \bar{x} $2\bar{x}$ $\frac{3}{4}$;
 $2x$ x $\frac{3}{4}$; \bar{x} x $\frac{3}{4}$

120_{IV} in (k) with $x_{0_{\text{IV}}} = 0.167$ and $z_{0_{\text{IV}}} = 0.050$

120_{V} in (k) with $x_{0_{\text{V}}} = 0.500$ and $z_{0_{\text{V}}} = 0.150$.

(The hexagonal elementary unit cell consists of 10 oxygen layers. A schematic representation is given in figure 1(a). In the unit cell there are two layers each containing three oxygen and one A ion. The A ions form a part of the close-packed oxygen framework, and in fact these just replace one oxygen ion in every fifth oxygen layer. Each A ion is surrounded by twelve oxygen ions, six of them in the same (0001) layer and three above and three below.

The B ions (Fe^{3+} or Al^{3+}) are located in the interstices formed in the close-packed structure of A and oxygen ions. There are three types of coordinations for the B ions.

(1) Octahedral, where each B ion is surrounded by six oxygen ions.

(2) Tetrahedral, where it is surrounded by four oxygen ions.

(3) Trigonal bipyramid, where it is surrounded by five oxygen ions, three in the same plane, one above and one below. This site is situated in the plane containing A ions.

This type of coordination is not present in spinels or any commonly known oxides. From considerations of the size of the B ion and the position of the neighbouring ions it appears that the three oxygen ions must be displaced outwards. The B ions at the octahedrally surrounded sites belong to the three different crystallographic positions, so that together with the tetrahedral and the trigonal bipyramid sites there are five non-equivalent crystallographic positions available for them.

The magnetoplumbite structure can also be visualized as consisting of spinel blocks separated by layers of A, B and oxygen ions as shown in the figure 1(b). In the spinel region four layers of cubic close-packed oxygen ions lie in infinite planes normal to the c axis, and the B ions occupy positions equivalent to those in the spinel structure. The A -- B -- O layer is a single plane of oxygen ions in which one of the four oxygen ions is replaced by A ions in such a way that triangles of oxygen ions are formed half of which contain the B ions.)

Magnetic Properties of Compounds of Magnetoplumbite Structure:

In this section we give a historical survey of the studies made in regard to the magnetic properties of the compounds of this class. These compounds can be classified under two heads for the description of their magnetic properties:

(1) Those which do not contain any magnetic ions
e.g. $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$, $\text{SrO} \cdot 6\text{Al}_2\text{O}_3$ and $\text{BaO} \cdot 6\text{Al}_2\text{O}_3$.

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(2) Those which contain magnetic ions e.g. $\text{SrO} \cdot 6\text{Fe}_2\text{O}_3$, $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$, $\text{PbO} \cdot 6\text{Fe}_2\text{O}_3$, etc. These compounds are ferrimagnetic and in what follows we will be interested in this class of compounds only.

Saturation Magnetization

The magnetic properties of $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ were first studied systematically by Went, Rathenau, Gorter and van Oosterhout⁵ (1951-52). As the compound exhibits a large magnetic anisotropy, no measurement of saturation magnetization was made in the hard direction of magnetization. The measurements of saturation magnetization along easy direction were made on a small single crystal by the method described by Rathenau and Snoek⁶ (1946).

The value at 0°K obtained by extrapolation corresponds to 44 Bohr magneton per unit cell. The authors arrived at a theoretical value of 40 Bohr magneton with the aid of a "Rule of Thumb" method⁷ based on Anderson's theory of superexchange interaction. The underlying idea was that the strength of interaction increased with the angle $\text{Me} - \text{O} - \text{Me}$ from a minimum for 90° to a maximum for 180° and decreased with the increase in $\text{Me} - \text{O}$ distance. The relative directions of the magnetic moments of different ions could be found by assigning an arbitrary direction to any arbitrary ion and by placing anti-parallel to it the moments of those surrounding ions for which the angle $\text{Me} - \text{O} - \text{Me}$ was largest and for which the distance $\text{Me} - \text{O}$ was about 2.5 \AA . The agreement between the experimental

and the calculated value was satisfactory considering the uncertainties involved in extrapolation and the crude assumptions in the rule of thumb.

Henry⁸ (1958) determined the magnetization of polycrystalline barium ferrite sample in the form of a rod 1.4 cm long. Measurements were made by applying fields upto 60,000 oersted at 295^o, 130^o, 4.2^o and 1.3^oK by moving the sample from the centre of one coil to the centre of another coil, the colinear coils being wound in series opposition with each other and in series with a calibrated ballistic galvanometer whose deflection was proportional to the magnetic moment of the sample. He found that the domain alignment was complete at about 30 KOe. The saturation magnetisation showed substantial difference from the values observed by Went et al.⁵ It was interesting to find that at low temperatures, the magnetization became independent of temperature, as to be expected from Nernst theorem, according to which the slope of magnetization vs temperature curve should tend to zero as temperature approaches absolute zero. The value of saturation moment at 0^oK came close to 40 Bohr magneton.

Bozorth and Kramers⁹ (1959) studied the saturation magnetization of oriented polycrystalline samples of $\text{Pb}_{0.6}\text{Fe}_2\text{O}_3$. The extrapolated value of saturation magnetic moment at $T = 0^\circ\text{K}$ and $H \rightarrow \infty$ was 38 Bohr magneton per unit cell. It was claimed that the uncertainty in this value was only of the order of a few per cent. Pauthenet and Guy Rimet¹⁰ (1959) measured the

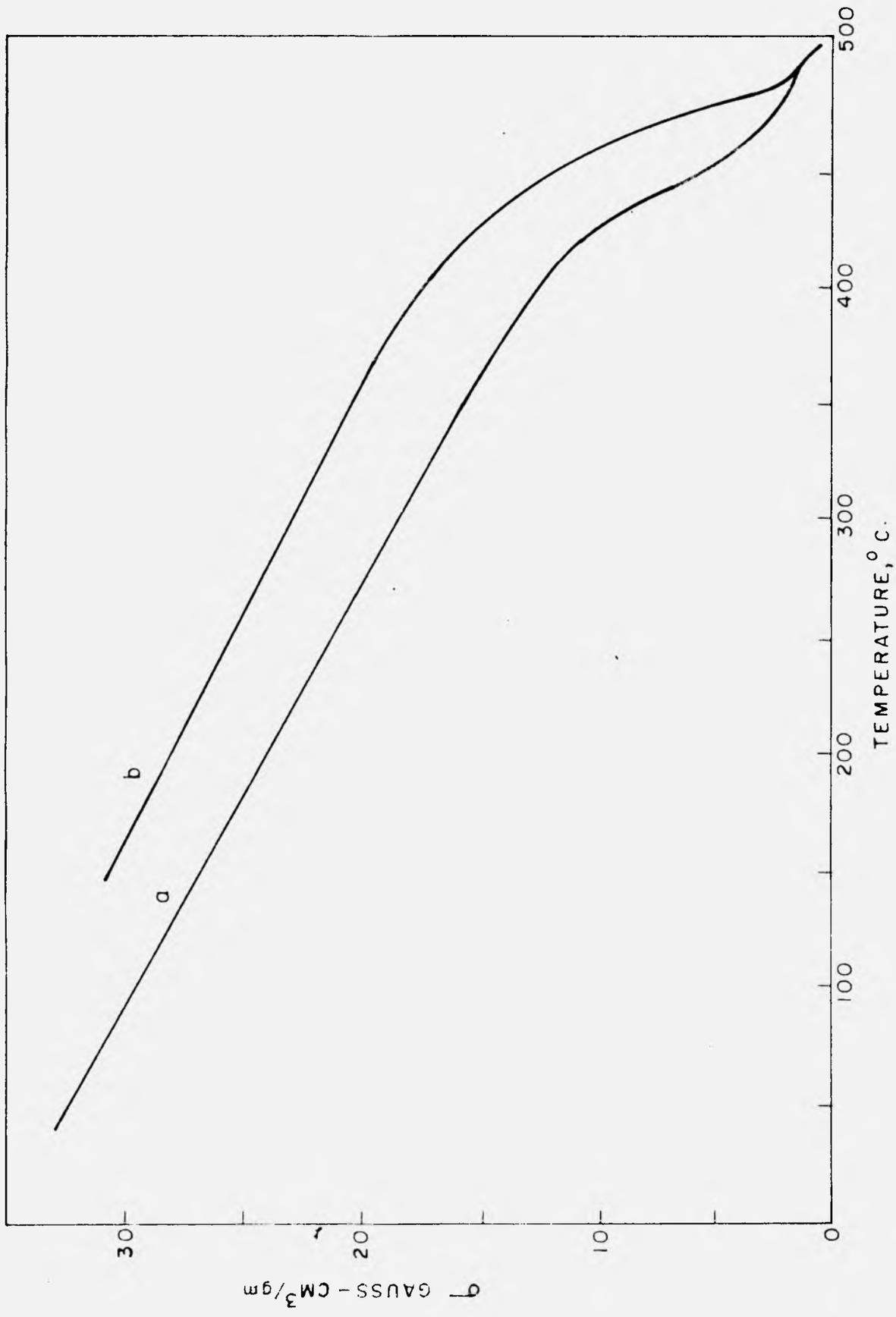


Fig. 2. MAGNETIZATION VS. TEMPERATURE FOR (a) BARIUM FERRITE AND (b) SODIUM LANTHANUM FERRITE. (POLYCRYSTALLINE SAMPLES)

variation of magnetization of single crystals of $\text{Pb}_{0.5}\text{Fe}_2\text{O}_3$ by applying fields upto 30,000 oersted in a direction perpendicular to the preferred direction of magnetization. The measurements were made at temperatures from 2.3° to 748°K . It was found that the fields of the order of 14,000 oersted completely aligned all the domains in the direction of the applied field. Magnetization was independent of temperature at low temperatures and the extrapolated value of saturation moment at 0°K was found to be 37.2 ± 0.4 Bohr magneton per unit cell. This was 7% lower than the theoretical value of 40 Bohr magneton.

Summergrad and Banks¹¹ (1957) measured the saturation magnetization of single crystals of sodium lanthanum ferrite ($\text{Na}_{\frac{1}{2}}\text{La}_{\frac{1}{2}}\text{Fe}_{12}\text{O}_{19}$). Measurements were made in the easy direction of magnetization by a modification of Rathenau and Snoek⁶ method down to 133°K . Results are plotted in figure 2. An extrapolation to 0°K of the straight line obtained gave a value of ≈ 45 Bohr magneton per unit cell. However, if Nernst theorem was taken into account, the value of saturation moment at 0°K changed to 43 Bohr magneton, which was approximately the same as that obtained by Went⁵ et al. for barium ferrite.

Frie, Schieber and Shtrikman¹² (1960) studied the saturation moment of the compound $\text{BaF}_{\frac{1}{2}}.2\text{FeO}.5\text{Fe}_2\text{O}_3$ in which four oxygen ions per unit cell of barium ferrite were replaced by F^{-1} ions. The value of saturation magnetic moment of this compound at room temperature was found to be 72 c.g.s. units/gm as compared to 67 c.g.s units/ gm

for $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$. This increase was explained by assuming that the Fe^{2+} ions occupied the $4f_2$ sites near the Ba^{2+} ions.

Heimke¹³ (1960) investigated the temperature dependence of saturation magnetization of ferrites of magnetoplumbite structure. An approximately linear curve was obtained. It was suggested that several spin arrangements besides the one given by Gorter were possible, with lower and higher values of magnetic moments per unit cell. If with increasing temperature transitions took place from one arrangement to the other, the observed linear behaviour of the magnetization vs temperature curve could be explained. It was thought that this would become similar to Langevin or one of the Neel type curves, if the interaction chain could be made unique by suppressing the rivalling interactions. This was attempted by replacing the Fe^{3+} ions of the octahedral sites on the either side of the oxygen layer containing the Ba^{2+} ions ($4f_2$ sites) by nonmagnetic ions. Under controlled conditions one out of the two $4f_2$ Fe^{3+} ions per unit cell was replaced by a Ti^{3+} ion, carrying one Bohr magneton. For this compound the magnetization vs temperature curve was altered below 0°C and its Curie temperature was lowered by about 80°C . The still remaining linear slope between 0°C and Curie temperature was supposed to be due to the fact that only one out of the two $4f_2$ Fe^{3+} ions had been replaced and hence the interaction chain was not yet unique.

Aharoni and Schieber¹⁴ (1961) made measurements of the magnetic moment on oriented samples of the ferrite $\text{La Fe}_{12}\text{O}_{19}$ ($\text{La}^{3+}\text{Fe}^{2+}\text{Fe}_{11}^{3+}\text{O}_{19}$) from liquid air temperature to its Curie point at 695°K in a field of 12,000 Oersted. The saturation magnetic moment at the lowest temperature was found to be 17.5 Bohr magneton as compared to 19 Bohr magneton for $\text{BaFe}_{12}\text{O}_{19}$ per formula weight. Curie temperature of the lanthanum compound was also lower by 30°C than that of the barium compound. The difference in the saturation magnetization of the two compounds had been explained by assuming that the 12 k sites were occupied by Fe^{2+} ions as nearest neighbours of the La^{3+} ions in the unit cell. This led to a decrease in the total magnetic moment. The lower value of Curie point was attributed to smaller exchange interaction with the divalent ion.

It will be clear from the above historical survey that the linear variation of saturation magnetization with temperature has not been yet explained satisfactorily. The main difficulty arises due to the presence of a large number of interactions between five different sub-lattices. Also it has not been yet conclusively established that Neel type of coupling with Gorter's arrangement of spins is present in these compounds. The agreement between the experimental values of saturation magnetic moment and that obtained from one Neel model can, at the best, be said to offer only an indirect basis for the above model.

Crystal Anisotropy

It is usually found that in a ferromagnetic specimen, the magnetization vector is bound to a certain preferred direction, known as the easy direction of magnetization and a finite field is required to turn it away from that direction. The anisotropy energy is defined by the value of the magnetization energy $\int H dM$ required to rotate the magnetization vector from an easy direction to a difficult direction. This energy for a hexagonal crystal is given by

$$F_k = K_1 \sin^2 \theta + K_2 \sin^4 \theta + K_3 \sin^6 \theta \cos 6(\phi + \psi)$$

where θ and ϕ are the usual polar angles with 0001 axis taken as z direction and ψ is the phase angle and can be made zero for suitably chosen axes. K's are the various anisotropy constants.

The experimental determination of these constants for barium ferrite was first carried out by Went⁵ et al. (1952). Since single crystals of this substance were not available, small crystallites obtained from polycrystalline material were oriented in a magnetic field and fixed on a glass plate in such a way that the hexagonal axis (the easy direction) was perpendicular to the surface of glass plate. The magnetization (BH) curves were then obtained with the field applied along the easy and the hard directions. The observed linear rise of magnetization with magnetic field for the hard direction showed that at room temperature all the higher order anisotropy constants K_2 , K_3 , etc. were very small compared to K_1 which was found to be

3×10^6 erg/cm³. By another method in which the crystal was allowed to make torsional oscillations in a strong field in such a way that the preferred direction oscillated in a plane containing the direction of magnetic field, the value of K was obtained as 3.3×10^6 erg/cm³ from the period of oscillation at $H=30K_0$ (Casimir et al.¹⁵, 1959).

Villers¹⁶ (1959) studied the magnetization of a single crystal of Pb_{0.6}Fe₂O₃ and evaluated various anisotropy constants, using the following expression for the anisotropy energy.

$$F_k = K_0 + K_1 \sin^2 \theta + K_2 \sin^4 \theta + K_3 \sin^6 \theta + K_4 \sin^8 \theta$$

where K_0 is ≈ 0 . A curve of F_k as a function of θ was drawn, the value of F_k for a particular angle θ was obtained by measuring the area between the magnetization curve for the easy direction and one for the angle in question. The following values of anisotropy constants were obtained at the room temperature.

$$K_1 = 2.2 \times 10^6; K_2 = -1.4 \times 10^6; K_3 = 1.6 \times 10^6;$$

$$K_4 = 1.0 \times 10^5.$$

Later, Pauthenet and Rimet¹⁰ (1959) studied the temperature variation of anisotropy constants for a single crystal of lead ferrite from 2.3°K to 748°K by plotting the magnetization curves in easy and hard directions by the method of Sucksmith and Thompson¹⁷ (1954). They used $F_k = K_1 \sin^2 \theta + K_2 \sin^4 \theta$ as the expression for the magnetocrystalline anisotropy

energy and obtained the values of K_1 and K_2 at different temperatures. Their K_2 value showed significant difference from that obtained by Villers¹⁶.

Summergrad and Banks¹¹ (1957) determined the anisotropy constants of the compound $\text{Na}_{\frac{1}{2}}\text{La}_{\frac{1}{2}}\text{Fe}_{12}\text{O}_{19}$ from the equation $F_k = K\sin^2\theta$. Measurements were made at room temperature on a single crystal by measuring the magnetization at various field strengths along the easy direction of magnetization and in a direction at right angles to it. The magnetization was measured with fields insufficient to saturate the samples and then the results were extrapolated to saturation. The value obtained for K at room temperature is 3×10^6 erg/cm³, which is exactly the same as for barium ferrite as determined by Went⁵ et al.

Smit¹⁵ (1959) had emphasized that although dipole-dipole interaction might give rise to a uniaxial anisotropy it gave a wrong order of magnitude for K in the case of barium ferrite. Thus this anisotropy presumably arose from spin orbit coupling in an excited state. Later he showed²⁴ that this interaction could possibly be attributed to the Fe^{3+} ion located at the trigonal bipyramid site, a site not present in the spinel structure. The small distance between Fe^{3+} ion and O^{2-} ion indicated an appreciable overlap of their wave functions. It was assumed that either Fe^{3+} ions went to the excited state $3d4s$ or they were partially present in Fe^{2+} configuration, i.e. one of the electrons of the oxygen ion was transferred to the metal

ion. He showed that

$$E_{S.O.} = - \epsilon \left[\frac{(4\lambda \cos \theta)^2}{\Delta E} + \frac{(4\lambda \cos \theta)^4}{(\Delta E)^3} \right] + \dots$$

where ϵ represented the total relative superposition of the two states $\psi_{\pm 2}$ and ΔE was the energy difference between the ground and the excited state. Assuming $\Delta E = 4000 \text{ cm}^{-1}$ and putting the experimental values of anisotropy energy and λ in the above equation, he got $\epsilon = 0.2$ and $K_2/K_1 = 0.01$.

Domains

In order to lower its demagnetizing energy, a ferromagnetic body divides ^{itself} into a number of domains, in which the magnetization vectors are parallel to the preferred directions, so that the demagnetizing field and hence the energy are as small as possible. In compounds of magnetoplumbite structure $A\text{Fe}_{12}\text{O}_{19}$ ($A = \text{Ba}, \text{Sr}$ or Pb) the c axis is the only easy direction of magnetization and hence the domains moments are tied along this direction. Thus mostly there are 180° domains in the above compounds. In particles of linear dimensions less than 10^{-6} cm domain boundaries cannot form (as the particles will be single domained) and the usual mechanism of magnetization by domain boundary displacement cannot occur. Instead any change of magnetization must be due to rotational processes. Such rotations are opposed by the magnetocrystalline anisotropy which is very high in these compounds. Thus if these compounds are ground

to a very fine particle size in a ball mill for a sufficient time, they will have very high coercivities.

Sixtus, Koromenbergand and Tenzer¹⁸ (1956) found that on application of magnetic field to barium ferrite the wall movement took place in samples with particle thickness down to 10^{-3} cm. For samples less than 5×10^{-4} the reversal of the magnetization took place through rotation process and both the above processes were effective in the particles of intermediate sizes.

Domain patterns of barium ferrite were also obtained by Pearson¹⁹ (1957), Bates²⁰ (1957) and Paulus²¹ (1957) using Bitter technique. Kooy²² (1958) studied the domains by means of Faraday effect. Craik and Griffiths²³ (1959) studied Bitter patterns of barium ferrite by a modified electron microscope technique. The observed wall thickness was $\approx 1 \times 10^{-5}$ cm, which agreed well with the calculated value of 0.7×10^{-5} cm by Smit and Wijn²⁴ (1959). The patterns showed a typical uniaxial configuration of 180° domains with reverse spikes. On the basal plane containing no easy direction of magnetization, a system of reverse spike terminations of variable configuration was observed.

More recently Kojima and Kimiyoshi²⁵ (1961) studied the magnetic domains of barium ferrite, after magnetizing it at various fields by Faraday effect on single crystal platelets prepared by Brixner method²⁶ (1959). They obtained Labyrinth pattern for demagnetized crystals, comparatively parallel

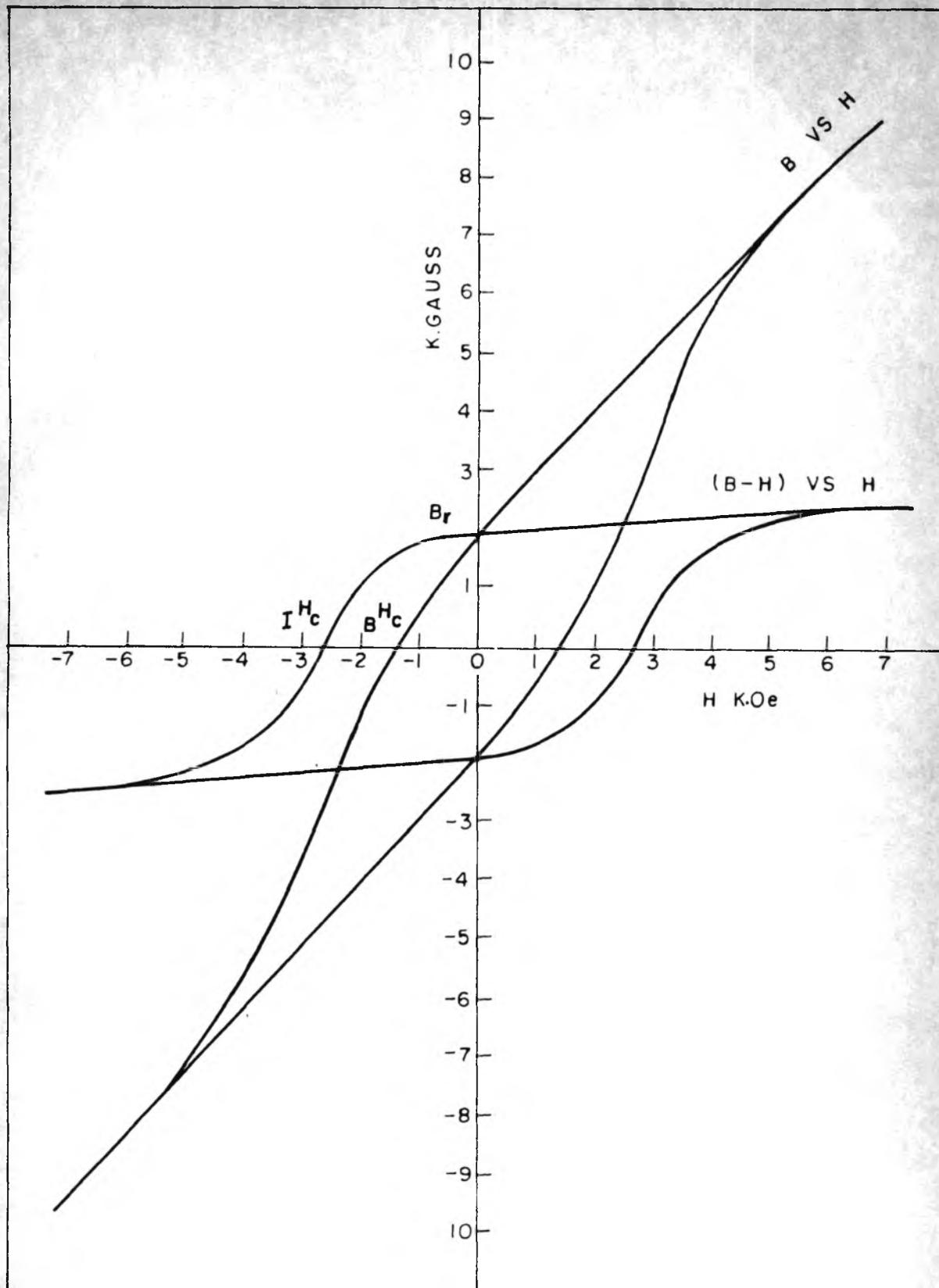


Fig. 3. HYSTERESIS LOOP OF A SAMPLE OF POTASSIUM LANTHANUM FERRITE AT ROOM TEMPERATURE

domains after magnetization at high fields, and cylindrical domains, which were stable at higher fields, trapped near crystal imperfections. Calculated thickness of the platelets from the domain width was in reasonable agreement with the value measured by microscope.

Permanent Magnet Properties:

The properties of a permanent magnet material can best be described with the aid of the magnetization curve (B against H) as shown in figure 3. The point B_r is known as remanent magnetization or remanence and H_c is the coercive force, i.e. the negative field required to make the induction or magnetization in the sample zero. One of the important properties of a permanent magnet is its high coercivity. In hexagonal ferrites this high coercivity is due to the high uniaxial anisotropy, hence these are useful as permanent magnet materials. Whenever a permanent magnet forms a part of a circuit in which there is an air gap, the magnet is subjected to a demagnetising field. It is, therefore, the second quadrant of the hysteresis loop that is of interest in studying permanent magnet materials. The maximum value of the product of B and H on this part of the curve, known as $(BH)_{\max}$ product is taken as a figure of merit of a permanent magnet. It is possible to operate at this maximum (B.H) point by properly arranging the magnet dimensions.

The first attempt to develop permanent magnets from such ferrites was made by Went et al⁵ (1952). The values of B_r , B_{H_c} and $(BH)_{max}$ obtained by them are 2000 gauss, 1500 oersted and 0.8×10^6 gauss oersted respectively for the sample sintered at 1300°C . The value of $(BH)_{max}$ is quite low as compared to 5×10^6 gauss oersted for Ticonal G. They also studied the temperature variation of coercive force of barium ferrite and found that it increased with temperature upto 250°C , after which it showed a steep fall upto the Curie temperature at 450°C . This type of variation in the coercive force was believed to be due to (i) decrease in the number of stable domain walls at high temperatures and (ii) increase in the mobility of these walls with rise in temperature. The two have opposing influence on the coercivity, in the lower temperature range the first predominates so the coercive force increases. At temperatures above 250°C the second predominates, leading to a decrease in the coercive force.

Sixtus et al¹⁸ (1956) also studied the variation of coercivity with temperature in the range -190° to 450°C on various oriented and unoriented samples of barium ferrite. All these showed a maxima at approximately 300°C . They compared the experimental curve with the theoretical curve obtained from the equation, $I_{H_c} = 0.48 (2k/I_s - 4 \sqrt{I_s})$ (Hunter²⁷). The agreement between the observed and theoretical curve was made very good by making certain assumptions such as (i) the grain radius r in the sample was equal to the critical radius r_0 at

300°C, and (ii) r_0 varied with temperature as $K^{\frac{1}{2}}/I_s$.

Quite independently of Dutch workers, a very similar programme by Fahlenbrach and others^{28,29} (1953-54) in Germany led to the development of sintered barium ferrite magnets. The magnetic properties were improved by applying magnetic field during sintering. Maximum coercive force obtained was 2000 oersted. However, it was reported that the magnetic properties of these substances were sensitive to temperature changes and hence inferior to Alnico type permanent magnets.

An improvement in the material soon followed from Philips Research Laboratory^{30,31} (1954). It was found out theoretically that for isotropic samples of barium ferrite, the remanence would be 2000 gauss i.e. about one half of the saturation magnetization. On the other hand, the value of remanence would be 4000 gauss and $(BH)_{\max} = 4.4 \times 10^6$ gauss oersted, i.e. the same as of a single crystal if all the crystallites of the material were aligned parallel by the application of a magnetic field during the pressing of reacted powders. An attempt to make oriented magnets was made and Ferroxdure I & II were obtained with properties given below:

		FERROXDURE	
		I	II
Remanence		3700 gauss	3000 gauss
$I H_c$		1200 oersted	2100 oersted
$(BH)_{\max}$		2.8×10^6 gauss oersted	2.1×10^6 gauss oersted
Working point	B	2600 gauss	1700 gauss
"	H	1000 oersted	1250 oersted
Curie temperature		450°C.	450°C.

Gordon³² (1956) investigated the preparation and properties of barium ferrite magnets in detail. The demagnetization curves were studied for three different samples prepared under different conditions. The first curve was obtained from a sample where the raw material was mixed, pressed and fired. The curve was a straight line with fullness factor $K = 0.25$ where $K = (BH)_{\max}/B_r \cdot H_c$. This was taken to indicate that there was an extreme randomness of grains. Remanence was low as the reaction took place only during firing and coercive force was limited mainly by the particle size of the component oxides. The second curve was obtained from samples prepared by firing the oxide mixtures, grinding the product, pressing it and finally sintering it. The fullness factor was greater than 0.25 which was taken to indicate that there was some orientation, presumably produced during the pressing before final sintering. The crystals have a plate like habit and hence they tend to get oriented under pressure. The third curve was obtained from a sample which was prepared as in curve second, except that magnetic field was applied before and during pressing. The remanence and $(BH)_{\max}$ showed a considerable improvement. The coercive force, on the other hand, showed some decrease. This was attributed to the size of the grain which was kept large to achieve better orientation.

Kubola and Okazuki³³ (1955) found that when a reverse field was applied to a magnetized polycrystalline rod of barium ferrite having a temperature gradient of 12-40°C per cm., those

parts which were either above or below 300°C were demagnetized first, showing that the coercive force was maximum at this temperature. This is more or less in agreement with the observations of Went et al⁵ (1952).

Suchet³⁴ (1956) investigated the formation of barium ferrite from barium carbonate and ferric oxide with special reference to the influence of sintering temperature and time and the effect of additives on density, grain size and magnetic properties of the products. It was suggested that at 700 - 800°C BaFeO₄ was first formed, which reacted with more Fe₂O₃ leading to the formation of BaFe₁₂O₁₉ at temperatures above 820°C. He developed an empirical function $f(t,T)$ which gave the relation between magnetic properties and sintering temperature T and time t. Above 1200°C the increase in t or T caused an enlargement of the particle size and led to a rapid deterioration of magnetic properties.

Stuijts³⁵ (1956) studied the sintering of barium ferrite magnets. Products with high apparent density and consisting of particles with a diameter below the critical value (1 μ) gave the best magnetic properties. High densities, as much as 95% of the ideal value were obtained by using non-stoichiometric compositions in which rapid transportation of the material during sintering was possible due to vacancies existing in the lattice. The crystallites could be kept small by using a high rate of heating and keeping the sample at the sintering temperature only for a short time. In this case the mechanism of sintering was believed to be plastic flow rather

than diffusion and gave high densities without crystal growth. It was also observed that the coercivity and more dramatically the remanence decreased with strong crystal growth. This observation is in agreement with that of Suchet³⁴ (1956).

The decrease in remanence does not appear to be due to the formation of a small amount of nonmagnetic phase during the sintering at high temperatures in view of the recent phase study of BaO - Fe₂O₃ system by Yasumase Goto and Toshio Takada³⁶ (1960). The hexagonal magnetoplumbite phase is stable in the composition range BaO.6Fe₂O₃ to BaO.5Fe₂O₃ at all temperatures upto its melting point. Also these authors did not observe any considerable loss of oxygen when the sample was heated in air at temperatures below the melting point. However, their technique would not be sensitive enough to detect small loss of oxygen and it appears that this may have a large effect on the magnetic properties of the samples because of the role of oxygen ions in superexchange interaction. The decrease in remanence on sintering at high temperatures may therefore be due to the loss of oxygen.

Sixtus et al¹⁸ (1956) studied the effect of particle size, packing density and sintering temperature on the intrinsic coercivity of oriented and unoriented barium ferrite samples. ΓH_c values were found to increase with the milling time in accordance with the predictions of the fine particle theory, while there was a decrease in its value when samples were oriented.

Gottardi³⁷ (1956) prepared barium ferrite magnets by precipitation of ferric and barium chloride solution in the ratio 6:1 by a solution of sodium hydroxide. The temperature and the pH of precipitation had a great effect on the magnetic properties of the resulting products. The optimum values were the temperature at boiling point and pH equal to 12.5. The precipitate was heated at 900°C for half an hour in an atmosphere of oxygen, pressed at 1000 Kgm/sq.cm. pressure and sintered at 1250°C.

Stablein³⁸ (1956) found that remanence, coercivity and $(BH)_{\max}$ of compressed and sintered $Ba_{0.6}Fe_2O_3$ and $Pb_{0.4}Fe_2O_3 \cdot SiO_2$ were better parallel to the direction of pressing than perpendicular to it. The higher values of magnetic properties in the direction of pressing were believed to be due to laminar shape of the powder particles which aligned themselves to some extent during pressing operation and led to "compression anisotropy" in the material.

Heimke³⁹ (1958) observed an anomaly in the magnetic properties of $Ba_{0.6}Fe_2O_3$ to which $CaO \cdot SiO_2$ was added to enhance the reactivity during the formation of the compound. On sintering the samples from 1120 to 1220°C it was found that the saturation magnetization and the remanence first increased with sintering temperature, then decreased to a minimum at 1180°C and finally increased again. No such anomaly was found in a sample in which equal amounts of $CaCO_3$ and SiO_2 were added. The effect in the former case was attributed to the transition of $CaO \cdot SiO_2$ from β to α state.

Ivascu, Rozenberg and Caarlen⁴⁰ (1960) studied the effect of pressure applied during pressing, intensity of magnetic field and final heat treatment on anisotropic barium ferrite magnets. Optimum conditions were found out for the composition $(BaO).(5.9Fe_2O_3).(0.035Bi_2O_3)$. $(BH)_{max}$ product of this anisotropic product was in the range of 2.0 to 2.5 x 10⁶ gauss oersted, four times larger than the isotropic material.

Substitutions and Additions in Hard Ferrites:

A number of studies have been made on the effect of substitutions in these ferrites. Replacements of all the three ions Fe^{3+} , (Ba^{2+}, Pb^{2+}) and O^{2-} have been attempted. The following table gives the substitutions of Fe^{3+} and Ba^{2+} or Pb^{2+} . The only replacement reported for O^{2-} is by F^{-1} .

Replacements of Fe^{3+}				Replacements of Ba^{2+} or Pb^{2+}	
M^{2+}	M^{3+}	M^{4+}	M^{5+}	M^{2+}	M^{3+}
Zn ²⁺	Al ³⁺	Ti ⁴⁺	V ⁵⁺	Ca ²⁺	La ³⁺
Mg ²⁺	Ga ³⁺	Ge ⁴⁺		Sr ²⁺	Pr ³⁺
Sn ²⁺	Mn ³⁺	Si ⁴⁺			Nd ³⁺
Co ²⁺	Cr ³⁺	Zr ⁴⁺			Sm ³⁺
Cu ²⁺	B ³⁺				Eu ³⁺
Ni ²⁺					

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Replacement of Fe^{3+} by Al^{3+} and Ga^{3+} ions:

The study of the magnetic properties of the system $Al_2O_3-Fe_2O_3-MO$ ($M = Ba, Sr$ or Pb) was first attempted by Kojima⁴¹ (1955) in the range $Fe_2O_3 + Al_2O_3 = 3.5$ to 6. The coercive force of the magnets prepared from these compounds increased with the addition of Al_2O_3 but the saturation magnetization decreased.

Guillaud and Villers⁴² (1956) measured the coercive force, saturation magnetization and the variation of B with H at 77° and $288^\circ K$ for $MO \cdot Al_2O_3 \cdot 5Fe_2O_3$ with $M = Ba^{2+}, Pb^{2+}$ or Sr^{2+} prepared by heating the oxides at $1200^\circ C$. The saturation magnetization was approximately 20 Bohr magnetons as compared to 40 Bohr magnetons per unit cell for the pure compound with no aluminium.

van Uitert⁴³ (1957) found a systematic decrease in the saturation magnetization as Fe^{3+} was replaced by Al^{3+} , indicating that Al^{3+} go to octahedral sites 2a and 12k. This would lead to complete compensation when, per formula unit, $4Fe^{3+}$ ions were substituted by Al^{3+} ions at the octahedral sites of the spinel block. That, in fact, appeared to occur in case of $BaAl_4Fe_8O_{19}$ where indirect evidence indicated the occurrence of such a point of compensation. The coercive force was found to increase with decrease in saturation magnetization (i.e. with increasing aluminium content). Ga^{3+} ions were also found to replace the octahedral Fe^{3+} ions.

Mones and Banks⁴⁴ (1958) studied the variation of magnetization of $BaFe_{12-2x}Al_xO_{19}$ and $BaFe_{12-x}Ga_xO_{19}$ on single

crystals and polycrystalline specimens. The compounds $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$ were found to be magnetic upto $x = 8$. Although, it was concluded that Al^{3+} ions went to the octahedral sites in the spinel blocks, their compensation point would indicate that all the octahedral sites were substituted with equal probability. Ga^{3+} appeared to occupy the tetrahedral sites at low concentrations of about 0.3 gm.atom/formula and beyond that it was distributed at random in the spinel blocks.

Kozlowski and Ziolkowski⁴⁵ (1958) found that at less than 15% Al_2O_3 in barium ferrite, the unit cell dimensions varied considerably while at concentration greater than this the changes were much smaller. In the first stage I_s and B_r decreased approximately linearly and the coercive force increased attaining a maximum of 5000 oersted at 14 mole per cent of Al_2O_3 substituted for Fe_2O_3 in $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$.

Bertaut et al^{46,47} (1958,59) concluded from saturation magnetization and x-ray intensity measurements that for the compositions $\text{BaO} \cdot 5\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$, two Al^{3+} occupied 2a sites and two occupied 12k sites in a unit cell, whereas for $\text{BaO} \cdot 3\text{Fe}_2\text{O}_3 \cdot 3\text{Al}_2\text{O}_3$ two Al^{3+} occupied 2a sites, nine 12k sites and one 4f₁ site. The magnetization curve showed a compensation point at six Al^{3+} per molecule and not at $x = 4$ as assumed by van Uitert⁴³ (1957). The x-ray and magnetic data for Ga^{3+} substituted compounds suggested that in $\text{BaO} \cdot 5\text{Fe}_2\text{O}_3 \cdot \text{Ga}_2\text{O}_3$ unit cell there were three Ga^{3+} at octahedral 12k sites and one Ga^{3+} at 4f₁ tetrahedral site. In the case of

Ba_{0.3}Fe₂O₃.3Ga₂O₃ where 50% of the Fe³⁺ were replaced by Ga³⁺, these Ga³⁺ occupied the following positions. Three Ga³⁺ at 4f₁ six Ga³⁺ at 12k, two Ga³⁺ at 2a and one Ga³⁺ at 4f₂ sites.

Bozorth and Kramer⁹ (1959) made a similar study on PbAl_xFe_{12-x}O₁₉. The saturation magnetization was measured down to liquid nitrogen temperature and the results were extrapolated to 0°K. The decrease of saturation magnetization with increasing Al³⁺ showed that initially Al³⁺ occupied 12k and 2a sites, however, at concentrations beyond x = 3 the saturation magnetisation did not appear to follow the expected behaviour for such replacements and it was more likely that Al³⁺ now went to different sites. In fact the compensation point was reached at x = 6 which was consistent with the value obtained by Bertaut⁴⁶ (1958).

It can be seen that the experimental evidence is definitely against substitution of tetrahedral Fe³⁺ by Al³⁺. However, it is not quite clear whether the substitution at the octahedral sites is only preferred at 12k and 2a sites in the spinel blocks or Al³⁺ are statistically distributed at all the octahedral sites 2a, 12k and 4f₂. It is possible that the distribution is sensitive to the method of preparation of the compound. For example, Mones and Banks⁴⁴ who had quenched their samples from the elevated temperatures where all the octahedral sites will be equally occupied, whereas Bozorth and Kramer⁹ used single crystals prepared by cooling at a very slow rate which enabled the Al³⁺ to move to the low energy positions.

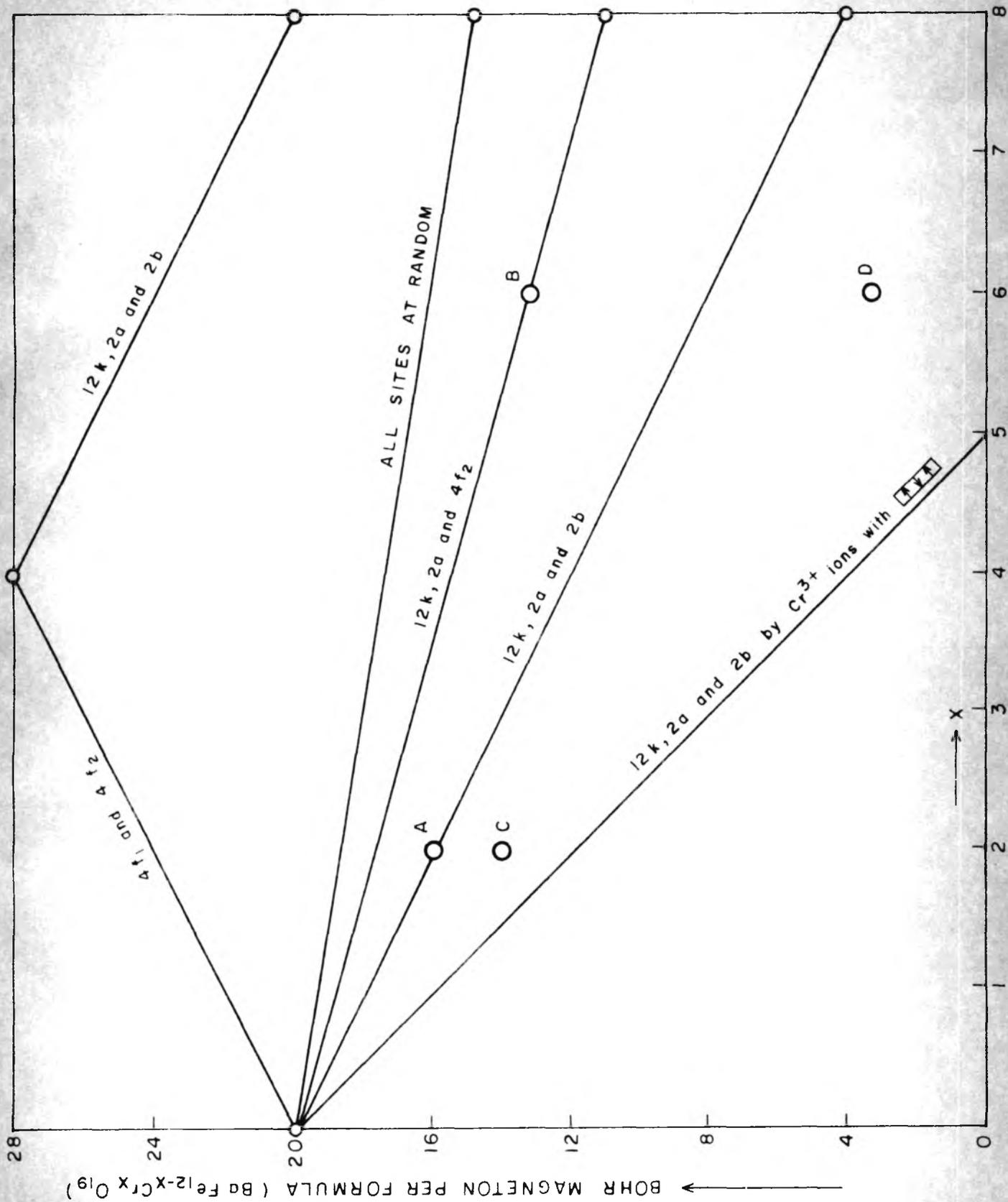


FIG. 4. THE EXPECTED VARIATION OF MAGNETIC MOMENT OF THE COMPOSITION BaFe_{12-x}Cr_xO₁₉ AS A FUNCTION OF X. THE SITES REPLACED BY Cr³⁺ IONS ARE INDICATED ON THE LINES.

Replacement by Cr^{3+} :

Brisi and Burdese⁴⁸ (1952-53) substituted Fe^{3+} by Cr^{3+} in hexagonal ferrites $\text{SrFe}_{12}\text{O}_{19}$ and $\text{BaFe}_{12}\text{O}_{19}$ and studied these by x-ray and magnetic methods. A maximum substitution of only about 50% of Fe^{3+} could be achieved in both cases.

Hiroshi Kojima^{49,50} (1956, 58) studied the effect of addition of Cr_2O_3 in the $\text{MO} - \text{Fe}_2\text{O}_3$ system, where $\text{M} = \text{Sr}, \text{Ba}$ or Pb . Some improvement in the magnetic properties was observed in the composition $\text{MO}.5\text{Fe}_2\text{O}_3$ by addition of 3% Cr_2O_3 . The addition had no effect on Curie temperature and the improvement in magnetic properties had been assumed to be due to increase in the apparent density and control of grain growth, rather than the formation of a new stronger ferromagnetic phase.

van Uitert⁴³ (1957) studied the substitution of Fe^{3+} in $\text{BaFe}_{12}\text{O}_{19}$ by Cr^{3+} . The specimens had the characteristic plate like habit of barium ferrite and the saturation magnetization was low as in the case of Al^{3+} and Ga^{3+} substitutions. Mones and Banks⁴⁴ (1958) and Kozlowski and Ziolkowski⁴⁵ (1958) also made substitutions of Fe^{3+} by Cr^{3+} in $\text{BaFe}_{12}\text{O}_{19}$. It was found that all magnetic properties decreased on increasing the chromium content, suggesting its preference for octahedral sites. At 10% substitution, crystals of new unidentified phase had been reported by the latter authors⁴⁵.

Figure 4 shows the expected variation of the saturation magnetization of $\text{BaFe}_{12-x}\text{Cr}_x\text{O}_{19}$ with increasing Cr^{3+} concentration. Cr^{3+} ions are supposed to have three spins per ion. The substitution of these ions at $4f_1$ and $4f_2$ sites should

increase the saturation magnetization, while at other sites they should decrease the same as shown in the figure. Bertaut *et al*^{47,48} (1958, 59) measured the saturation magnetization of $\text{Sr}0.5\text{Fe}_2\text{O}_3.\text{Cr}_2\text{O}_3$ and $\text{Sr}0.3\text{Fe}_2\text{O}_3.3\text{Cr}_2\text{O}_3$ samples and the results are given by the points C and D in the figure 4. Based on the cation distribution as determined by neutron diffraction, the expected values of the saturation magnetization are given by points A and B. The observed values are considerably lower and it is possible that a part of the Cr^{3+} at 12k and 2a sites are present in the lower spin state. However, it is not clear whether Cr^{3+} in the octahedral field will prefer the low spin state. As a matter of fact, there are various alternative locations for the low spin Cr^{3+} which would give the experimentally observed values, and further work would be required to settle the point.

Addition of B_2O_3 :

Kojima^{49,50} (1956-58) studied the effect of addition of B_2O_3 in the system $\text{MO} - \text{Fe}_2\text{O}_3$ ($\text{M} = \text{Ba}, \text{Sr}$ or Pb). It was found that the magnetic properties of the system improved when small quantities (upto 3%) of B_2O_3 were added in the composition $\text{Fe}_2\text{O}_3/\text{MO} = 5$. The improvement was thought of as due to increase in the apparent density of the material.

Substitution by Zn^{2+} ions:

Mones and Banks⁴⁴ (1958) studied the substitution of Fe^{3+} ions in barium ferrite by Zn^{2+} ions. The polycrystalline

samples used for measurements of magnetization were slowly cooled (100°/hr) from high temperatures. The only zinc compound having BaFe₁₂O₁₉ structure was BaFe₁₁ZnO_{18.5} while BaFe_{11.6}Zn_{0.6}O₁₉ showed some x-ray reflections of ZnO. The magnetization values of zinc compounds were higher than those of pure compounds, showing that the Zn²⁺ ions occupied the tetrahedral sites which was consistent with the behaviour of these ions in the spinels.

Substitution and addition of CoO, MgO, SnO₂, BeO, CaO, CuO, NiO and V₂O₅:

Hiroshi Kojima^{49,50} (1956-58) studied the effect of partial replacement of Fe₂O₃ by CoO, MgO, SnO₂, CdO, NiO and V₂O₅ in the oxide magnets of barium ferrite type. It was found that CdO, SnO₂, CoO and CuO were quite uneffective in improving the magnetic properties while V₂O₅ had a harmful effect.

Rutkowska⁵¹ (1957) studied the addition of CaO, MgO, BeO to BaFe₁₂O₁₉ by sintering the samples at 1050°, 1150° and 1250°C in air. These oxides when added upto 10% had an injurious effect on the magnetic properties of hexagonal ferrites. CaO of these oxides was found to be least harmful.

Kozlowski and Ziolkowski⁴⁵ (1958) investigated the effect of addition of CaO and NiO to Ba_{0.6}Fe₂O₃. With the addition of less than 5% CaO and NiO, the resulting products were of one phase only and although they still possessed the

characteristics of a permanent magnet, their magnetic properties were inferior to that of the pure compound. With more than 5% addition, a new soft magnetic phase, isomorphic with $\text{BaFe}_{12}\text{O}_{19}$ upto 20% addition appeared with decreased values of I_r and H_c , especially in the products sintered at high temperatures. With more than 40% addition, the barium ferrite type structure disappeared with the formation of new compounds.

It emerged from the later work of Braun⁵² (1957) that divalent cations like Mg^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} and Zn^{2+} can be taken by the $\text{BaO} - \text{Fe}_2\text{O}_3$ system to give structures, W, Z and Y type where $W = \text{BaFe}_2^{2+} \text{Fe}_{16}^{3+} \text{O}_{27}$, $Y = \text{Ba}_2\text{Zn}_2^{2+} \text{Fe}_{12}^{3+} \text{O}_{22}$, $Z = \text{Ba}_3\text{Co}_2^{2+} \text{Fe}_{24}^{3+} \text{O}_{41}$. These are soft magnet materials with a plane of easy magnetization.

Addition of TiO_2 , GeO_2 , SiO_2 and ZrO_2 :

Kojima^{41,49,50} (1955, 56, 58) investigated the effect of addition of TiO_2 , GeO_2 , ZrO_2 and SiO_2 on the magnetic properties of the system $\text{MO} - \text{Fe}_2\text{O}_3$ ($M = \text{Ba}, \text{Sr}$ or Pb). With TiO_2 addition the study was made in the range $(\text{Fe}_2\text{O}_3 + \text{TiO}_2)/\text{MO} = 4$ to 9 . ^{Some improvement in magnetic properties was found at $n=4$.} This had been assumed as a result of the shift in the point of maximum magnetic properties as a result of the combination of MO with TiO_2 . A considerable improvement in the magnetic properties was found in the above system with $M = \text{Ba}$ or Sr with the addition of GeO_2 and SiO_2 at $\text{Fe}_2\text{O}_3/\text{MO} = 5$. Curie points of these compositions were not changed by these additions and the improvement in the magnetic properties was thought to be due to the increase in the density of the samples. In the

case of $\text{PbO}-\text{Fe}_2\text{O}_3$ system the best properties were obtained with GeO_2 or SiO_2 additions at $\text{Fe}_2\text{O}_3/\text{PbO} \approx 4$ to 5 when the samples were reacted at 900°C for two hours and sintered at $950^\circ - 1150^\circ\text{C}$ for 15 minutes. The properties of these improved $\text{PbO} - \text{Fe}_2\text{O}_3$ magnets were comparable to those of BaO or $\text{SrO}-\text{Fe}_2\text{O}_3$ magnets.

Pawlek and Reichel⁵³ (1957) studied the magnetic properties of the system $\text{PbO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$. These investigations revealed the favourable effect of small additions of SiO_2 on the permanent magnet properties of this system. The best composition consisted of 25.2 PbO .74 Fe_2O_3 and 0.8% SiO_2 . When reacted in air at 950°C followed by sintering at 1100°C , it gave remanence equal to 2450 gauss and coercivity of 2000 Oe.

Addition of Bi_2O_3 :

Takei and Sugimoto⁵⁴ (1955) studied the effect of Bi_2O_3 addition to $\text{MO}.6\text{Fe}_2\text{O}_3$ with $\text{M} = \text{Pb}, \text{Sr}$ or Ba . It was found that the $(\text{BH})_{\text{max}}$ improved by 20-30% and the mechanical strength by 2-3 times. Curie temperature, however, remained unchanged. These effects were attributed to lower melting point of Bi_2O_3 which accelerated the sintering. Microscopic examination did not reveal any new phases.

Okamura and his collaborators⁵⁵ (1955) measured the magnetic properties of $\text{MO}.6\text{Fe}_2\text{O}_3$ (with $\text{M} = \text{Ba}, \text{Sr}$ or Pb) compounds containing Bi_2O_3 additions. It was found that for lead compound the best magnetic properties were observed at

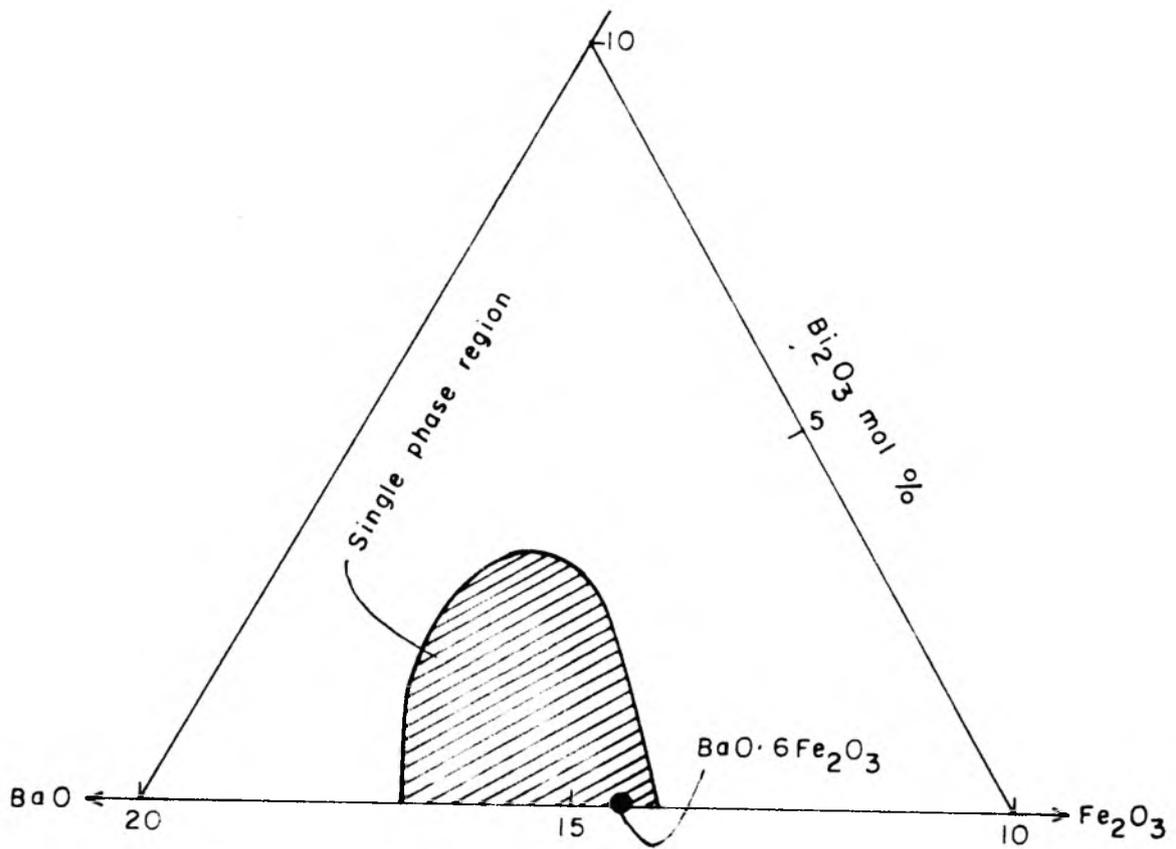


Fig.5. MAGNETOPLUMBITE SINGLE PHASE REGION IN THE TERNARY SYSTEM BaO - Bi₂O₃ - Fe₂O₃.

$\text{Fe}_2\text{O}_3/\text{PbO} = 4.5$. The magnetic saturation and remanence values of strontium compound increased by the addition of Bi_2O_3 only in the range $\text{Fe}_2\text{O}_3/\text{SrO} \approx 6$, but $I_H C$ decreased. The results for barium ferrite were in agreement with those of Sugimoto⁵⁴ (1955). It was concluded that the sintering velocity of these oxide magnets was accelerated by the addition of bismuth oxide.

The effect of Bi_2O_3 additions on barium ferrite magnets was also studied by Kozlowski and Ziolkowski⁴⁵ (1958). They, in agreement with the previous workers, found that barium ferrite containing Bi_2O_3 sintered well at 1000°C and had densities ≈ 5.2 gm/c.c. Furthermore, the crystal growth was also inhibited. At 2 mole percent and beyond, a new phase was reported. Additions of less than 2% of Bi_2O_3 increased $I_H C$ by approximately 25%. The unit cell changes were greater at 2-5% addition and practically nil at 5-10%. Also the change in Curie temperature was only 30°C at 10% Bi_2O_3 .

Sugimoto and Takei⁵⁶ (1960) studied the reaction yield and volume and weight changes during formation of barium ferrite containing Bi_2O_3 . The residual induction B_r was found to be maximum at 5% Bi_2O_3 , when the reaction temperature was 900°C and sintering temperature 1100°C . Study of the ternary system $\text{BaO}-\text{Fe}_2\text{O}_3-\text{Bi}_2\text{O}_3$ was made by microscopic observations and x-ray diffraction analysis. A very narrow single phase region in the vicinity of $\text{Ba}_0.6\text{Fe}_2\text{O}_3$ was observed and the phase diagram obtained by them is reproduced in figure 5. In the single phase region, variations in lattice constants and Curie temperature,

if any, were very small.

Substitution of Ba²⁺ ions:

Deschamps and Bertaut⁵⁷ (1957) attempted to substitute Ba²⁺ ions in BaFe₁₂O₁₉ with rare earth ions, La³⁺, Pr³⁺, Nd³⁺, Sm³⁺ and Eu³⁺. The solubility limits for these ions were found to be respectively 0.7, 0.4, 0.3, 0.1 and 0.1 times the mole fraction of barium at 1400°C. However, no magnetic measurements were made.

Substitution of O²⁻ ions:

Substitution of oxygen ions by fluorine ions was partially achieved by Schieber and Shtrikman¹² (1960). The new compound had the chemical formula BaF₂.2FeO.5Fe₂O₃, the magnetic properties of which have already been described earlier (p.7).

It is clear from a review of the earlier work that the understanding of various factors involved in the formation and stabilization of magnetoplumbite structure is still incomplete. In the present work a systematic attempt has been made to synthesize new compounds of this structure with ions of different sizes and electronic configurations in order to know the influence of these on the stability of such compounds. The effect of impurities on the magnetic properties of these hard ferrites has also been investigated in some detail. In what follows we give a description of the experimental techniques employed in these studies, followed by a discussion of the results obtained.

CHAPTER II

EXPERIMENTAL TECHNIQUES

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Preparation of samples:

Ferric oxide (α -Fe₂O₃) is the chief starting material for the preparation of all ferrites. Except for the synthesis of hexagonal ferrites containing lanthanum, ferric oxide used was obtained by precipitating ferric hydroxide Fe(OH)₃ from an aqueous solution of A.R. grade ferric chloride (FeCl₃) with liquor ammonia. The precipitate was made free from chloride ions by washing it with hot water containing ammonium nitrate for several days in a centrifuge and was then calcined at 650°C for four hours to decompose it to ferric oxide. Chemically pure, brown precipitated, ferric oxide supplied by B.D.H. England was employed for the preparation of ferrites containing lanthanum, for the reasons to be given later. The x-ray diffraction patterns of both these samples gave the same d values as reported for α -Fe₂O₃ in the A.S.T.M. x-ray data card file.

The other compounds used for the preparation of the ferrites under study were of A.R. grade purity except for silver oxide, silicon dioxide, stannic oxide, cobalt oxide and zirconium oxide, which were of C.P. grade only. In order to remove any moisture present, these compounds were heated to 300°C for two hours before weighing them on a Mettler balance. Zinc oxide and lanthanum oxide were, however, heated to 500° and 1000°C respectively to decompose any carbonates present. The weighed compounds were thoroughly mixed under alcohol in an agate mortar with pestle till these appeared homogenous. The mixture was

dried in an oven at 100°C and transferred to a platinum crucible. The reaction was carried on at temperatures ranging from 800° to 1350°C for various durations in an electric furnace using silicon carbide rods as heating elements. The temperature of the furnace was automatically controlled within $\pm 10^\circ$ by means of a chopper bar type mercury switch regulator and was indicated on a 16" pyrometer, operated by a Pt - Pt 13% Rh thermocouple kept inside the furnace. The calibration of the thermocouple was done by determining the melting points of potassium chloride (770°C) sodium chloride (800°C) and silver metal (960°C).

Normally the furnace took about three hours to attain a temperature of 1350°C from room temperature and more than twelve hours for the reverse cycle. All the heat treatments were carried on in an atmosphere of air and the specimens were cooled in the furnace. The reacted hard masses were broken into small pieces in a clean steel mortar and then ground in a ball mill under distilled water for various durations. The cylindrical stainless steel can of the ball mill (length 8" and diameter 6") contained ten steel balls of one inch diameter and fifty balls of half an inch diameter. The can rotated at a speed of sixty revolutions per minute by a half H.P. continuous operation motor. On completion of grinding the slurry was poured out in a beaker along with the washings from the can and dried on a hot plate.

X-ray Examination:

The reacted powders were examined by x-ray powder diffraction technique to check the completion of the reaction and to determine their crystal structure. The samples were filled in thin glass capillary tubes and Debye Scherrer patterns were taken on a G.E.C. XRD3 X-ray machine using M_o-K_{α} radiation ($\lambda = 0.709 \text{ \AA}$) filtered through a zirconium foil, in a 14 cm camera. The d values were calculated in the usual manner with an accuracy of $\pm 0.2\%$.

Pellet Formation:

About 2.5 grams of the ball milled sample was made into a thick paste by thoroughly mixing it in an agate mortar with a 2% solution of polyvinyl acetate in acetone which acted as a binder and lubricant. The paste was transferred into the barrel of a die fabricated out of die steel bar. The pressures upto 15,000 lbs per square centimeter were applied to the plunger in a Carver laboratory press fitted with a calibrated pressure gauge. The pressure was released after one minute and the pellet removed by applying the pressure in the opposite direction. Use of vacuum during pressing was found to be unnecessary. The binder made the pellets rugged and they could easily be removed from the die without developing any cracks. Several other binders such as a solution of paraffin wax in benzene, polyvinyl alcohol in water, polyvinyl chloride in cyclohexanone, etc. were also tried but found to be inferior to the polyvinyl acetate binder. Mostly cylindrical pellets

of about one centimeter length and half centimeter diameter were made but for certain special measurements, such as the determination of remanence along different directions at right angles to each other, pellets with a rectangular cross-section were also pressed.

These pellets were sintered by keeping them on a platinum foil in the electric furnace by first raising the temperature very slowly upto 800°C to burn away the binder and then raising it at a fast rate upto the desired sintering temperature by adjusting the input power. Sintering was done at temperatures from 600°-1350°C for various durations, after which the furnace was switched off and the pellets were slowly cooled in the furnace itself.

The sintered pellets were weighed in a Mettler balance and their dimensions measured with a micrometer screw gauge. The apparent densities of these pellets were then calculated from their weights and bulk volumes. Weights of all the pellets sintered below 1000°C were determined after the completion of the magnetic measurements because they had to be heated at 1000°C to burn away the binder completely.

A coil of a single layer of 75 turns (B coil) was wound round each pellet with enamelled copper wire No. SWG 46 by manually operating a winding machine fitted with an automatic counter. The ends of the coil were cleaned with a fine emery paper and connected to a ballistic galvanometer (B.G.) circuit to be described below.

Magnetic Measurements:

(A) Tracing of hysteresis loop: The measurements of magnetic induction and the magnetizing force were based on the principle that there was an e.m.f. induced in a coil, whenever there was a change in the amount of flux linked with this coil. Let N be the number of turns possessed by the coil and ϕ the instantaneous value of the flux linked with these turns. The instantaneous value of e.m.f. will be $e = Nd\phi/dt$ and $edt = Nd\phi$. Let the coil circuit be closed and let R be the resistance of this circuit. Dividing by R we get $edT/R = Nd\phi/R$ or $idt = Nd\phi/R$ where $e/R = i$, the instantaneous value of current induced in the circuit. Integrating

$$\int_0^t idt = N/R \int_{\phi_2}^{\phi_1} d\phi \quad \text{or} \quad q = N/R(\phi_1 - \phi_2)$$

where q is the quantity of electricity made to pass through the circuit due to a flux change ($\phi_1 - \phi_2$). Thus it is clear that if q is measured, the change in flux linked with the coil can be determined. A ballistic galvanometer, which is capable of integrating the quantity idt can be used to measure the changes in flux when calibrated for this purpose. With this instrument the magnetic flux cannot be measured directly because only changes in flux and not the steady flux produce the galvanometer deflections. The value of the total flux is, therefore, inferred from the measurement of the change in flux

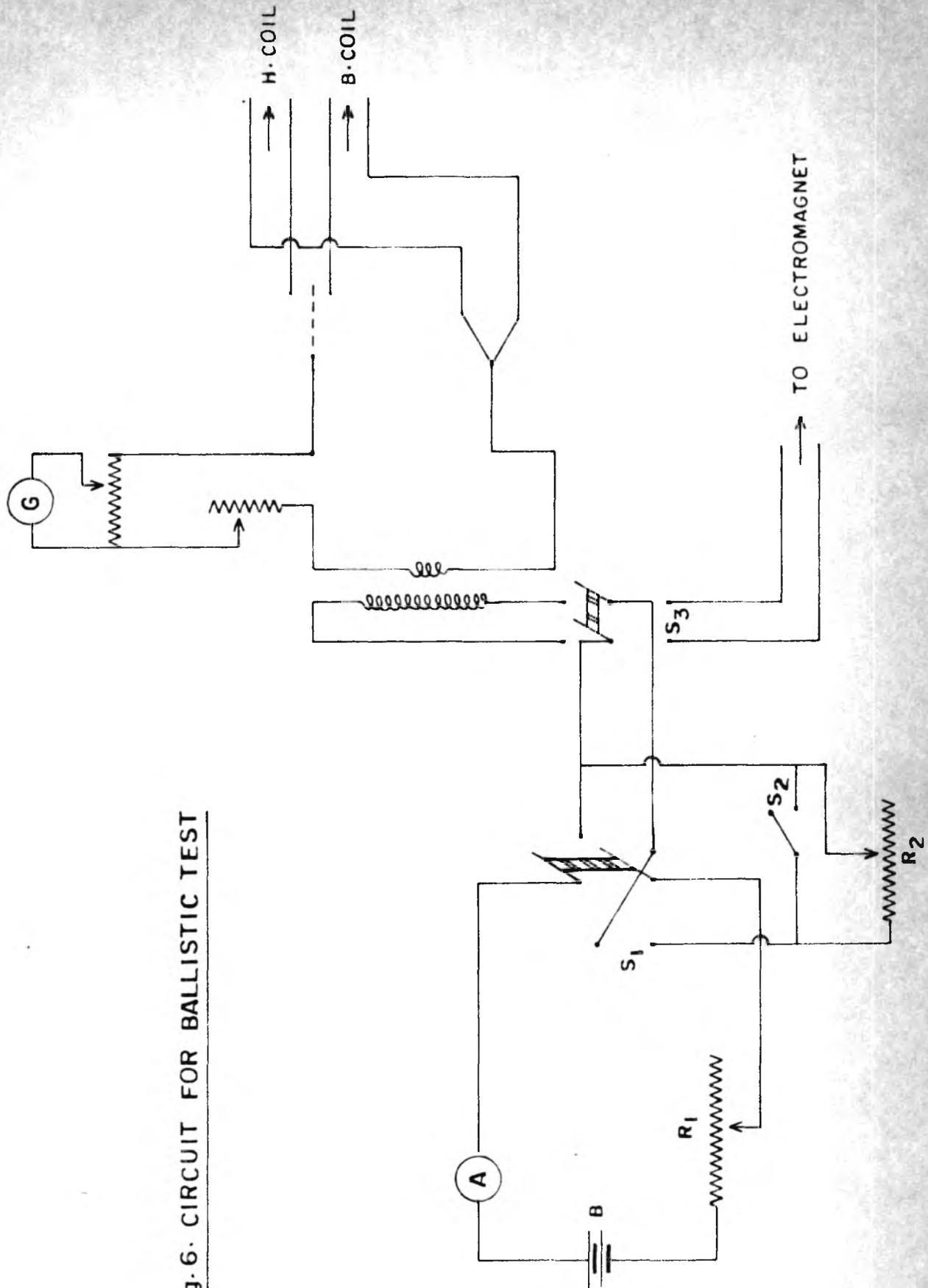


Fig. 6. CIRCUIT FOR BALLISTIC TEST

which can be produced by changing the magnetizing current. The value of B is determined by dividing the total flux with the cross-section area of the coil.

(B) Calibration of the ballistic galvanometer: The calibration of the ballistic galvanometer having a natural period of 28 seconds was done with the help of a standard air core solenoid consisting of a long single layer coil of enamelled copper wire SWG 19 wound on a one meter long brass pipe having a diameter equal to three inches. The winding was uniform and the number of turns per inch axial length was 23.4 so that a uniform magnetic field H, given by the relation $H = 4\pi NI/10L$ Oersted was produced at the centre of the solenoid on passing current through it. (N = total number of turns in the solenoid, L = length in centimeters and I = current in amperes). At the centre of the solenoid and coaxial with it was kept a small secondary coil of 800 turns of thin copper wire and known mean cross section area. The secondary coil was connected to the B.G. and a known current could be passed through the solenoid from a set of twelve 6 Volt batteries. An e.m.f. producing the galvanometer deflection was induced in the secondary coil when the current in the solenoid was reversed by a reversing switch as shown in the figure 6. The number of line turns producing this deflection was obtained from the known value of H at the centre of the solenoid and the number of the turns and the dimensions of the secondary coil. The values of the galvanometer deflections for different values of line turns

associated with the secondary coil were obtained by reversing different known currents through the solenoid. The average number of line turns required to produce 1 mm. deflection on the B.G. scale, kept at a distance of one meter was thus calculated.

As the current passing through the B.G. circuit depended on its resistance, the secondary coil used for its calibration was permanently included in its circuit. Thus the exact conditions of calibration were always reproduced in the subsequent magnetic measurements.

(C) B-H Measurements: The test pellet with ends ground smooth and parallel and having a B coil wound round it was tightly clamped in the adjustable gap of a massive electromagnet with rectangular pole faces tapered at an angle of 60° so as to make the magnetic field between them as nearly uniform as possible. The clamping of the pellet was done in such a way that a good magnetic contact was made at both its ends and it was completely enclosed in soft iron, without leaving air gaps. This provided a closed low reluctance path for the magnetic flux. The magnet was energized by twelve 6-Volt lead accumulators which were constantly charged as the power was drawn from them. To determine the value of the magnetic field acting on the pellet, a small H coil of 100 turns and known cross-section area, wound on a nonmagnetic material was placed very close to it. Both these coils could be alternately brought into the circuit of the B.G. with the help of a selector switch. The current in

the two coils of the electromagnet, which were connected in series, could be increased, decreased or reversed by a suitable arrangement of switches as shown in figure 6.

The B-H measurements were made upto a maximum field of 7000 oersted. In what follows the magnetization measured at this field will be called the saturation magnetization. The magnetizing current corresponding to this above field was reversed a few times to bring the specimen in the cyclic state. Since only the changes in B could be measured and not the full value of B itself, it was necessary to choose one point, the tip of the hysteresis loop (H_{\max} , B_{\max}), as the point of reference and then measure the change in B when the specimen was taken from this magnetic state to some other state. By opening the switch S_1 , of figure 6, the flux density in the specimen was reduced to remanent magnetization, B_r . The deflection of the B.G. with B coil in the circuit was, therefore, that corresponding to a flux change $\Delta \phi$ equal to $(\phi_{\max} - \phi_{B_r})$. Since the galvanometer was calibrated to be direct reading for line-turns, the total change in the magnetic lines was obtained by dividing the line-turns by 75, i.e. the number of turns in the B coil. The change in the number of lines per unit area, i.e. ΔB , was calculated by dividing it with the cross-section area of the specimen. By subtracting this value of ΔB from B_{\max} , B_r , the remanence was obtained.

To determine other points on the loop, use was made of the resistance R_2 by opening the switch S_2 . If, with switch

S_1 on the left hand contacts, S_2 was opened, the magnetizing force got reduced from H_{\max} to some value H' depending upon the magnitude of R_2 . The value of H' was determined in the same way by noting the deflection on switching off the current corresponding to H' , with H coil in the B.G. circuit. Any point on the loop between the tip point and the remanence point could thus be reached by adjusting R_2 to a suitable value. After each measurement, the specimen was always brought back to the reference point ($B_{\max} \cdot H_{\max}$). Points on the loop corresponding to a negative magnetizing force H'' could be found out in the same way by placing S_1 on the right hand contacts, adjusting R_2 to a suitable value with S_2 open, and noting the galvanometer deflection when S_1 was reversed. The value of H'' was determined in the same way as described above for H' .

B and H values determined at various points along the cycle were plotted to give a hysteresis loop from which could be determined the induction coercivity $B_H H_c$ and remanence B_r of the material. The value of intrinsic coercivity $I_H H_c$ was determined from the plot of B-H against H.

The following precautions were taken during these measurements:

- (a) Stray fields, especially from parts of electrical circuit in which the current changed during observation were avoided by using folded leads in such a way that their magnetic effects were mutually cancelled.
- (b) The specimen was clamped between the magnetic poles in such a way that it was free from mechanical strains.

(c) Heating of the specimen during measurement was avoided by cooling it with a stream of air. Actually the apparatus required about 500 Watts to produce a field of 7000 oersted and had a considerable radiating surface and heat capacity. The temperature rise of the specimen was negligible.

(d) Whenever induction is measured by means of a stationary coil surrounding the specimen, the space between the coil and the test sample should be as small as possible. However, it cannot be reduced to zero and this introduces some error in measurements. This error was minimized by using a single layer coil of a very thin copper^{wire} (diameter 0.0024").

(e) Some errors were introduced due to leakage of flux at points where the sample made contact with the yoke. Moreover, the yoke did not entirely fulfil its purpose of joining the ends of the pellets magnetically. These effects tended to produce demagnetization, i.e. made H somewhat less than its actual value. However, the demagnetization effects were so small on account of low permeability of the test sample ($\mu < 5$) and low saturation magnetization that they were neglected.

A small error, which is inherent in measurements involving stationary coils, however, remained because the values of B and H were calculated as the difference between two relatively large quantities.

The values of the various magnetic properties such as saturation magnetization, remanence and coercivity were determined fairly accurately after taking the above-mentioned precautions. The measured values of pure barium ferrite compared well

with those quoted in the literature.

(D) Curie Temperature Measurements: For determining Curie temperatures of the ferrites, the test sample in the form of a sintered cylindrical rod, (length ≈ 1 cm, dia ≈ 1 cm) kept in a thin walled copper crucible, was suspended with the aid of a steel spring and a quartz rod into a vertical tube furnace of one inch diameter. The purpose of the quartz rod was to keep the steel spring out of the furnace to avoid its expansion during heating. A ten inch long mild steel rod with diameter slightly less than one inch was introduced into the furnace from its lower end so that the distance between the upper end of the rod, which was tapered down to one centimeter, and the suspended sample was only half centimeter. The mild steel rod was magnetized by passing a current of 5 amps through a coil of 1500 turns of copper wire fitted at its lower end. The rod pulled the sample towards itself, making an electrical contact between the copper crucible and the mild steel rod. This in turn completed the circuit of an indicator bulb which was made on and off as the contact was made or broken respectively. The test sample remained attached to the magnetized rod at temperatures below Curie point, but as soon as it passed through that point, the spring action pulled it up and the indicator lamp went off. The furnace was heated at a rate of approximately five degrees per minute in the region of Curie temperature. The temperature of the sample was determined by means of a chromel-alumel thermocouple kept close to it, inside the copper

crucible. The uncertainty in the values of Curie temperature measured by this method was estimated as $\pm 5^\circ$.

Shrinkage Measurements:

To study the effect of certain additives on the linear shrinkage of the ferrites during sintering, the pellets of the reacted materials were pressed under a pressure of 3000 lbs/sq. cm. in the form of rods of two centimeter length and one centimeter diameter. The test rod was placed at the bottom of a vertical silica tube with its lower end closed and surrounded by a furnace capable of going upto 1000°C . A quartz rod resting on the test rod was kept vertical inside the silica tube by means of a brass cap fitted at its upper end. The furnace was slowly heated from room temperature to 1000°C and the temperature was measured by means of a Pt-Pt.13% Rh thermocouple attached to the tube at its bottom. Any changes in the height of the quartz rod due to the shrinkage or expansion of the test sample during its sintering were measured by means of a spherometer, the tip of whose screw was resting on the top of the quartz rod which was coated with a paste of metallic silver to make it electrically conducting. An indicator bulb was connected in a circuit consisting of a dry cell, variable resistance, milliammeter, spherometer and the conducting part of the quartz rod. As soon as the tip of the spherometer touched the quartz rod, the milliammeter showed a deflection and the reading on the spherometer scale was recorded. The readings were taken at various temperatures as the heating was

going on. Knowing the original length of the test rod, it was thus possible to calculate the per cent linear change during sintering.

Surface area Measurements of Iron Oxide Powders:

Nitrogen adsorption method was used for determining the specific surface areas of ferric oxide samples obtained by different methods. The principle of this method involves the evaluation of the quantity of gas which is taken up by one gram powder to cover all its available surface with gas-layer of one molecule in thickness. If this quantity of gas q_0 is expressed in gm. moles, then the specific surface area is given by $S_w = q_0 NA.$, where N is the Avogadro's number (6.02×10^{23}) and A is the area occupied by one nitrogen gas molecule (16.2×10^{-20} sq. meters). The amount of gas adsorbed depends upon the pressure as well as on the temperature. Experimentally one studies adsorption as a function of pressure at a constant temperature (B.P. of liquid nitrogen). Multilayer theory of Brunauer, Emmett and Teller⁵⁸ (1938) satisfactorily explains the adsorption phenomenon of gases on solid surfaces and can be summed up in the following equation:

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \frac{P}{P_0}$$

where V is the volume of the gas adsorbed at 0°C and one atmosphere pressure, P is the equilibrium pressure, P_0 is the saturation vapour pressure of the gas at the temperature of the

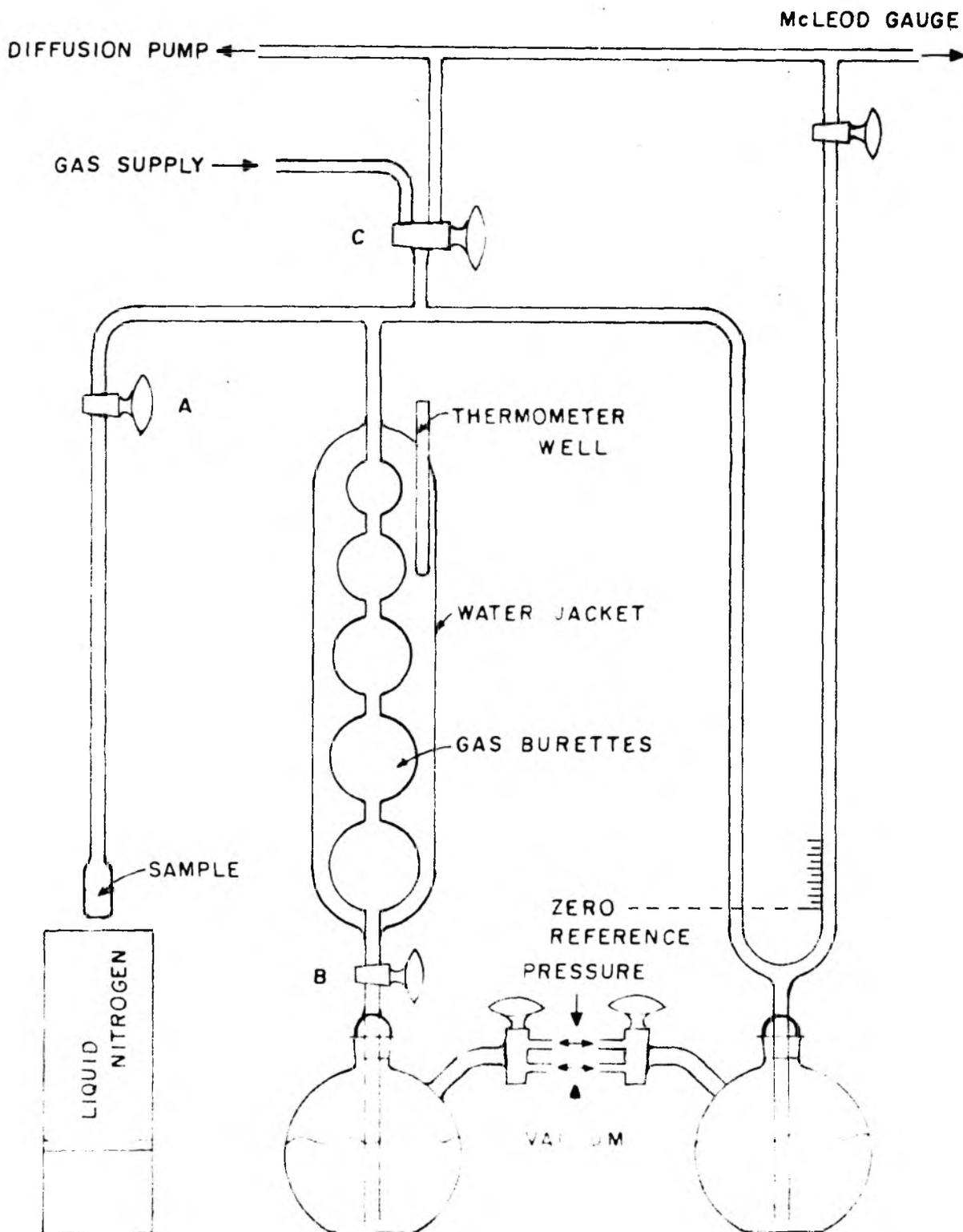


Fig.7. THE APPARATUS USED FOR SURFACE AREA MEASUREMENTS

adsorbent, C is a constant related to the heat of adsorption and V_m is the volume of the gas required to cover the entire surface of the solid with a single layer of one molecule thickness. Of these quantities P , P_0 and V are determined experimentally and V_m and C are obtained by plotting $P/V(P_0 - P)$ against P/P_0 which yields a straight line, with slope $(S) = C - 1/V_m C$ and intercept $(I) = 1/V_m C$, hence $V_m = 1/S + I$ and the surface area (sq.meters) = $4.38 V_m$ (cc s.t.p.)

Apparatus used for such measurements is shown in figure 7. The volumes of various bulbs in the burette were determined by mercury calibration before the apparatus was assembled and the volume between stopcock A and zero reference of the manometer was determined by filling it with helium gas at various pressures and using the relation $PV = RT$. The commercial nitrogen gas used for adsorption studies was purified by passing it through columns of silica gel, hot copper filings at 350°C , soda asbestos and finally through activated charcoal at liquid nitrogen temperature. The measurements followed the following steps:

(1) Pretreatment of the sample: Before starting the adsorption the sample was degassed at room temperature in a vacuum of 2×10^{-5} mm of mercury for two hours to remove any adsorbed gases or vapours.

(2) Dead space measurement: Helium gas at liquid nitrogen temperature is not adsorbed by solids. Dead space i.e. the free space upto stopcock A not occupied by powder was therefore determined by admitting spectroscopically pure helium gas

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supplied by British Oxygen Company into the adsorption bulb after surrounding it by liquid nitrogen bath. After the measurement, the liquid nitrogen bath was removed and the gas was pumped out of the system. Stopcock A was then closed and the bath replaced.

(3) Determination of the isotherm: The system was again evacuated to a pressure of 2×10^{-5} mm of mercury and purified nitrogen gas was admitted to the burette with stopcock A closed. By determining the pressure and the temperature of the burette, this volume was converted to standard conditions. With the liquid nitrogen bath surrounding the adsorption bulb, stopcock A was opened. After allowing sufficient time for equilibrium to be established, the pressure was again determined. From these data, simple calculations enable us to arrive at the volume of the gas adsorbed.

By allowing the mercury to fill the various bulbs of the burette the volume of the system was altered by known amounts and hence several points were taken in succession repeating the above procedure.

The calculation of the surface area was done by plotting a graph of $P/V(P_0 - P)$ against P/P_0 and finding out the value of V_m as described above and substituting it in the relation $S_w = 4.38 V_m$ sq. meters.

CHAPTER III

RESULTS AND DISCUSSION

III. 1 : Silver and Thallium Lanthanum Ferrites	... 48
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SILVER AND THALLIUM LANTHANUM FERRITES

Ferrites of magnetoplumbite structure find useful application as permanent magnet materials. Recently some new compounds of the general formula $AFe_{12}O_{19}$ (where A ion is a combination of Na^{1+} , K^{1+} or Rb^{1+} and La^{3+} with an average valency 2) belonging to this group have been reported¹¹. However, all these contained A ions having a rare gas electronic configuration ($s^2.p^6$). Attempts were made to prepare new compounds of the above structure with A ions of different sizes and electronic configurations, with a view to understand the factors that govern the formation and stability of these compounds. Silver lanthanum ferrite ($Ag_{\frac{1}{2}}La_{\frac{1}{2}}Fe_{12}O_{19}$) containing Ag^{1+} ions with d^{10} configuration and radius 1.26 \AA was successfully synthesized. Cu^{1+} ions with d^{10} configuration and radius equal to 0.96 \AA on the other hand did not form this structure. Further investigations in the same direction led to the formation of thallium lanthanum ferrite ($Tl_{\frac{1}{2}}La_{\frac{1}{2}}Fe_{12}O_{19}$), another new ferrimagnetic compound of the same series with Tl^{1+} ions having s^2 electronic configuration and radius 1.47 \AA . The results of structural and magnetic measurements of these new compounds are described below.

SILVER LANTHANUM FERRITE

Kinetics of Reaction: Silver lanthanum ferrite was formed by the solid state reaction between the component oxides at elevated temperatures as described in chapter II. It was

observed that only brown precipitated ferric oxide (α - Fe_2O_3) supplied by B.D.H., England and that formed by the thermal decomposition of ferric oxalate ($\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 5\text{H}_2\text{O}$) at 200°C for one hour could form the desired hexagonal silver lanthanum ferrite $\text{Ag}_{\frac{1}{2}}\text{La}_{\frac{1}{2}}\text{Fe}_{12}\text{O}_{19}$. The following other varieties of ferric oxide were tried but they consistently gave negative results. The desired compound was not formed even upto 1350°C in detectable amounts, beyond that ferric oxide, Fe_2O_3 , progressively changed to Fe_3O_4 .

(1) Spectroscopically pure α - Fe_2O_3 supplied by Johnson Mathey and Co., London.

(2) α - Fe_2O_3 supplied by Howard and Co., England.

(3) α - Fe_2O_3 prepared by decomposition of A.R. grade ferrous sulphate at 700°C .

(4) α - Fe_2O_3 prepared by precipitation of A.R. grade FeCl_3 by ammonia and heating the precipitate at 650°C . In this case a partial formation of the compound was detected by x-ray diffraction.

(5) γ - Fe_2O_3 supplied by C.K. Williams and Co., U.S.A.

All these different samples of ferric oxide did, however, form barium ferrite when heated with appropriate proportions of BaCO_3 at 1000°C . Since the spectroscopically pure and other specially prepared ferric oxides gave negative results, it appeared probable that special reactivity of some samples could be attributed to large specific surface areas and the associated bulk imperfections like point defects, dislocations, and lattice strains⁵⁹. Surface area measurements

of some selected samples of ferric oxide were, therefore, carried on by nitrogen gas adsorption method at liquid nitrogen temperature as described earlier. The results are given in table I.

T A B L E I

SPECIFIC SURFACE AREAS OF SAMPLES OF FERRIC OXIDE OBTAINED BY DIFFERENT METHODS

Sample	Surface area in sq.m/gm.	Reactivity
Ferric oxide obtained ⁶⁰ by decomposition of ferric oxalate at 200°C	300	Ferrite formed completely at 1300°C in a few hours.
Brown precipitated BDH ferric oxide	73	-do-
Ferric oxide formed by precipitating (FeOH) ₃ with subsequent decomposition at 650°C.	25	Only partial formation took place on prolonged heating at 1300°C.
Ferric oxide obtained by decomposition of ferrous sulphate at 700°C.	11	No ferrite formation was observed even on prolonged heating at 1350°C.

The specific surface area appears to exhibit a good correlation with the reactivity and samples having surface areas greater than 50 sq.meters/gm. appear to be appropriate. Further evidence to this effect will be provided in chapter ~~II~~ 2 when the formation of sodium and potassium lanthanum ferrites is discussed.

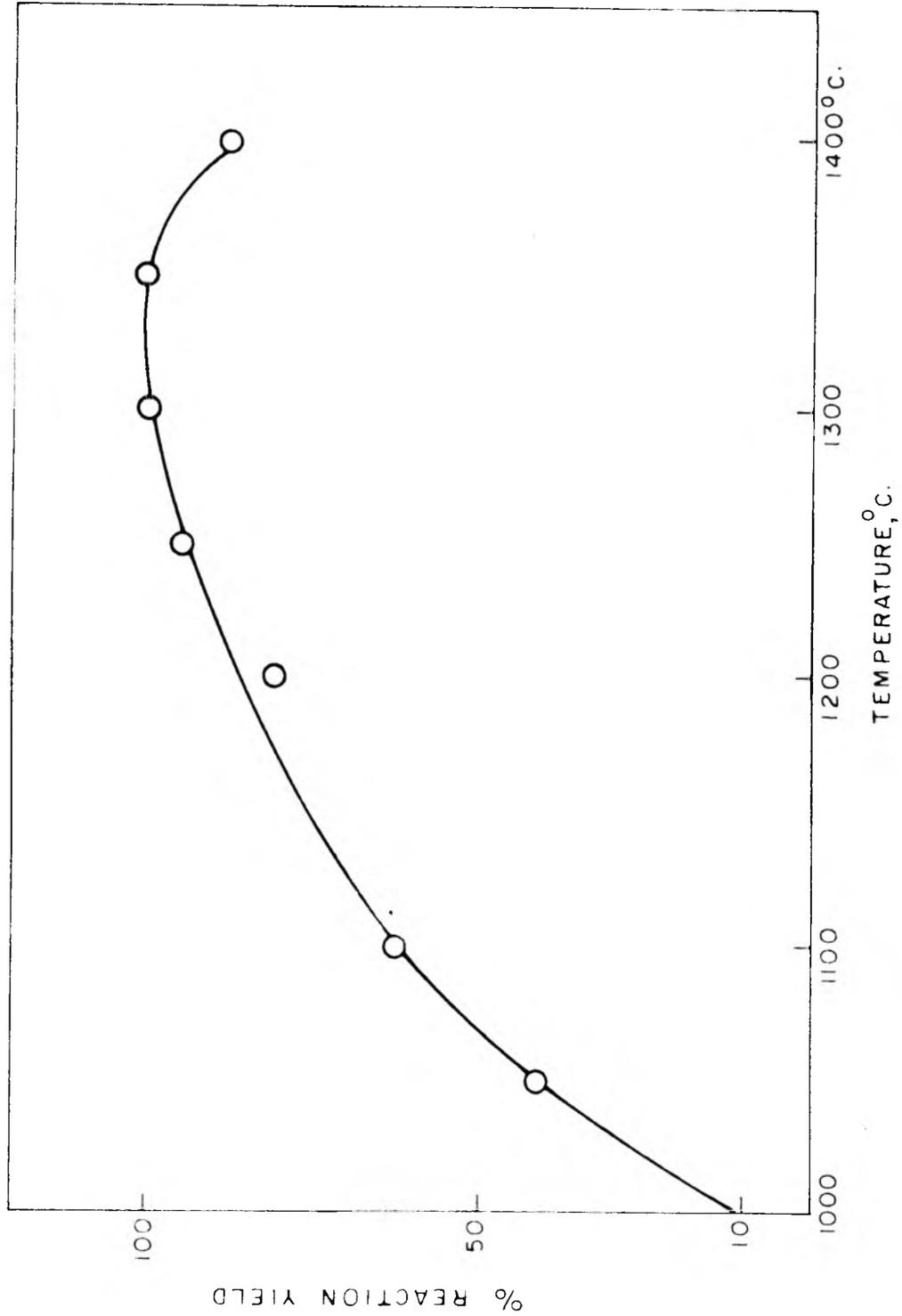


Fig.8 THE VARIATION OF YIELD OF SILVER LANTHANUM FERRITE AS
A FUNCTION OF REACTION TEMPERATURE

The rate of the reaction of the formation of silver lanthanum ferrite was determined from the values of the saturation magnetization of the samples reacted at different temperatures for various durations. Using the saturation magnetization per gram, σ_s , for a completely reacted sample (as established by x-ray diffraction), the extent of the reaction was found out for other samples assuming that the observed value of σ was directly proportional to the percentage of magnetoplumbite phase. The effect of temperature on the percent reaction yield is shown in figure 8. The reaction is completed at 1300°C in three hours while under similar conditions barium ferrite formation is complete at 1000°C only. The cause of this difference in the reaction temperature of these two compounds will be discussed in the next chapter.

The saturation magnetization decreases on heating the samples at 1350°C and, furthermore, all these samples become electrically conducting. The increase in the conductivity can be attributed either to the (i) formation of highly conducting Fe_3O_4 or (ii) replacement of some Fe^{3+} ions by Fe^{2+} ions in silver lanthanum ferrite due to a small loss of oxygen. This would give rise to an increased conductivity as is observed in any mixed valence semiconductor⁶¹. Electrons jump from one ion to another of different valency and contribute to the electric conduction. It appears that the decrease in the saturation magnetization would exclude the first possibility as the saturation magnetization per gram of Fe_3O_4 is of the same

order as that of silver lanthanum ferrite. This conclusion is also supported by the absence of any Fe_3O_4 lines which were specially looked for in the x-ray diffraction patterns of the samples heated beyond 1300°C .

On the other hand, the second case would give rise to decrease in the saturation magnetization due to two possible causes (i) the magnetic ordering of spins on different ions takes place by superexchange interaction through the intermediate oxygen ions. Hence the removal of oxygen ions is bound to decrease the interaction and may cause a local disorder of spins, (ii) the presence of Fe^{2+} would also cause a decrease in the saturation magnetization if their spins are unfavourably oriented. It was observed that the increase in conductivity was more marked when the samples were heated at 1350°C in the form of pellets pressed under a pressure of 3000 lbs/sq.cm. The powder samples, when heated at 1350°C and cooled in air, did not show much rise in conductivity. This indicates that when a powder sample was cooled in air, it got reoxidized to the parent silver lanthanum ferrite, whereas this was not possible in pressed pellets. Long heating (about 20 hours or more) at 1300°C also caused a similar decrease in the magnetic properties and increase in electrical conductivity for the same reasons. The results of the magnetic measurements on samples heated at 1300°C for different durations are summarized in table 2.

T A B L E 2

EFFECT OF REACTION TIME AT 1300°C ON THE SATURATION MAGNETIZATION OF SILVER LANTHANUM FERRITE..

Reaction time hours	$4\pi I_s$ gauss	density gms/cc.	σ gauss-cm ³ /gm.
1	1600	3.68	34.5
3	1640	3.68	35.5
6	1650	3.67	35.8
16	1580	3.59	35.1
20	1560	3.56	34.7
30	1515	3.55	33.9
40	1485	3.54	33.3

X-ray Results: The reflection intensities and interplanar spacings (d) as obtained from Debye-Scherrer pattern of a sample of silver lanthanum ferrite formed at 1300°C are presented in table 3. The corresponding values for pure lead ferrite (Adelskold²) are also included. It can be seen that the two compounds are isomorphous, thus the reflections could be easily indexed on the basis of a hexagonal unit cell.

The calculated values of the unit cell dimensions are $c = 22.85 \text{ \AA}$; $a = 5.85 \text{ \AA}$ and $c/a = 3.9$. No superstructure lines were observed and it is likely that no ordering of Ag^{1+} and La^{3+} takes place.

T A B L E 3

X-RAY RESULTS FROM SILVER LANTHANUM FERRITE REACTED AT 1300°C.

$Ag_{\frac{1}{2}}La_{\frac{1}{2}}Fe_{12}O_{19}$			$PbFe_{12}O_{19}$		Adelskold
d(A°)	Relative* intensity	hkl	d(A°)	Relative intensity	
2.940	M	110	2.940	M	
			2.880	W	
			2.850	W	
2.750	S	107	2.760	S	
2.610	S	114	2.620	S	
			2.550	VW	
2.510	M	108	2.510	VW	
2.420	M	203	2.420	M	
			2.310	VW	
2.330	VW	00,10	2.290	W	
2.220	M	205	2.230	S	
2.118	VW	206	2.125	M	
			2.101	VW	
2.067	VW	118	2.059	VW	
			1.937	W	
1.910	VVW	210	1.920	VW	
		00,12	1.867	VW	
			1.815	VW	
1.800	VVW	209	1.809	W	
			1.778	VW	
			1.710	VW	
1.686	M	300	1.698	W	
			1.631	VW	
			1.670	VW	
1.652	M	217	1.664	S	
1.620	M	304	1.630	M	
1.606	MS	20,11	1.619	M	
			1.602	VW	
			1.593	VW	
1.524	VVW	20,12	1.535	VW	
			1.478	VW	
1.464	MS	220 & 10,15	1.473	S	
			1.470	VW	
			1.463	VW	
			1.457	VW	
			1.441	VW	
1.412	VVW	21,11	1.420	W	
1.372	VW	10,16	1.387	M	
			1.376	VW	

* S = Strong, W = Weak, M = Medium, V = Very.
The intensities follow the order of S > MS > M > W > VW > VVW.

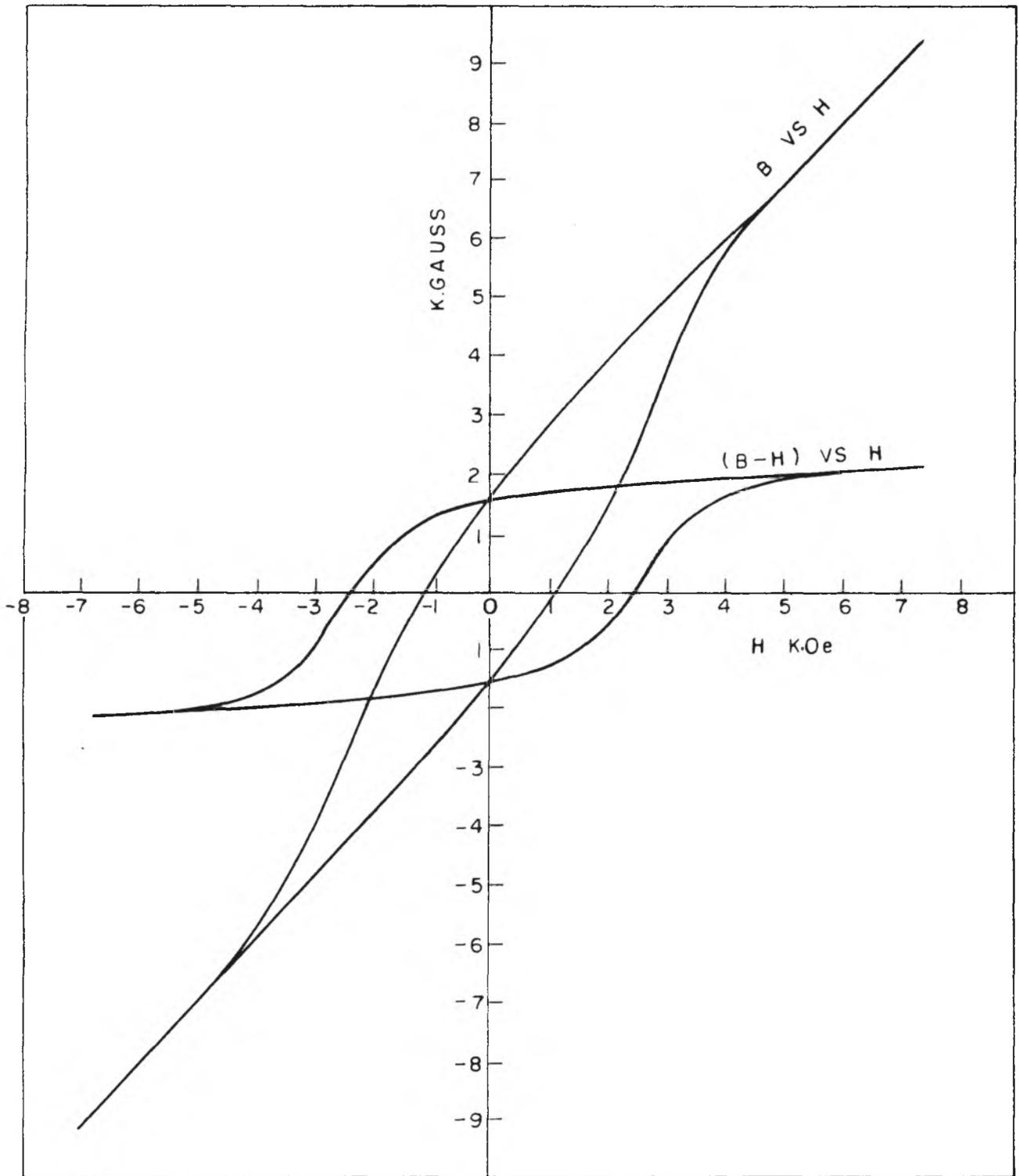


Fig.9. HYSTERESIS LOOP OF A SAMPLE OF SILVER-LANTHANUM FERRITE AT ROOM TEMPERATURE

MAGNETIC PROPERTIES

B-H Measurements: The variation of induction, B, with applied magnetic field, H, was measured for samples prepared under different conditions. The values of $4\pi I_s$ (at $H = 7000$ Oe); remanence, B_r , induction coercivity, B_{H_c} , intrinsic coercivity, I_{H_c} , density, d, and saturation magnetization per gram, σ , for the samples reacted at 1300°C , ball milled for 15 hours and pressed into pellets under a pressure of 3000 lbs/sq.cm. are presented in table 4. As will be explained in the next chapter, the ball milled samples of silver lanthanum ferrite and thallium lanthanum ferrite decompose at 900°C , so the pellets were heated at a fast rate when passing through the above mentioned temperature range in order to bring them to the desired sintering temperature. The saturation magnetization per gram at room temperature was calculated from I_s using the relation $\sigma = I_s/d$. A B-H plot for one of the samples sintered at 1300°C is shown in figure 9.

A number of compounds with varying ratios of $(\text{Ag}_2\text{O} + \text{La}_2\text{O}_3) : \text{Fe}_2\text{O}_3$ were formed and their magnetic properties studied. These compounds have the general formula $(\text{Ag}_{\frac{1}{2}}\text{La}_{\frac{1}{2}})0. x\text{Fe}_2\text{O}_3$ where x ranges from 5 to 7. X-ray diffraction results showed that all these formed homogeneous single phase products with magnetoplumbite structure when reacted at 1300°C . The intensities of diffraction peaks were nearly identical with that of the pure silver lanthanum ferrite, $(\text{Ag}_{\frac{1}{2}}\text{La}_{\frac{1}{2}})0.6\text{Fe}_2\text{O}_3$

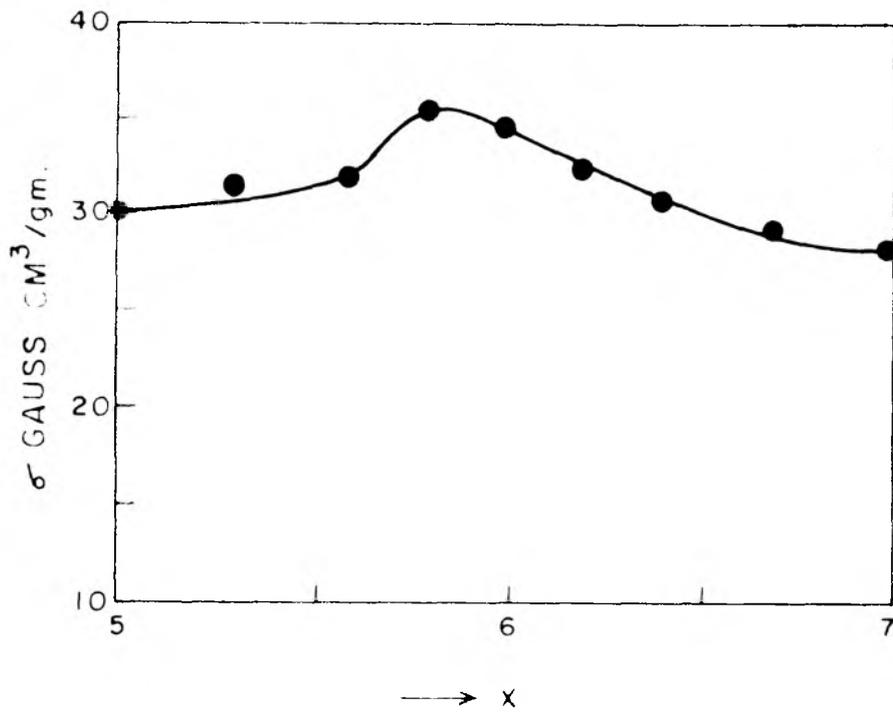
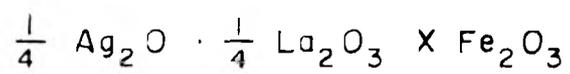


Fig. 10. THE VARIATION OF σ WITH X IN THE COMPOSITION



hence no attempt could be made to find out location of vacancies or interstitials created by the departure from the stoichiometry.

T A B L E 4

MAGNETIC PROPERTIES OF SILVER LANTHANUM FERRITE AS A FUNCTION OF SINTERING TEMPERATURE.

SAMPLES WERE REACTED AT 1300°C, BALL MILLED FOR 15 HOURS AND PRESSED UNDER A PRESSURE OF 3000 Lbs/Sq. Cm.

Sintering temp. °C	$4\pi I_s$ gauss	B_r gauss	BH_c Oersted	I^H_c Oersted	density gm/cc.	σ gauss-cm ³ /gm.
1100	835	735	700	4300	3.51	19.0
1200	1475	1295	1000	3550	4.58	25.4
1300	2105	1595	1100	2450	4.99	33.7
1350	2170	1535	900	1750	4.99	34.6

The magnetic properties were determined and the results are summarised in table 5. Figure 10 shows the variation of saturation magnetisation per gram as a function of x. The saturation magnetization shows a maxima at $x = 5.8$ instead of 6. This behaviour is also observed in barium ferrite⁵⁵ and may be due to the possibility that Fe^{3+} ion vacancies in the lattice are created at the favourable sites. The optimum value for x arise from the fact that at lower x there would be many vacancies causing a decrease in the super-exchange interactions. In other words, in certain localised regions the ordered chains of magnetic dipoles are terminated so frequently that in effect they become a random array of

dipoles, which causes a decrease in the magnetic moment. At higher x values we would have Fe³⁺ ions either outside the magnetoplumbite structure or at sites where they would not form a part of the magnetic ordered array so that they merely have the dilution effect causing a decrease in the magnetic moment.

T A B L E 5

MAGNETIC PROPERTIES OF THE COMPOSITIONS $\frac{1}{4}\text{Ag}_2\text{O} \cdot \frac{1}{4}\text{La}_2\text{O}_3 \cdot x\text{Fe}_2\text{O}_3$
 REACTED AT 1300°C AND GROUND FOR 15 HOURS WHEN
 x VARIED FROM 5 TO 7.

x	$4\pi I_s$ gauss	B_{H_c} Oersted	I_{H_c} Oersted	density gm/c.c.	$\frac{\sigma}{\rho}$ gauss cm ³ / gm.
5.0	1850	1325	2600	4.86	30.2
5.3	1920	1400	2700	4.86	31.3
5.6	1940	1510	2800	4.86	31.8
5.8	2150	1575	2800	4.85	35.2
6.0	2075	1530	2800	4.78	34.4
6.2	1910	1430	2800	4.75	32.0
6.4	1800	1375	2750	4.70	30.5
6.7	1720	1280	2700	4.71	29.0
7.0	1650	1200	2700	4.70	28.0

Curie Temperature: Curie temperature of silver lanthanum ferrite was found to be 435 ± 5°C as compared to 450°C for barium ferrite. It is felt that the lower values of this compound can be attributed to small structural changes associated with the incorporation of ions of slightly

different radii^{62,63} compared to Ba^{2+} ions. It is plausible to suggest that this causes slight changes in the $Fe^{3+} - O^{2-} - Fe^{3+}$ angles in the neighbourhood of these ions. The super-exchange interaction is fairly sensitive to changes in these angles and hence a change in Curie temperature is understandable.

Effect of addition of bismuth oxide & Aluminium oxide: It is well known that bismuth oxide improves the magnetic properties of barium ferrite to a considerable extent⁵⁵. The effect of this compound on silver lanthanum ferrite was, therefore, studied. 5% bismuth oxide, Bi_2O_3 , was added to the mixture before the reaction and the pellets were pressed and sintered at various temperatures as described earlier. It was found that the magnetic properties showed a marked deterioration in these samples. The values of $4\pi I_s$, B_r , B_{H_c} , H_c and density for these samples containing Bi_2O_3 are given in Table 6. The x-ray diffraction pattern of the sample heated at $1300^\circ C$ for 3 hours was analysed and it was found to have lines attributable to free $\alpha - Fe_2O_3$ and metallic silver.

The same result was obtained if silver lanthanum ferrite was first formed by heating the constituent oxides at $1300^\circ C$ and then bismuth oxide was added to it and the pellets made. The results of the magnetic measurements on the pellets sintered at different temperatures are reproduced in table 7.

T A B L E 6

EFFECT OF Bi_2O_3 AND Al_2O_3 ON THE MAGNETIC PROPERTIES OF SILVER LANTHANUM FERRITE PELLETS SINTERED AT 1300°C . Bi_2O_3 WAS ADDED TO THE MATERIAL BEFORE THE REACTION.

Starting composition	Sintering temp. $^\circ\text{C}$	$4\pi I_s$ gauss	B_r gauss	B_{Hc} Oe	I_{Hc} Oe	density gm/c.c.
$(\text{Ag}_2\text{O})_{\frac{1}{2}} (\text{La}_2\text{O}_3)_{\frac{1}{2}}$	1100	770	705	650	4000	5.03
$(\text{Fe}_2\text{O}_3)_6 (\text{Bi}_2\text{O}_3)_{0.12}$	1200	930	865	650	3100	5.06
	1300	1030	960	650	1900	5.06
	1350	1050	900	600	1000	5.06

$(\text{Ag}_2\text{O})_{\frac{1}{2}} (\text{La}_2\text{O}_3)_{\frac{1}{2}}$						
$(\text{Fe}_2\text{O}_3)_{6-x} (\text{Al}_2\text{O}_3)_x$						
x = 0.2	1300	1285	1040	850	4100	4.90
x = 0.4	1300	955	760	675	4300	4.86
x = 0.7	1300	570	450	400	4300	4.82
x = 1.0	1300	250	210	175	4500	4.85

T A B L E 7

MAGNETIC PROPERTIES OF SILVER LANTHANUM FERRITE WHEN 5% Bi_2O_3 WAS ADDED TO IT AFTER THE REACTION AT 1300°C . PELLETS WERE PRESSED WITHOUT BALL MILLING THE MATERIAL.

Sintering temp. $^\circ\text{C}$	$4\pi I_s$ gauss	density gm/c.c.	σ gauss Cm^3/gm .
"as-pressed"	1640	3.68	35.5
500	1640	3.68	35.5
900	1315	3.73	28.0
1000	1095	3.78	23.0
1150	1230	4.16	23.5

On comparison with the samples free from Bi_2O_3 , it can be concluded that Bi_2O_3 reacts with La_2O_3 from the magnetoplumbite phase forming a more stable double oxide of lanthanum and bismuth. The magnetoplumbite phase which is no longer stable without lanthanum oxide decomposes partially into the constituent oxides. It is, however, interesting to note that the density increases considerably in the presence of Bi_2O_3 . In fact the increase is almost as large as that observed in the case of barium ferrite when bismuth oxide is added to it. The effect of this impurity on the ferrites containing lanthanum will be discussed later in greater detail in chapter IV.3.

Similar results were obtained when substitution of Fe^{3+} ions by Al^{3+} ions was attempted. The x-ray results indicated the decomposition of silver lanthanum ferrite and the magnetic properties showed a rapid decrease with increasing Al^{3+} concentration. The results are included in table 5. LaAlO_3 is known to be a stable compound with perovskite structure⁶⁴. It is likely that this is more stable compound of lanthanum as compared to silver lanthanum ferrite so that the latter decomposes to give the former in the presence of Al^{3+} ions.

THALLIUM LANTHANUM FERRITE

Thallium lanthanum ferrite $Tl_{\frac{1}{2}}La_{\frac{1}{2}}Fe_{12}O_{19}$ was prepared by reacting a mixture of thallous nitrate, lanthanum oxide and α -ferric oxide (1:1:24) at temperatures $1100^{\circ}C - 1300^{\circ}C$ in air. The conclusion that thallium ions stay as monovalent Tl^{1+} in the magnetoplumbite structure and do not change to the trivalent Tl^{3+} state during the course of the solid state reaction at elevated temperatures is based on the following indirect arguments.

(1) The electronic configuration of the monovalent thallium ion is 2.8. 18.32. 18.2 and the $6s^2$ electrons in the last orbital form an inert pair which gives them an extra stability. Thus compounds of monovalent thallium are more stable than the trivalent thallium and thallic salts are oxidizing agents.

(2) If during the reaction Tl^{1+} ions get oxidized to Tl^{3+} ions, the corresponding number of ferric ions will have to be reduced to the divalent ferrous state, which may not be easy under the conditions of reaction.

X-ray Results:

The x-ray powder diffraction pattern of thallium lanthanum ferrite was found to be identical with that of the corresponding silver compound showing it to be isomorphous with the latter. The values of the cell constants as calculated from the diffraction peaks on the basis of a hexagonal unit cell are $a = 5.89$, $c = 23.4$.

Kinetics of Reaction: The percent reaction yield of thallium lanthanum ferrite at different reaction temperatures was determined by the procedure described earlier. The results are summarized in the table 8.

T A B L E 8.

REACTION YIELD OF THALLIUM LANTHANUM FERRITE AT DIFFERENT TEMPERATURES.

Reaction temp. °C.	$4 \pi I_s$ gauss	d gm/cm.	σ gauss.cm ³ /gm	% yield
1100	485	3.25	11.8	32
1200	1270	3.32	30.4	82
1300	1570	3.37	37.0	100
1350	1475	3.37	34.8	94

It can be seen that the reaction is completed at 1300°C in three hours. Here again, as in the case of silver lanthanum ferrite, the reaction temperature is higher than that of barium ferrite. In fact the reaction temperature of all similar ferrites containing lanthanum is found to be higher than the corresponding compounds of barium, strontium or lead. The reason for this difference in the reaction temperature will be discussed in some detail in chapter 4.3.

Curie Temperature: Curie temperature of thallium lanthanum ferrite as determined by the method reported earlier had been found to be 430 ± 5°C. This value is comparable to the other compounds having the same general formula.

B-H Measurements: The material reacted at 1300°C was ground under water in the ball mill for 15 hours. Pellets for making magnetic measurements were pressed from the ground sample under a pressure of 3000 lbs/sq.cm. These pellets were sintered at various temperatures as described earlier. The results of the magnetic measurements for sintering temperatures higher than 1100°C are reported in table 9. The results obtained from pellets sintered at lower temperatures are included in the next chapter.

T A B L E 9.

MAGNETIC PROPERTIES OF THALLIUM LANTHANUM FERRITE AT DIFFERENT SINTERING TEMPERATURES ABOVE 1100°C.

Sintering temp. °C.	$4 \pi I_s$ gauss	B_r gauss	$B H_c$ Oersted	$I H_c$ Oersted	density gm/c.c.	σ gauss.cm ³ /gm.
1100	935	820	750	3700	3.42	21.8
1200	1495	1230	1000	3400	4.15	28.6
1300	2140	1630	1300	2700	4.79	35.5
1350	2260	1600	1100	2050	4.85	37.0

Addition of Bismuth Oxide: 5% bismuth oxide was added to the reacting components before the reaction and the magnetic measurements were made in the usual way. It was found that this addition spoiled the magnetic properties as reported earlier for studies on silver lanthanum ferrite. The results are summarized in table 10.

T A B L E 10.

EFFECT OF Bi_2O_3 ADDITION ON THE MAGNETIC PROPERTIES
OF THALLIUM LANTHANUM FERRITE

Sintering temp. °C.	$4\pi I_s$ gauss	B_r gauss	$B_c^{H_c}$ Oersted	$I_c^{H_c}$ Oersted	density gm/c.c.
1100	860	740	700	3500	4.95
1200	1150	950	750	3150	5.01
1300	1400	1120	750	2250	5.04
1350	1440	1120	700	1750	5.05

The reason for this decrease in saturation magnetization on addition of Bi_2O_3 will also be discussed in detail in the next chapter.

It appears that the size rather than the electronic configuration of the A ions in the compounds $\text{AFe}_{12}\text{O}_{19}$ is the deciding factor of the stability of the magnetoplumbite phase. Table 11 summarizes the results of the attempts to form magnetoplumbite compounds together with the radii of the A ions used. A weighted average of the radii has been taken in the case of A ions consisting of a combination of two ions of different radii. It can be seen that the positive results are obtained only in the case of A ions with radii in the range of 1.06 to 1.40 Å. The ion $(\text{Cs}_{\frac{1}{2}}^{1+} + \text{La}_{\frac{1}{2}}^{3+})$ with radius equal to 1.41 is bigger and $(\text{Cu}_{\frac{1}{2}}^{1+} + \text{La}_{\frac{1}{2}}^{3+})$ and $(\text{Li}_{\frac{1}{2}}^{1+} + \text{La}_{\frac{1}{2}}^{3+})$ ions are smaller than required for the formation of a stable magnetoplumbite phase. Summergrad and Banks¹¹ had tried to synthesize the compound $\text{Na}_{\frac{1}{2}} \text{Pr}_{\frac{1}{2}} \text{Fe}_{12}\text{O}_{19}$ and analogous compounds using Sm^{3+} and Gd^{3+} in place of La^{3+} ions. They attributed

the failure to form these compounds to unfavourable reaction conditions. However, it would now seem that the real cause for the negative results is possibly the small ionic radii of the A ions used (table II). It is expected that the compounds $K_{\frac{1}{2}}Pr_{\frac{1}{2}}Fe_{12}O_{19}$ ^{$\times K Sm_{\frac{1}{2}}Fe_{12}O_{19}$} on the other hand would be formed with the magnetoplumbite structure as the radii of the A ions in these cases have the values 1.20 Å and 1.17 Å⁰ respectively.

T A B L E 11.

RADII OF A IONS IN THE HEXAGONAL FERRITES. AN AVERAGE HAD BEEN TAKEN WHEN THE A ION CONSISTED OF TWO IONS OF DIFFERENT RADII. P AND N STANDS FOR POSITIVE & NEGATIVE RESPECTIVELY.

Composition	A ion	Ionic radius \AA	Result	Reference
$\text{Cs}_{\frac{1}{2}}\text{La}_{\frac{1}{2}}\text{Fe}_{12}\text{O}_{19}$	$(\text{Cs}_{\frac{1}{2}}^{1+} + \text{La}_{\frac{1}{2}}^{3+})$	1.41	N	11
$\text{BaFe}_{12}\text{O}_{19}$	Ba^{2+}	1.34	P	2
$\text{Rb}_{\frac{1}{2}}\text{La}_{\frac{1}{2}}\text{Fe}_{12}\text{O}_{19}$	$(\text{Rb}_{\frac{1}{2}}^{1+} + \text{La}_{\frac{1}{2}}^{3+})$	1.31	P	11
$\text{Tl}_{\frac{1}{2}}\text{La}_{\frac{1}{2}}\text{Fe}_{12}\text{O}_{19}$	$(\text{Tl}_{\frac{1}{2}}^{1+} + \text{La}_{\frac{1}{2}}^{3+})$	1.31	P	present work
$\text{K}_{\frac{1}{2}}\text{La}_{\frac{1}{2}}\text{Fe}_{12}\text{O}_{19}$	$(\text{K}_{\frac{1}{2}}^{1+} + \text{La}_{\frac{1}{2}}^{3+})$	1.23	P	11
$\text{PbFe}_{12}\text{O}_{19}$	Pb^{2+}	1.20	P	2
$\text{Ag}_{\frac{1}{2}}\text{La}_{\frac{1}{2}}\text{Fe}_{12}\text{O}_{19}$	$(\text{Ag}_{\frac{1}{2}}^{1+} + \text{La}_{\frac{1}{2}}^{3+})$	1.20	P	present work.
$\text{LaFe}_{12}\text{O}_{19}$	La^{3+}	1.14	P	14
$\text{SrFe}_{12}\text{O}_{19}$	Sr^{2+}	1.12	P	2
$\text{Na}_{\frac{1}{2}}\text{La}_{\frac{1}{2}}\text{Fe}_{12}\text{O}_{19}$	$(\text{Na}_{\frac{1}{2}}^{1+} + \text{La}_{\frac{1}{2}}^{3+})$	1.06	P	11
$\text{Cu}_{\frac{1}{2}}\text{La}_{\frac{1}{2}}\text{Fe}_{12}\text{O}_{19}$	$(\text{Cu}_{\frac{1}{2}}^{1+} + \text{La}_{\frac{1}{2}}^{3+})$	1.05	N	present work
$\text{Na}_{\frac{1}{2}}\text{Pr}_{\frac{1}{2}}\text{Fe}_{12}\text{O}_{19}$	$(\text{Na}_{\frac{1}{2}}^{1+} + \text{Pr}_{\frac{1}{2}}^{3+})$	1.02	N	11
$\text{Na}_{\frac{1}{2}}\text{Sm}_{\frac{1}{2}}\text{Fe}_{12}\text{O}_{19}$	$(\text{Na}_{\frac{1}{2}}^{1+} + \text{Sm}_{\frac{1}{2}}^{3+})$	0.99	N	11
$\text{Li}_{\frac{1}{2}}\text{La}_{\frac{1}{2}}\text{Fe}_{12}\text{O}_{19}$	$(\text{Li}_{\frac{1}{2}}^{1+} + \text{La}_{\frac{1}{2}}^{3+})$	0.91	N	11
$\text{Na}_{\frac{1}{2}}\text{Gd}_{\frac{1}{2}}\text{Fe}_{12}\text{O}_{19}$	$(\text{Na}_{\frac{1}{2}}^{1+} + \text{Gd}_{\frac{1}{2}}^{3+})$	0.80	N	11

CHAPTER III

III. 2 : Sodium and Potassium Lanthanum
Ferrites ... 67

SODIUM AND POTASSIUM LANTHANUM FERRITES

Summergrad and Banks¹¹ synthesized new compounds of the formula $A_{\frac{1}{2}}^{1+}La_{\frac{1}{2}}^{3+}Fe_{12}O_{19}$ where A is an alkali metal ion K^{1+} , Na^{1+} or Rb^{1+} . Measurements of saturation magnetic moment of these compounds gave a value of 44 Bohr magneton when extrapolated to absolute zero. This compared favourably with the value 40 Bohr magneton observed for barium ferrite and that calculated on the basis of Anderson's theory of superexchange interactions⁷.

Although saturation magnetisation at absolute zero depends only on the spin arrangements, the coercivity and the variation of magnetic induction, B, with applied field, H, are properties which to a large extent depend on the conditions of preparation and subsequent treatments given to the samples. These properties are important from the point of view of application of the compounds as permanent magnet materials. A detailed study was, therefore, made on sodium and potassium lanthanum ferrites to investigate the effect of different conditions of preparation.

KINETICS OF REACTION

Effect of Surface Area: Out of many different samples of ferric oxide used for the preparation of these ferrites, positive results were obtained only with the samples having specific surface areas greater than 50 sq.meters/gm as was found in the case of preparation of silver and thallium lanthanum ferrites. The percent reaction yield x at different

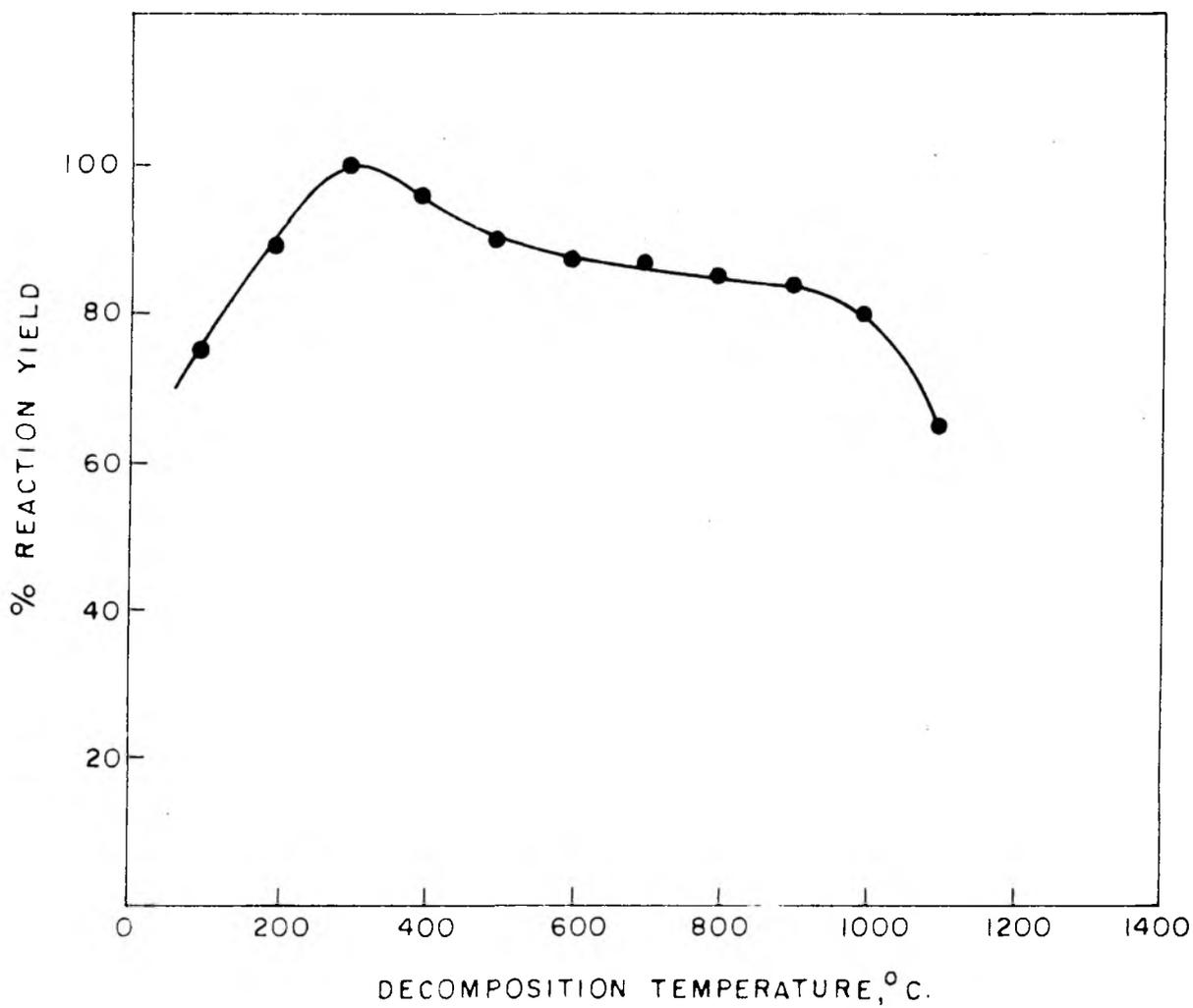


Fig. II. REACTION YIELD OF SODIUM LANTHANUM FERRITE AS A FUNCTION OF DECOMPOSITION TEMPERATURE OF FERRIC OXALATE

temperatures was calculated by the method already described, using the formula $x = \frac{\sigma}{\sigma_{max}} \times 100$ where σ_{max} was the maximum value of magnetization/gm and was assumed to correspond to complete reaction (40 c.g.s. units for sodium lanthanum ferrite).

Ferric oxide obtained by thermal decomposition of ferric oxalate possesses large specific surface area if the decomposition is carried out at low temperatures⁶⁰ ($\sim 300^{\circ}\text{C}$). The surface area decreases with the increase of decomposition temperature and becomes very small if this temperature exceeds 1000°C . The yield of sodium lanthanum ferrite formed at 1300°C from different samples of ferric oxide obtained by decomposition of ferric oxalate at various temperatures for half an hour was studied. The results are reproduced in table 12 and the variation of the reaction yield as a function of decomposition temperature of ferric oxalate is shown in figure 11. The maximum yield of sodium lanthanum ferrite is obtained from ferric oxalate sample heated at approximately 300°C . This appears to be due to the fact that at lower temperatures the decomposition of oxalate to oxide may only be partial whereas at higher temperatures the decomposition is complete but the surface area decreases. At decomposition temperatures beyond 1000°C the sintering of ferric oxide formed starts giving much bigger particles, hence the reaction yield decreases abruptly.

The effect of surface area of ferric oxide on the formation of sodium lanthanum ferrite can also be seen from the result of an experiment in which $\text{Fe}(\text{OH})_3$ obtained by the

T A B L E 12

REACTION YIELD OF SODIUM LANTHANUM FERRITE USING FERRIC OXIDE
OBTAINED BY THERMAL DECOMPOSITION OF FERRIC
OXALATE AT DIFFERENT TEMPERATURES.

Oxalate decom- position temperature (°C)	$4 \times I_s$ gauss	Density gm/c.c.	σ gauss.cm ³ / gm.	Reaction yield per cent
100	1320	3.49	30.0	75
200	1525	3.41	35.6	89
300	1710	3.40	40.0	100
400	1645	3.39	38.6	96
500	1530	3.38	36.0	90
600	1465	3.33	35.0	87
700	1465	3.33	35.0	87
800	1420	3.32	34.0	85
900	1380	3.27	33.6	84
1000	1220	3.02	32.0	80
1100	985	3.01	26.0	65

precipitation of FeCl₃ with ammonia was decomposed by heating it at 650°C for eight hours. The eight-hour heating decreased the surface area of the oxide considerably. This sample was ball milled for various durations. Since the surface area increases with the grinding time, samples of various areas were obtained. Sodium lanthanum ferrite was prepared from them by reacting them at 1300°C for 3 hours with the other component oxides (or carbonates). The values of reaction yield for these different samples are summarized in table 13. The reaction

T A B L E 13

THE EFFECT OF INITIAL GRINDING TIME OF FERRIC OXIDE ON THE
REACTION YIELD OF SODIUM LANTHANUM FERRITE

Grinding time hrs.	$4 \pi I_s$ gauss	density gm/c.c.	σ gauss.cm ³ / gm	Reaction yield percent.
0	210	3.51	4.8	12
20	585	3.52	13.2	33
40	795	3.52	18.0	45
60	1070	3.55	24.0	60
80	1270	3.55	28.4	71
100	1330	3.56	29.6	74
118	1310	3.57	29.2	73

yield increases with the grinding time of ferric oxide upto about hundred hours, after which it remains practically constant. The initial increase is due to the increase in the surface area of ferric oxide. After a certain time, about one hundred hours in the present case, an equilibrium is reached⁵⁹ and further grinding has no effect on the surface area of the powder, therefore, there is practically no increase in the reaction yield of sodium lanthanum ferrite. It is interesting to note that the reaction yield never becomes 100%, indicating that the ferric oxide sample heated at 650°C for a few hours possesses specific surface area less than 50 sq.meters even after grinding it in a ball mill for several hours.

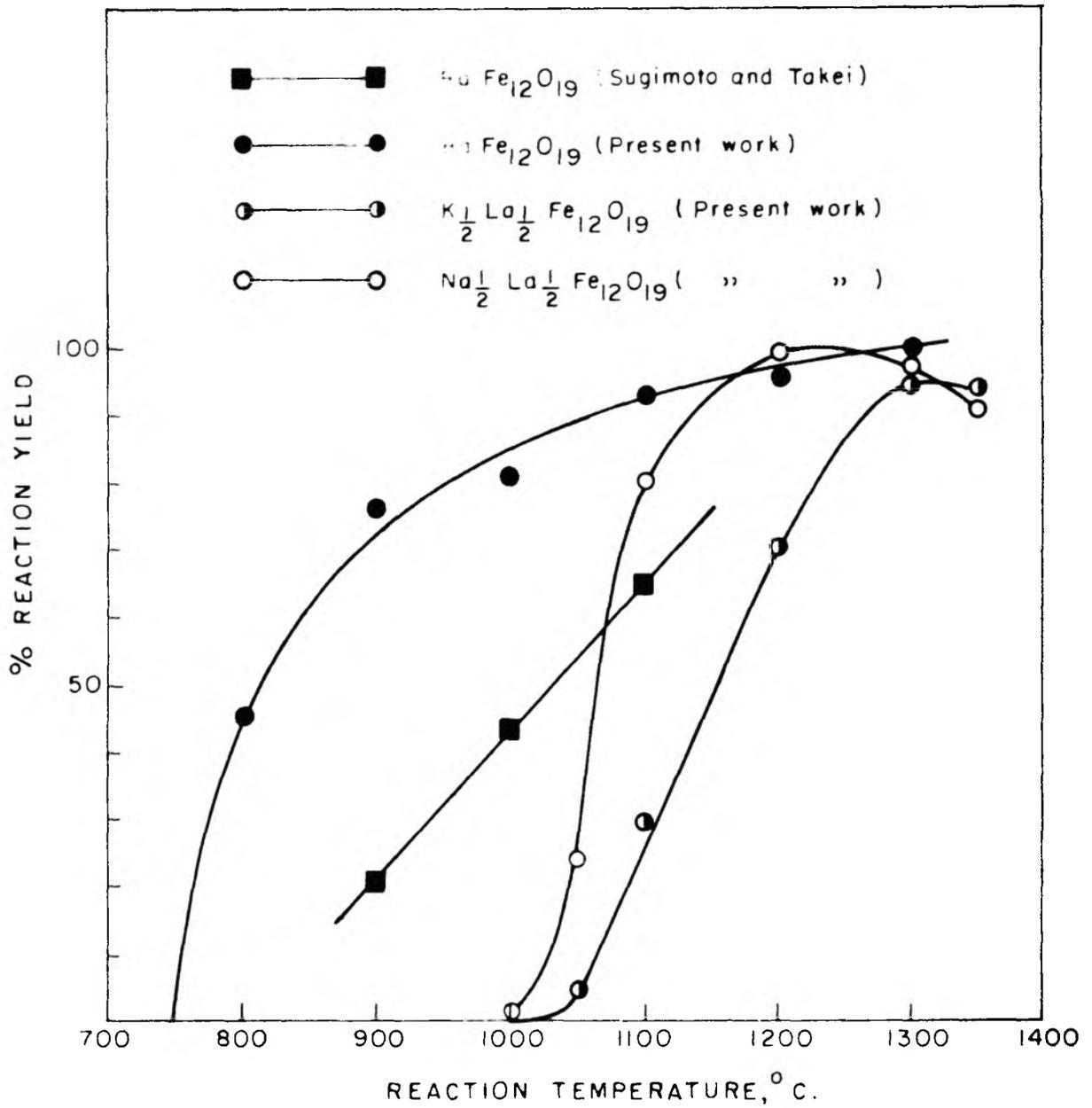


Fig.12. VARIATION OF REACTION YIELD WITH TEMPERATURE OF SODIUM AND POTASSIUM LANTHANUM FERRITES

Effect of Temperature: In order to determine the effect of temperature on the reaction yield of sodium and potassium lanthanum ferrites, B.D.H. ferric oxide and the other component oxides or carbonates were reacted for three hours at different temperatures. The results are given in table 14 and the variation of the percent yield with reaction temperature is shown in figure 12.

T A B L E 14

REACTION YIELD OF SODIUM AND POTASSIUM LANTHANUM FERRITES AT DIFFERENT TEMPERATURES

Composition	Reaction Temp. °C	$4 \pi I_s$ gauss	density gm/c.c.	σ gauss. cm ³ /gm	Percent yield
$Na_{\frac{1}{2}}La_{\frac{1}{2}}Fe_{12}O_{19}$	1000	35	3.30	0.8	2
	1050	405	3.34	9.6	24
	1100	1380	3.42	32.0	80
	1200	1730	3.46	39.8	99
	1300	1730	3.52	39.0	97
	1350	1615	3.57	36.0	90
$K_{\frac{1}{2}}La_{\frac{1}{2}}Fe_{12}O_{19}$	1000	0	3.20	X	X
	1050	80	3.26	2.0	5
	1100	530	3.30	12.8	32
	1200	1220	3.30	29.4	73
	1300	1685	3.35	40.0	100
	1350	1635	3.30	39.4	98

It can be seen that the "effective yield" increases with temperature and attains a maximum value at 1200°C for sodium lanthanum ferrite and at 1300°C for potassium lanthanum ferrite. Beyond these temperatures the "effective yield" started decreasing. These ferrites, like silver lanthanum ferrite, are also formed at higher temperatures as compared to barium ferrite. In the case of barium ferrite it is known that the rate of reaction is controlled by the rate of decomposition of barium carbonate³⁴ which is one of the starting materials for its preparation. In order to determine whether in this case also the rate of decomposition of sodium or potassium carbonate influenced the rate of formation of these ferrites, sodium lanthanum ferrite was synthesised using sodium peroxide (Na_2O_2 decomposition temperature 460°C) and sodium acetate (CH_3COONa decomposition temperature 324°C) instead of sodium carbonate as one of the starting materials. The rate of formation of sodium lanthanum ferrite was found to be the same in all the three samples containing different sodium compounds as the source of sodium ions, thus indicating that the higher reaction temperature of these ferrites is due to some other reason. As will be reported shortly, these ferrites are unstable at the temperatures 900-1000°C and decompose into the constituent oxides or binary compounds such as alkali metal ferrite or lanthanum ferrite. This probably is the reason for their reaction temperatures being higher than 1000°C. The results of similar studies on barium ferrite by Sugimoto and Takei⁵⁶ and by us are also included in the figure 12. The

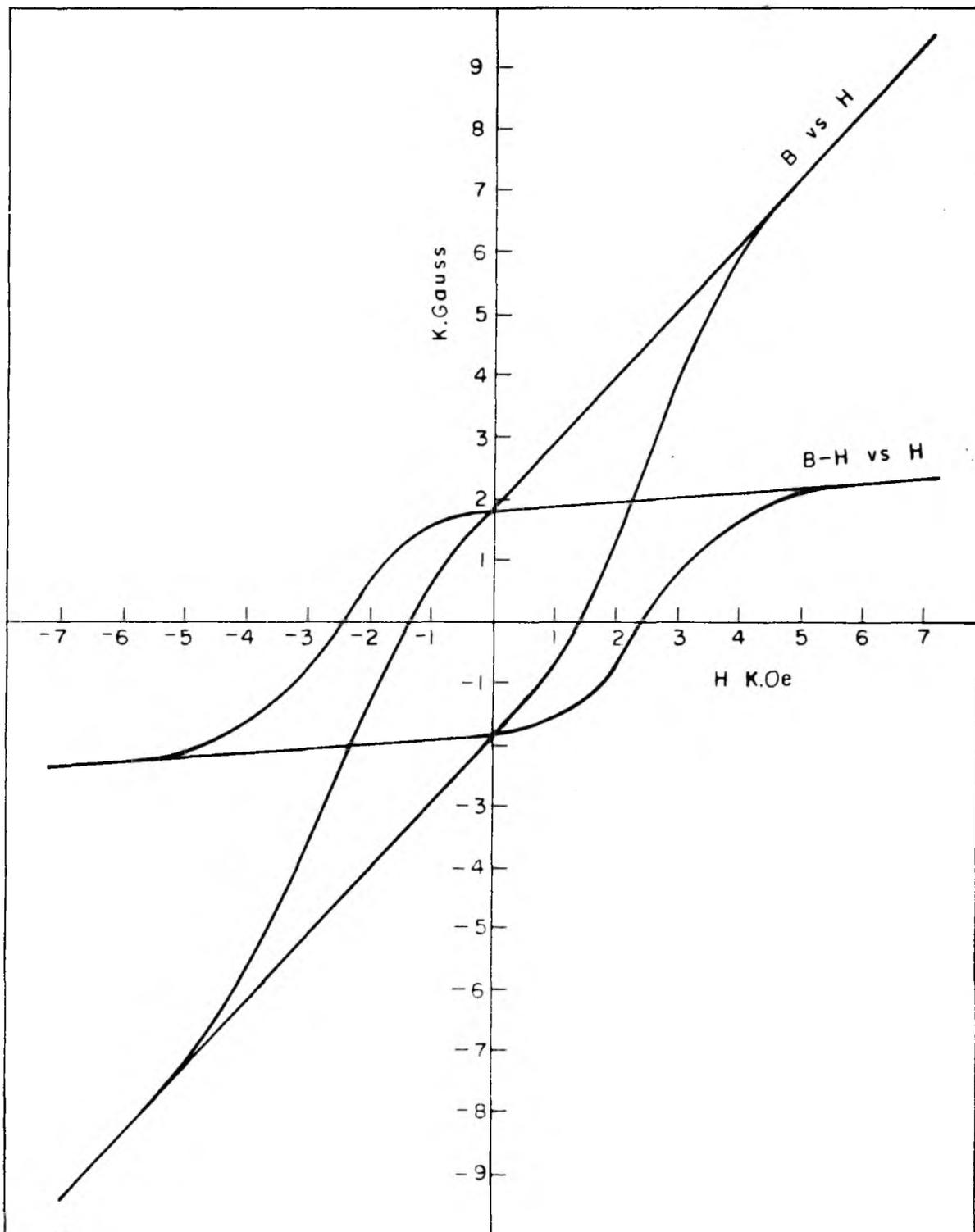


Fig.13. HYSTERESIS LOOP OF A SAMPLE OF SODIUM LANTHANUM
FERRITE AT ROOM TEMPERATURE

difference between their and our value of the barium ferrite reaction yield seems to arise from the fact that they had compared $4\pi I_s$ rather than σ (I_s/d) which is a true index of the amount of the magnetoplumbite phase present.

The reason for the decrease in x beyond 1300°C in the case of alkali metal lanthanum ferrites seems to be the same as described earlier for silver lanthanum ferrite.

MAGNETIC PROPERTIES

B-H Measurements: The variation of B and $B-H$ as a function of the applied field, H , was obtained for samples of sodium and potassium lanthanum ferrites prepared as described earlier and sintered at various temperatures upto 1350°C after grinding them for 15 hours and pressing into pellets under a pressure of 3000 lbs/sq.cm. Typical results are shown in figure 13 for sodium lanthanum ferrite and figure 3 for potassium lanthanum ferrite when sintered at 1300°C for one hour. The remanent induction, B_r , the induction coercivity, $B H_c$, and the intrinsic coercivity, H_c , were obtained from these graphs. The magnetization per gram, σ , was calculated from the formula $\sigma = I_s/d$ c.g.s. units as reported earlier. The values of these parameters for both the compounds sintered at various temperatures are presented in table 15.

Saturation Magnetization: Figures 14(a) and 14(b) show the variation of B_r and σ as a function of sintering temperatures for sodium lanthanum ferrite. One can see some interesting

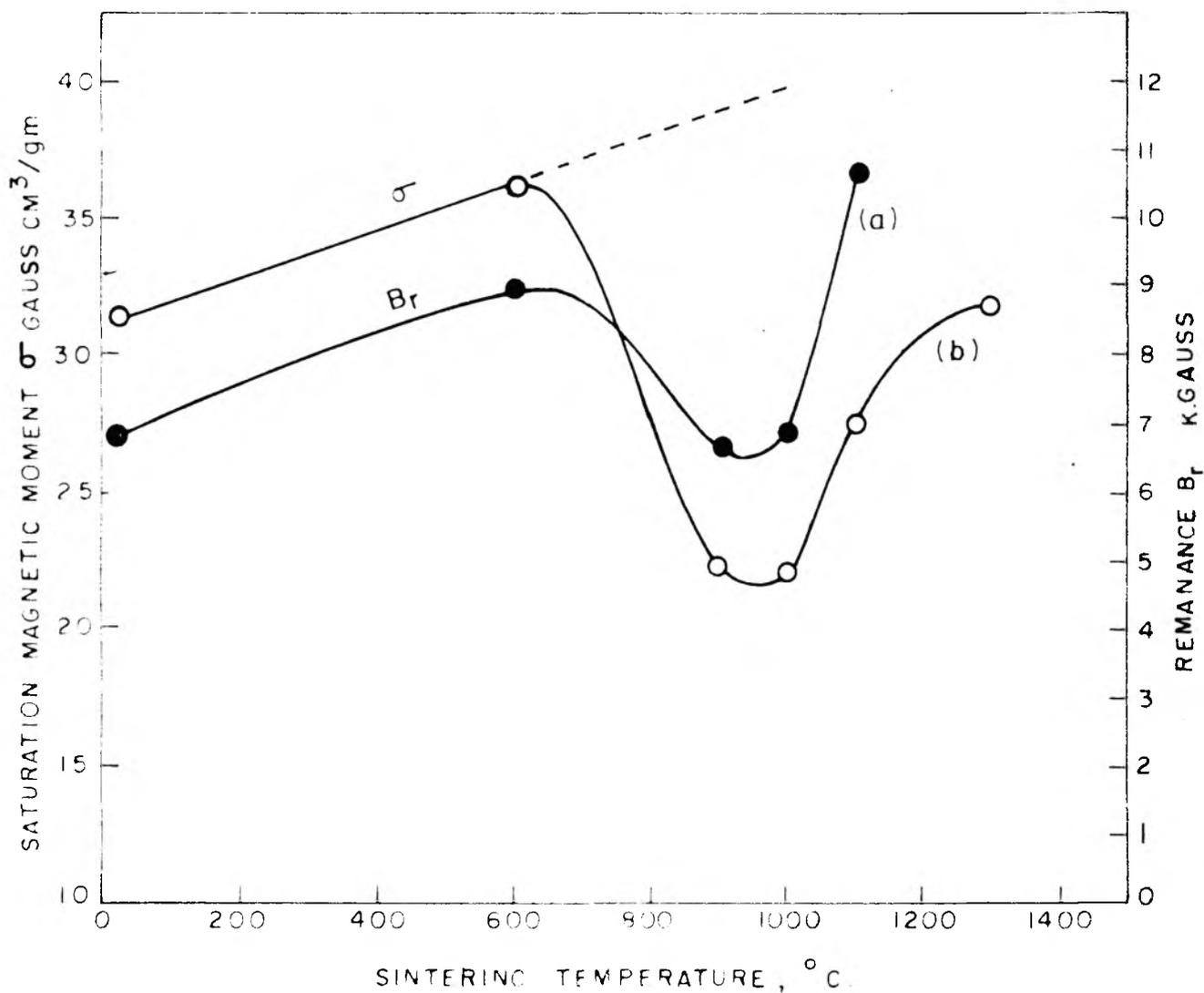
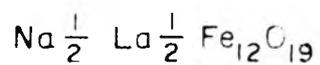


Fig.14.VARIATION OF SATURATION MAGNETIC MOMENT AND REMANACE AS FUNCTION OF SINTERING TEMPERATURE OF



T A B L E 15

MAGNETIC PROPERTIES OF SODIUM AND POTASSIUM LANTHANUM FERRITES
SINTERED AT DIFFERENT TEMPERATURES
(INDEPENDENT PELLETS WERE USED FOR EACH MEASUREMENT)

Composition	Sintering Temp. °C.	$4\pi I_s$ gauss	B_r gauss	B_c^H Oersted	I_c^H Oersted	density gm/cc	σ gauss cm ³ /gm.
$Na_{\frac{1}{2}}La_{\frac{1}{2}}Fe_{12}O_{19}$	"As-pressed"	1045	685	500	1550	2.67	31.5
	600	1205	900	600	1750	2.69	36.2
	900	765	670	600	3400	2.76	22.4
	1100	1430	1175	1050	3900	3.82	29.8
	1200	1840	1570	1400	3650	4.39	31.4
	1300	2325	1830	1350	2500	4.83	38.2
	1350	2300	1644	750	1100	4.83	37.4

$K_{\frac{1}{2}}La_{\frac{1}{2}}Fe_{12}O_{19}$	"As-pressed"	920	605	450	1600	2.53	29.3
	600	1000	715	550	1800	2.56	31.4
	900	610	585	500	2700	2.61	18.9
	1100	1169	985	800	3000	3.09	30.0
	1200	1007	1655	1300	3000	3.91	38.8
	1300	2445	1920	1400	2600	4.63	42.0
	1350	2510	1869	1100	1750	4.88	41.0

features. First, the "as-pressed" samples prepared after grinding fully reacted samples ($\sigma = 40$ gauss-cm³/gm) show a considerable decrease in σ value to about 30 units. This increases on heating and tends to approach the original value as shown by the

dotted line in figure 14. Secondly, B_r and σ start falling from 800°C upwards, attain a minimum at 900-1000°C and then rise again at higher temperatures upto 1300°C. The minimum values of B_r and σ obtained at 900-1000°C depend upon the duration of heating at these temperatures. If the heating is done for only one hour the values were 670 gauss and 22.4 gauss cm³/gm. respectively whereas after heating for 24 hours the values fell down to 455 gauss and 15.3 gaussxcm³/gm respectively for a sample of sodium lanthanum ferrite. A similar behaviour was observed in the case of potassium compound and also for silver and thallium lanthanum ferrites. The results of magnetic measurements on the last two compounds when the same pellets were sintered upto 1200°C are summarized in the table 16.

Regarding the first observation, it is clear that this lower value cannot be attributed to a partial decomposition because the x-ray diffraction pattern does not give any evidence of the same. Also it cannot be attributed to a loss, of the orientation achieved during pressing. If this had been the cause the original value would not have been restored on heating at relatively low temperatures of the order of 600 or 650°C, as was observed.

In order to check whether the relationship $\sigma = I_s/d$ was applicable to dilute magnetic systems, various samples containing different proportions of sodium lanthanum ferrite and an inert non-magnet material (α -Fe₂O₃) were prepared and pressed into pellets. The values of $4 \pi I_s$ for different

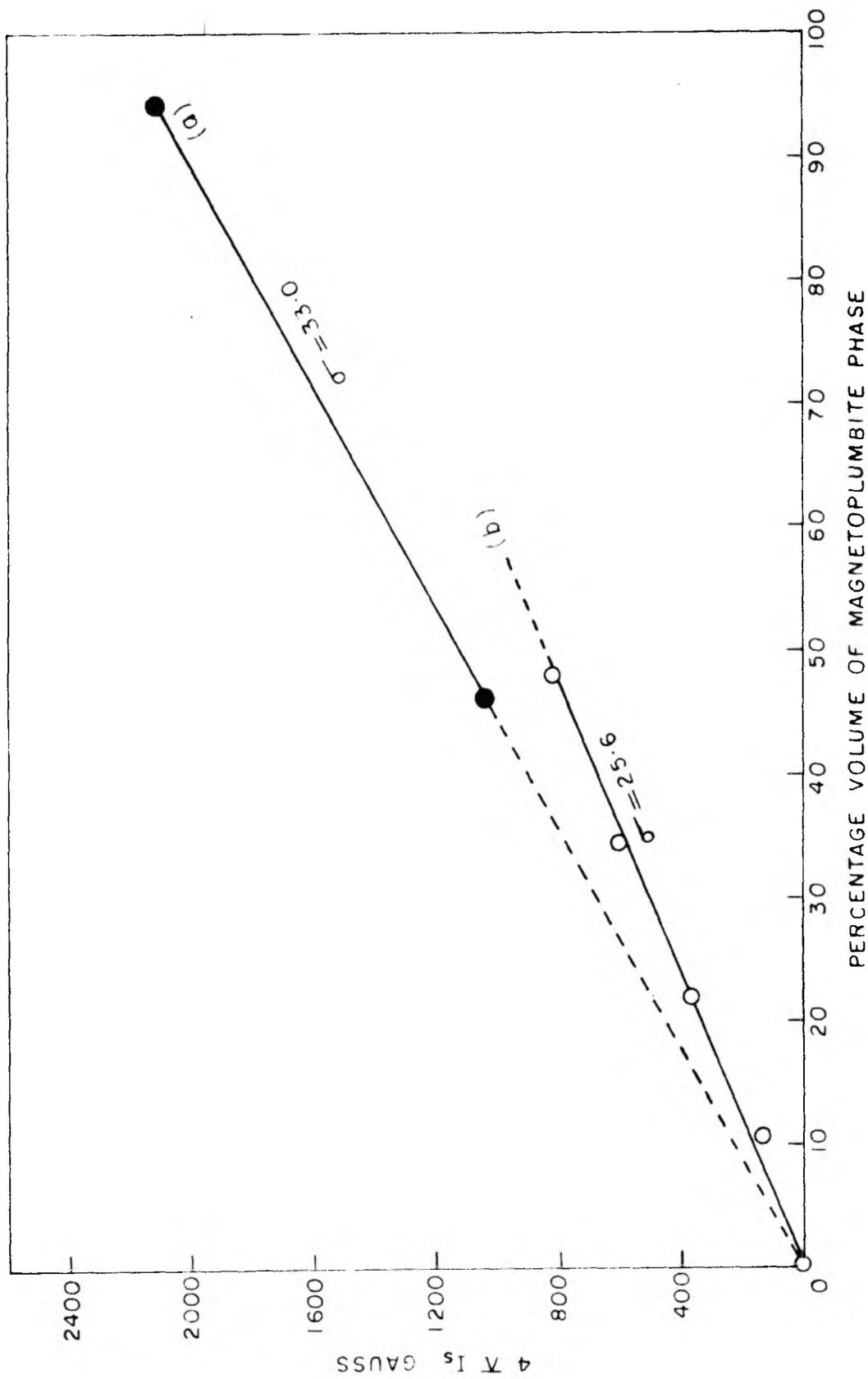


Fig. 15. EFFECT OF VOLUME DILUTION OF THE MAGNETIC PHASE ON BULK SATURATION MAGNETISATION

T A B L E 16

RESULTS OF MAGNETIC MEASUREMENTS ON SILVER AND THALLIUM LANTHANUM
FERRITES, USING THE SAME PELLET FOR MEASUREMENTS AT EACH
SINTERING TEMPERATURE

Composition	Sintering Temp. °C.	$4\pi I_s$ gauss	B_r gauss	B^H_c Oersted	I^H_c Oersted	density gm/cc	σ gauss cm ³ /gm
$Ag_{\frac{1}{2}}La_{\frac{1}{2}}Fe_{12}O_{19}$	"As-pressed"	645	475	350	1150	2.41	21.2
	600	1045	720	500	1200	2.47	33.6
	900	360	330	300	4000	2.49	11.5
	1100	890	750	700	3700	3.86	18.3
	1200	1090	970	800	3300	4.43	19.5
$Tl_{\frac{1}{2}}La_{\frac{1}{2}}Fe_{12}O_{19}$	"As-pressed"	910	625	450	1150	2.43	29.5
	600	1160	795	550	1200	2.49	37.0
	900	500	470	400	4000	2.52	15.7
	1100	835	740	650	3350	3.78	17.8
	1200	1000	850	700	2850	4.19	19.0

samples show (Fig.15(a)) the expected linear variation against the composition (percent magnetic material). The σ value calculated from the above equation remains constant. Another linear plot (Fig.15(b)) with different slope (ie. different σ) is obtained for samples heated at 600°C or 1300°C. This establishes that the value of σ decreases on grinding and is restored on heating at 600°C. That this decrease in saturation moment is recovered by heating the samples at low temperature is further confirmed by the results of the experiment in which

a sample of sodium lanthanum ferrite ground for 15 hours in a ball mill was heated first at 600°C, then mixed with usual binder and pressed into a pellet. The value of this sample was 36 gauss.cm³/gm, and it is comparable with the earlier values obtained at 600°C. This experiment also indicates that a loss of orientation could not be the cause of the above mentioned decrease in σ values, because in that case pellet formation after heating at 600°C should not have shown an increased σ value. Any link between improvement in σ with ferromagnetic to paramagnetic transition at Curie temperature was also ruled out by heating the pellet at many temperatures below and above the Curie point. No significant difference was observed. The improvement abruptly appeared at 600-650°C.

Although it is not possible to explain this behaviour precisely, it appears possible that the low σ values are due to some disorder brought about in the crystal due to grinding⁶⁵. The surface imperfections are readily removed, hence the improvement at 600°C is understandable.

In order to find the cause of decrease in σ in samples heated at 900-1000°C x-ray diffraction patterns were obtained from samples heated at different temperatures. It was found that upto 700°C magnetoplumbite was the only phase present. At 900-1000°C the pattern indicated a mixture of magnetoplumbite and α -Fe₂O₃, the lines due to the latter being more prominent. In fact the colour of the sample changed from the black colour of magnetoplumbite to the dark brown of α -Fe₂O₃.

At 1300°C a partial reformation of magnetoplumbite phase was observed. In samples heated at 900°C, lines due to some compounds of lanthanum or sodium were especially looked for but were not present. It can be seen that in partially decomposed sample of this ferrite (~50% decomposition), the proportion of lanthanum or sodium compounds would be less than five percent, hence it is not surprising that their lines were not observed. Blank experiments were carried out in which mixtures of $\text{La}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ (1:1) and $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ (2:1) were heated at 900°C for one hour. In both the cases compound formation was observed by x-ray diffraction, indicating that these would, indeed, be present in the decomposed samples of sodium, potassium, silver or thallium lanthanum ferrites heated at 900-1000°C.

In an attempt to see whether the decomposition at 900-1000°C and recombination at 1200-1300°C were completely reversible processes, various cycles of heating between the two temperatures (900°C and 1100-1300°C) were carried out. The results are given in table 17. Results of similar measurements on silver and thallium lanthanum ferrites are also included in this table. It can be seen that the σ values do go up and down at 1100°C and 900°C repeatedly on unsintered pellets or powdered samples. However, the original value of σ was never achieved once the sample was heated at 900°C for a long time. Such samples even after grinding in an agate mortar and heating at 1300°C for 6 hours gave a σ value of only 33 gauss.cm³/gm for

T A B L E 17

EFFECT OF REVERSIBLE HEATING CYCLES ON THE MAGNETIC PROPERTIES
OF SODIUM, POTASSIUM, SILVER AND THALLIUM LANTHANUM FERRITES

Composition*	Sintering Temp. °C.	$4 \pi I_s$ gauss	density gm/c.c.	σ gauss.cm ³ /gm.
$Na_{\frac{1}{2}}La_{\frac{1}{2}}Fe_{12}O_{19}$	900	495	2.57	15.3
	1100	890	3.85	18.4
	900	820	3.85	16.9
	1200	1120	4.46	20.0
	900	1120	4.46	20.0
	1300	1335	4.87	22.3
	900	1335	4.87	22.3
$K_{\frac{1}{2}}La_{\frac{1}{2}}Fe_{12}O_{19}$	900	610	2.56	18.9
	1100	870	3.34	20.7
	900	820	3.34	19.5
	1200	1545	4.23	29.0
	900	1485	4.23	27.9
	1300	1815	4.77	30.3
	900	1660	4.77	27.8
$Ag_{\frac{1}{2}}La_{\frac{1}{2}}Fe_{12}O_{19}$	900	360	2.49	11.5
	1100	730	3.52	16.4
	900	645	3.52	14.5
	1200	1050	4.63	18.0
	900	1005	4.63	17.2
	1300	1300	5.05	20.4
	900	1300	5.05	20.4
$Tl_{\frac{1}{2}}La_{\frac{1}{2}}Fe_{12}O_{19}$	900	500	2.52	15.7
	1100	835	3.72	17.8
	900	775	3.72	16.5
	1200	1075	4.19	20.4
	900	1045	4.19	19.8
	1300	1330	4.67	22.6
	900	1260	4.67	21.4

* Samples were ground, pressed and alternately sintered at 900°C and higher temperatures. Measurements were made on the same pellet at each temperature.

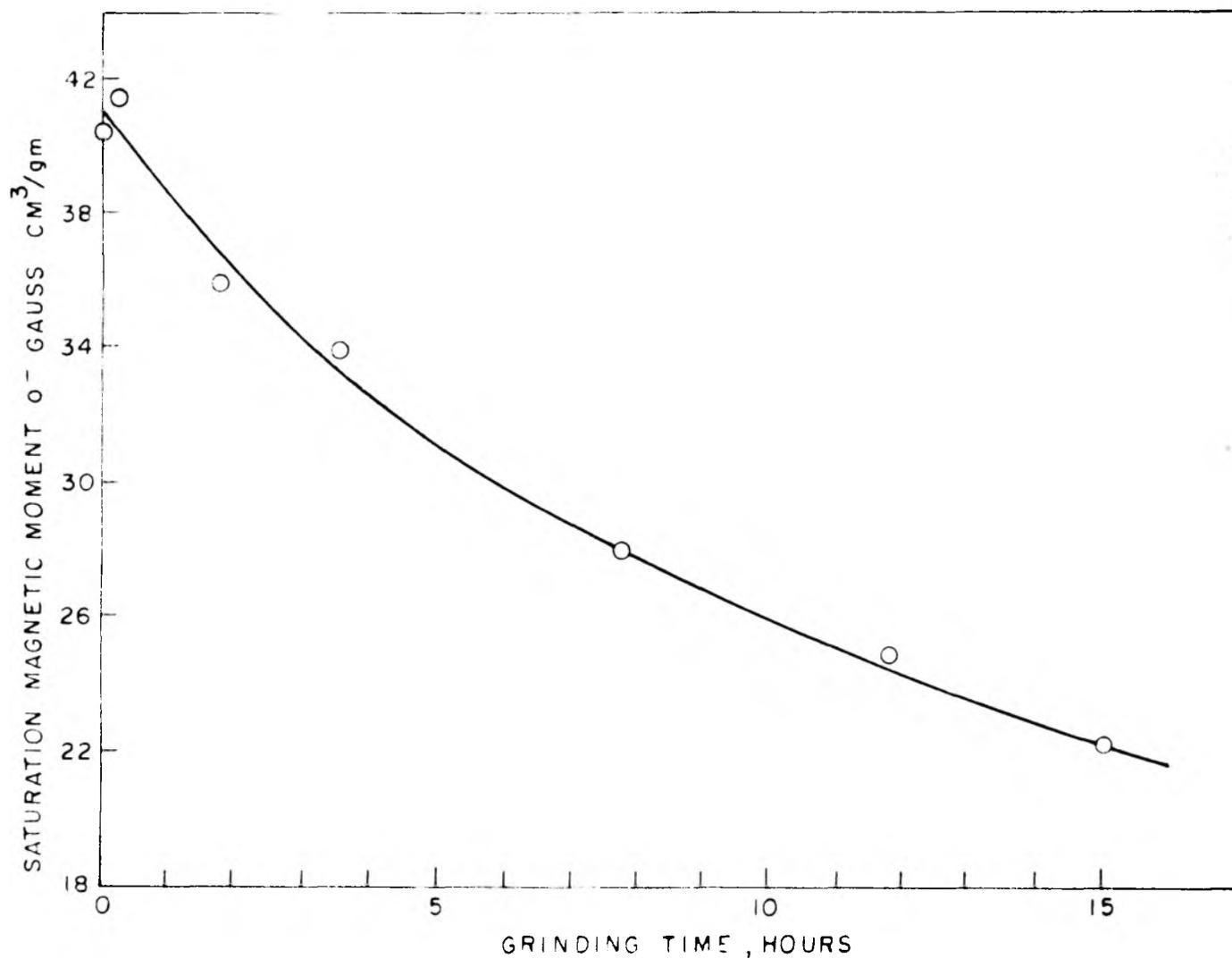


Fig 16. SATURATION MAGNETIC MOMENT AS A FUNCTION OF INITIAL GRINDING TIME FOR SAMPLES OF SODIUM LANTHANUM FERRITE HEATED AT 900 ° C. FOR 90 MINUTES

sodium lanthanum ferrite (original value 40), showing that the reaction remained incomplete. This clearly indicates that the λ - Fe_2O_3 obtained on decomposition at 900°C was of unreactive form, i.e. of low surface area.

It is also interesting to note that if pellets of completely reacted samples are quickly raised to 1350°C and sintered to a high density ($\sim 75\%$) and then lowered to 900 - 1000°C and subjected to a prolonged heating, no decomposition is observed. Similarly no decomposition is observed on heating the reacted samples at 900°C before grinding them in the ball mill. This indicates that the decomposition might be dependent on the particle size of the ferrite. The effect of particle size distribution was, therefore, investigated in some detail. Samples of sodium lanthanum ferrite were ground in a ball mill for different durations upto 15 hours. They were pressed into pellets and heated at 900°C for one and a half hours. The saturation magnetization was measured as usual and the results of the measurements are given in table 18.

The effect of grinding on σ can be seen from fig.16. Since the saturation magnetization per gram is proportional to the percentage of the magnetoplumbite phase, this curve indicates that the grinding facilitates decomposition.

Although this curve does not give a quantitative idea of the dependence of the decomposition on the actual particle size distribution, it points out qualitatively that smaller particles decompose faster than bigger ones. In fact it is quite likely that only particles below a certain critical

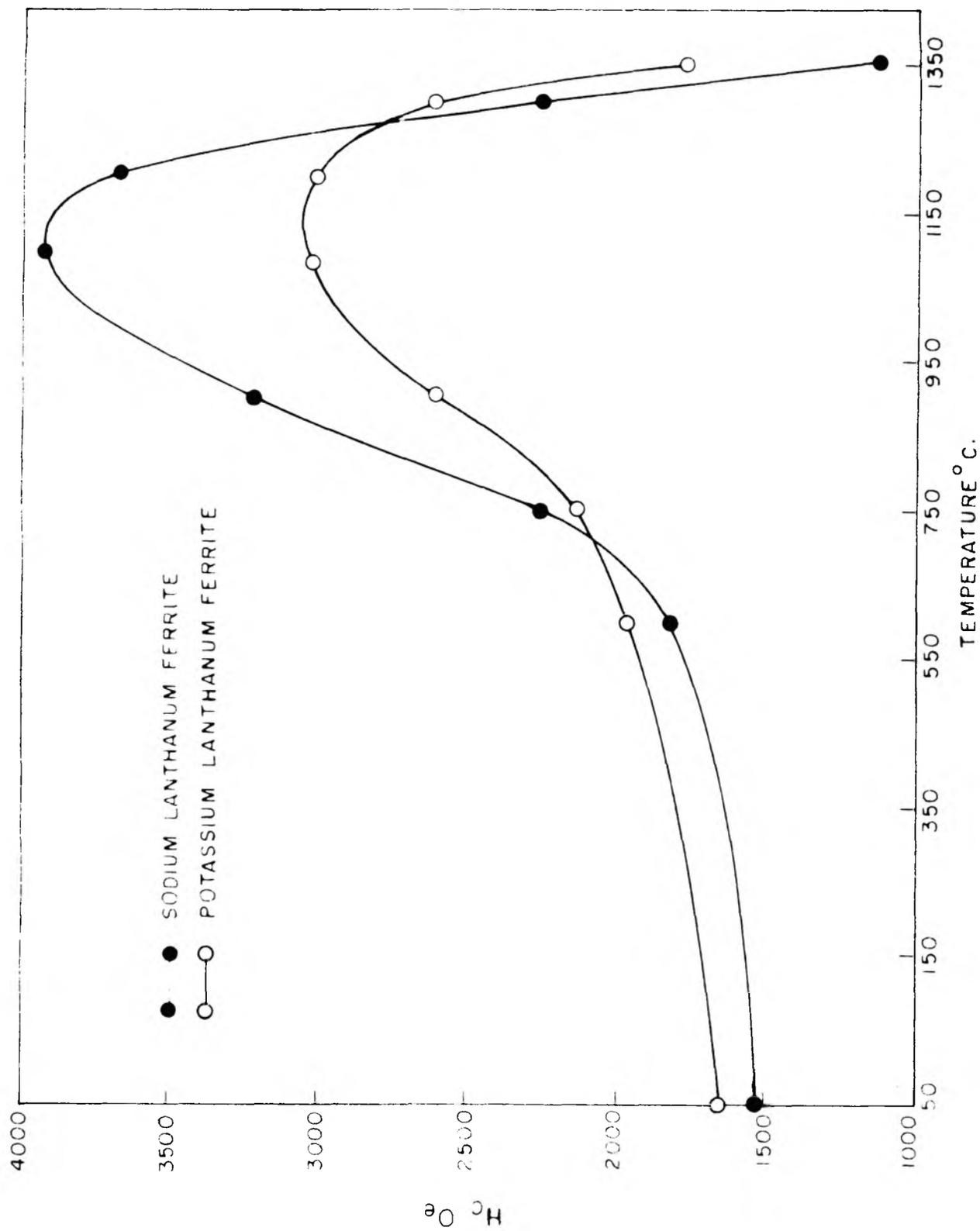


Fig.17. THE VARIATION OF INTRINSIC COERCIVITY OF SODIUM AND POTASSIUM LANTHANUM FERRITES AS A FUNCTION OF TEMPERATURE.

T A B L E 18

EFFECT OF INITIAL GRINDING ON THE DECOMPOSITION OF SODIUM
LANTHANUM FERRITE AT 900°C FOR $1\frac{1}{2}$ HOURS

Initial grinding time (hours)	$4 \pi I_s$ gauss ^s	density gm/c.c.	$\bar{\sigma}$ gauss.cm ³ /gm.
0	1650	3.25	40.4
1/4	1680	3.20	41.2
2	1380	3.05	36.0
3 1/2	1290	3.01	34.0
8	1055	3.00	27.9
12	920	2.97	24.8
15	825	2.95	22.2

diameter are capable of decomposing. Thus, increased grinding would convert more and more particles to below this critical diameter so that decomposition would increase with increasing grinding time.

Coercivity: Figure 17 shows the variation of intrinsic coercivity I_{H_c} as a function of sintering temperatures. For sodium lanthanum ferrite the intrinsic coercivity increased with temperature upto 1150°C, from where it started diminishing. A similar trend was observed for potassium lanthanum ferrite, although the maximum was observed at 1250°C. At all temperatures the coercivity of potassium compound was less than that of sodium lanthanum ferrite.

The decrease in $I H_c$ beyond a certain temperature can be attributed to more and more particles exceeding the critical domain size due to the increase in particle size during sintering. Whereas the magnetization changes in single domain particles can take place only through reversals and rotations in high fields, those in bigger particles can take place in much lower fields because of domain wall motion.

The steep rise in $I H_c$ in the range 800-1000°C is interesting. Since this temperature compares favourably with the decomposition temperature of the magnetic phase, it is plausible to suggest that the decomposition leaves the remaining mass of the magnetoplumbite phase with a much smaller particle size. If the decomposition starts from the surface and proceeds inwards, a fifty per cent decomposition would leave the final particle diameter about twenty percent less than the initial diameter. This may be enough to account for the observed increase in coercivity. It is even likely that the decomposition does not only proceed on the surface but in the bulk as well. This would lead to much smaller particles.

A similar decomposition may well explain a parallel increase in coercivity of barium ferrite observed around 800-1000°C¹⁸. However, in this case a difficulty arises due to the fact that no evidence to confirm this decomposition has so far been obtained from x-ray or saturation magnetization measurements. Therefore, this could only be taking place in traces. In order that such a trace decomposition has any effect on the particle size, it has to propagate through the body of the

crystallites leading to a sub-division of the particles.

Curie Temperature: Curie temperature of sodium and potassium lanthanum ferrites has been found to be 440°C. This value compares well with that obtained by Summergrad and Banks¹¹ and that of silver and thallium lanthanum ferrites as reported in the last chapter.

Effect of addition of bismuth oxide: As in the case of silver and thallium lanthanum ferrites, the addition of bismuth oxide to sodium and potassium lanthanum ferrites deteriorated considerably their saturation magnetization despite the fact that the increase in density was of the same order as that observed in barium ferrite. 5% Bi₂O₃ was added to the reacting mixture before the reaction at 1300°C for three hours and pellets were pressed applying a pressure of 3000 lbs/sq.cm. after grinding the mixtures for fifteen hours. Results of the magnetic measurements of samples sintered at various temperatures are given in table 19. The origin of this change will be discussed in chapter III.3.

It is thus concluded from the above experiments that although the alkali metal lanthanum ferrites are similar to barium ferrite with respect to crystal structure and magnetic properties such as saturation magnetization, coercivity and Curie temperature, there is a large difference in regard to their stability at elevated temperatures. The decomposition to the other oxides in the temperature range 900-1000°C raises the temperatures at which these compounds have to be heated

T A B L E 19

EFFECT OF Bi_2O_3 ADDITION ON THE MAGNETIC PROPERTIES OF SODIUM
AND POTASSIUM LANTHANUM FERRITES

Composition	Sintering Temp. °C.	$4\pi I_s$ gauss	B_r gauss	B^H_c Oersted	I^H_c Oersted	density gm/cc	σ gauss. cm ³ /gm
Sodium lanthanum ferrite	1100	980	890	800	4450	4.95	15.7
containing 5% bismuth oxide	1200	1555	1255	1100	3000	4.96	25.0
	1300	1635	1355	1000	2200	4.95	26.2
	1350	1670	1280	650	1300	4.95	26.8

Potassium lanthanum ferrite	1100	905	830	750	3400	4.70	15.3
containing 5% bismuth oxide	1200	1500	1150	1000	2700	4.92	24.2
	1300	1590	1210	950	2200	4.95	25.5
	1350	1620	1200	700	1800	4.95	26.0

for complete reaction and sintering. This puts these compounds at a disadvantage as compared to barium ferrite. Also the advantage associated with the addition of bismuth oxide is not available for these compounds.

CHAPTER III

III. 3 : Effect of Impurities on Hard Ferrites ... 85

EFFECT OF IMPURITIES ON HARD FERRITES

After the usefulness of the hexagonal ferrites as permanent magnet materials had been established, various attempts were made by several workers to improve their quality by certain additions and substitutions. A summary of the past work is already described in chapter I. It will be recalled that Okamura⁵⁵ observed that small amounts of bismuth oxide enhance the saturation and remanent magnetization of barium ferrite, $\text{Ba}_0.6\text{Fe}_2\text{O}_3$, considerably. Whereas pure unoriented polycrystalline sample of barium ferrite sintered at 1100°C showed a saturation magnetization ($4\pi I_s$) 2100 gauss, remanence (B_r) 1500 gauss and coercivity (I_{H_c}) 3000 oersted, another identical sample containing $1\frac{1}{2}$ percent bismuth oxide had the corresponding values as 3600 gauss, 2300 gauss and 3750 oersted respectively. In an attempt to explain this remarkable observation, a detailed study of the effect of this and other impurities on barium and other hard ferrites has been made. In what follows the results, together with some plausible conclusions regarding the role of these impurities are reported.

Effect of Impurities on Barium Ferrite: Barium ferrite samples containing various impurities listed in column I of table 20 were formed by solid state reactions at 1000°C as described earlier. The products, on examination by x-ray diffraction, revealed that in all cases the magnetoplumbite phase was formed completely. No diffraction lines attributable to the impurity phase could be detected, presumably because their concentrations were too low.

T A B L E 20

EFFECT OF IMPURITIES ON THE MAGNETIC PROPERTIES OF BARIUM FERRITE
SAMPLES SINTERED AT 1100°C FOR HALF AN HOUR

Impurity	$4 \pi I_s$ gauss	B_r gauss	B^H_c Oersted	I^H_c Oersted	density gm/cc	σ gauss. cm ³ /gm
nil	2035	1630	1300	2800	3.66	44.2
5%Na ₂ B ₄ O ₇ · 10H ₂ O	2140	1620	1025	2350	4.45	38.2
5%CuMn ₂ O ₄	2375	1855	1200	2500	3.98	47.4
5%PbO	2980	2260	1600	2800	4.87	48.6
5%Bi ₂ O ₃	3280	2525	2100	2900	5.12	50.9

After grinding the reacted samples for 15 hours in a ball mill, pellets were pressed under a pressure of 3000 lbs/sq.cm. These pellets were sintered at 1100°C for half an hour and then subjected to magnetic measurements. The values of $4 \pi I_s$, B_r , B^H_c , and I^H_c for these products are given in the columns 2,3,4 and 5 respectively of this table. It is seen that magnetic properties improve on the addition of small amounts of low melting oxides. This increase is mainly due to the increase in the density of the samples because $4 \pi I_s = \sigma \times d$ where σ is the saturation magnetization per gram in c.g.s. units and d is the density of the pellets. The values of densities of these samples are given in column 6 of the above mentioned table. The increase in density of these samples is caused by greater volume shrinkage of their pellets as compared to the pellets of pure barium ferrite. The measurements of linear shrinkage of these samples

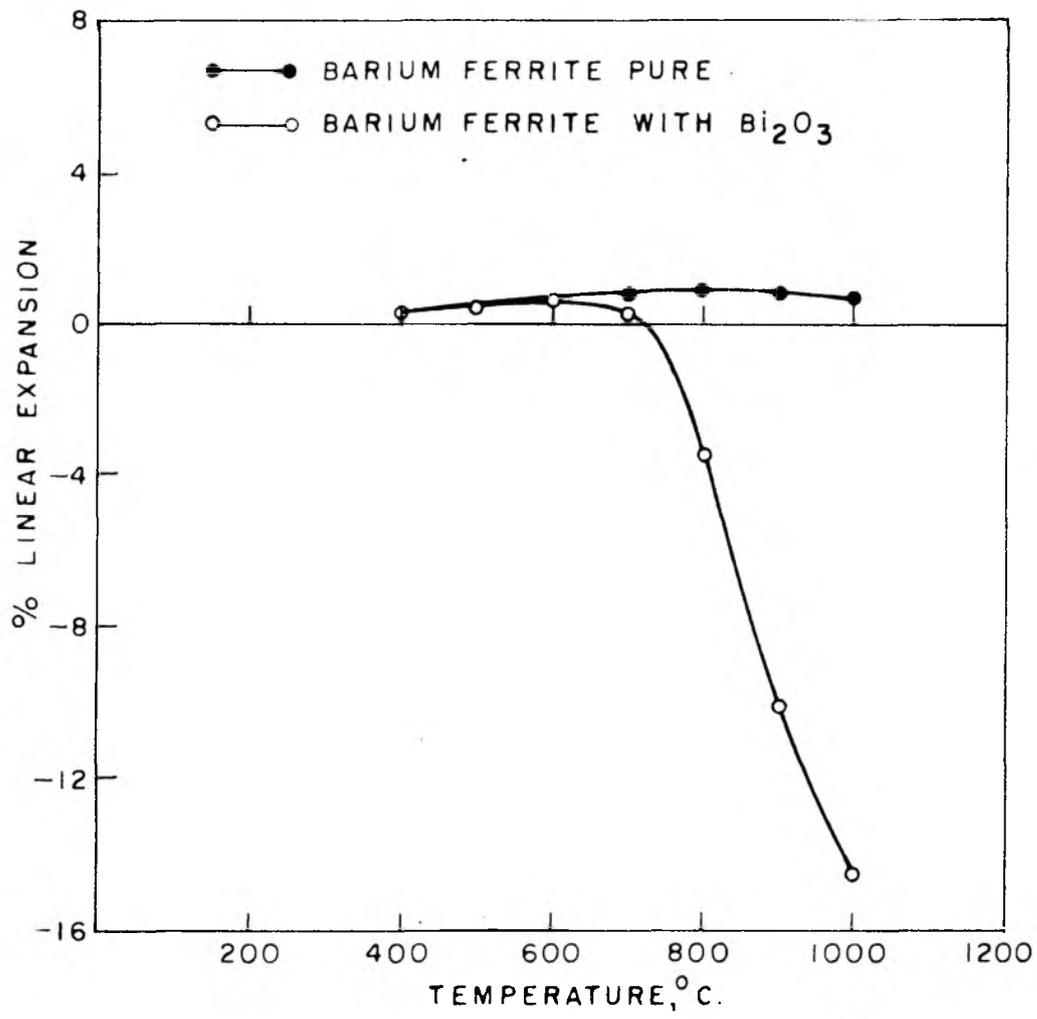


Fig.18. LINEAR SHRINKAGE ON HEATING SAMPLES OF BARIUM FERRITE WITH AND WITHOUT Bi₂O₃

during sintering were done as described earlier on 2 cm long rods pressed from samples reacted at 1000°C for 4 hours and ball milled under water for 10 hours. Figure 18 shows the variation of percent linear shrinkage of a sample of pure barium ferrite and that containing 6% Bi_2O_3 with the sintering temperature. It can be seen that the linear shrinkage, hence the density of the samples containing Bi_2O_3 increases at a rate much faster than in the case of pure compound. Similar results of shrinkage measurements on barium ferrite were also obtained by Sugimoto and Takei⁵⁴. The increased density is mainly responsible for higher value of $4\pi I$ in the impurity doped samples. However, the entire increase in $4\pi I$ cannot be attributed to the increase in density because in that case σ values (column 7; table 19) which are independent of density should have remained constant. This indicates some other changes in the samples which are responsible for changes in σ values. Thus σ for pure barium ferrite sintered at 1100°C has a value of 44 c.g.s. units, whereas those containing CuMn_2O_4 (M.P. $\sim 1000^{\circ}\text{C}$), PbO (M.P. 888°C) and Bi_2O_3 (M.P. 860°C) show an increase to 48, 49 and 51 units respectively and that containing borax, (M.P. 75°C) shows a decrease to 38 units. In the case of bismuth oxide, where the increase in σ is maximum, three probable causes for the increase can be thought of.

(1) At elevated temperatures bismuth oxide helps to increase the slight orientation produced in the pellets at the time of pressing them. Barium ferrite particles are platelets with their easy direction of magnetization perpendicular to the

plane of the plate. When the pressure is applied the platelets tend to lie flat, perpendicular to the direction of pressing. This introduces a partial anisotropy³² (compression anisotropy) which would increase at elevated temperatures if such rightly oriented particles grow at the cost of the remaining misaligned particles. With increase in orientation σ is also expected to increase.

(2) The presence of bismuth oxide helps in the formation of ferromagnetic phase. It is expected that in the temperature range in which the reaction of barium ferrite is carried out, bismuth oxide would exist as a liquid and this would furnish an easy path for the ions of the reacting oxides to diffuse and react, thus removing any unreacted oxides which might be present due to incomplete reaction at 1000°C.

(3) Bismuth ions, Bi^{3+} , from bismuth oxide replace those Fe^{3+} ions which have their magnetic moments antiparallel to the net magnetic moment of the unit cell.

The fact that the process (1) is partially responsible for the increase in σ has been established with the aid of the following results. Cubical pellets (~ 1 cm x 1 cm x 1 cm) were prepared from the reacted and ground samples of pure barium ferrite and that containing 5% Bi_2O_3 . These were sintered at various temperatures and magnetic measurements were made to determine the values of remanence in the direction of pressing (B_R^{\parallel}) and that in the direction at right angles to this direction (B_R^{\perp}). The value of the ratio $B_R^{\perp} / B_R^{\parallel}$ should be 1 for a completely random sample and zero for a completely oriented

sample³¹. The observed values for this ratio for these two samples when sintered at various temperatures are given in table 21. It can be seen that there is a small orientation already introduced during the pressing of the pellets and is nearly the same for both the samples. However, on heating at 900°C, the orientation has increased by about seven percent in the sample containing Bi₂O₃ whereas no change takes place in the other sample. This difference increases to about ten percent at 1200-1300°C. Thus the observed difference in σ of barium

T A B L E 21

CHANGE IN ORIENTATION DURING SINTERING OF BARIUM FERRITE SAMPLES WITH AND WITHOUT BISMUTH OXIDE

Composition	Sintering Temp. °C.	B_r^{\parallel} gauss	B_r^{\perp} gauss	$\frac{\perp}{\parallel}$ B_r / B_r
Pure barium ferrite	"As pressed"	1150	1075	0.935
	600	1210	1130	0.935
	900	1320	1230	0.935
	1000	1440	1345	0.935
	1100	1745	1630	0.934
	1200	1950	1820	0.933
Barium ferrite containing 5% bismuth oxide.	"As pressed"	1325	1250	0.942
	600	1360	1280	0.940
	900	1840	1640	0.891
	1000	2220	1930	0.870
	1100	2350	2015	0.859
	1200	2430	2060	0.848

ferrite with and without bismuth oxide ($\approx 15\%$, see table 20) can mainly be attributed to the difference in the degree of orientation. It is interesting to note that the orientation grows rapidly at 900°C , a temperature very close to the melting point of Bi_2O_3 , which would indicate that the presence of a molten phase helps in the growth of rightly oriented crystals at the cost of the wrong ones.

As pointed out above the increased orientation explains only a part of the improvement. This is also brought about by the following experiment. Mixtures of BaCO_3 and Fe_2O_3 (1:6) and that of BaCO_3 , Fe_2O_3 and Bi_2O_3 (1:6:0.12) were heated at different temperatures from 800 - 1300°C for four hours, pressed into pellets without ball milling them and sintered at 800°C for one hour. This last temperature was particularly chosen to exclude any increase in orientation, in bismuth oxide doped samples, which starts only around 900°C . The results of the magnetic measurements are given in the table 22. Even under these conditions the samples containing Bi_2O_3 give a larger σ value, showing that either process (2) or (3) mentioned above is also taking part in the improvement of these samples. It is not possible to rule out one or the other conclusively but the following indirect evidence suggests that the process (2) is less likely.

(a) There is no x-ray evidence of the presence of any unreacted phase in barium ferrite samples free from Bi_2O_3 . So the question of bismuth oxide increasing the reaction yield apparently does not arise.

T A B L E 22

SATURATION MAGNETIZATION OF BARIUM FERRITE SAMPLES WITH AND WITHOUT BISMUTH OXIDE WHEN REACTED AT VARIOUS TEMPERATURES AND SINTERED AT 800°C.

Composition	Reaction Temp. °C	$4 \pi I$ gauss	density gm/c.c.	σ gauss.cm ³ /gm
Pure barium ferrite	800	725	3.03	18.9
	900	1485	3.29	35.9
	1000	1905	3.56	42.5
	1100	1980	3.60	43.7
	1200	2095	3.70	45.0
Barium ferrite containing 5% bismuth oxide	800	860	2.90	23.6
	900	1610	3.29	38.9
	1000	2160	3.77	45.5
	1100	2320	3.81	48.2
	1200	2405	3.84	49.7

(b) The subsequent measurements using PbO instead of lead Bi₂O₃ showed no such improvement in σ when sintered below the melting point of PbO. If merely a molten phase was necessary to bring about the increased reaction, an equivalent improvement should have been observed in this case as well. On the other hand if substitutional replacement is taking place, no improvement could be expected in this case because Pb²⁺ ions will merely replace Ba²⁺ ions without in any way affecting the net magnetic moment of the unit cell. The replacement of Ba²⁺ ions by Bi³⁺ ions accompanied by a change in the valency of adjacent

Fe^{3+} ions to Fe^{2+} ions at the $4f_1$ or $4f_2$ sites, the improvement would be of the order of 10%, which agrees with the experimental observation. The ionic radius of Bi^{3+} is 0.96 \AA , so tetrahedral sites can accommodate them without much distortion.

It is interesting to note that in barium ferrite samples containing 5% Bi_2O_3 the coercivity τH_c has not fallen (infact, it has shown a slight increase) although the density has increased by about 40% as can be seen in table 20. The increase in density is usually associated with increase in grain size. This leads to a fall in coercivity because the demagnetization in bigger particles takes place through domain reversals as well as wall movements, whereas in small particles of less than the single domain size, domain reversal is the only feasible process which takes place at much higher magnetic fields. The increase in density can become consistent with the increase in coercivity if we assume that on melting, bismuth oxide provides a surface layer on each particle and acts as a cementing agent which joins the adjacent particles while maintaining a magnetic insulation at the inter-grain junctions. This hinders the formation of domain walls at the junctions, so that, effectively the particles continue to be single domained despite the high apparent density of the pellets.

The behaviour of barium ferrite containing five percent lead oxide, PbO , also fits in with the above picture. The replacement of Ba^{2+} ions by Pb^{2+} ions does not lead to any change in σ , so that the only improvement possible is through the increase

in orientation. This was confirmed experimentally with the similar decrease in the value of the ratio $B_r^\perp / B_r^\parallel$ in the neighbourhood of the melting point of PbO, just as was observed in the case of barium ferrite sample containing Bi_2O_3 . A ten percent increase due to this cause should give a value of 48-49 units for σ , which agrees well with the experimental value. It appears that in samples containing copper manganite, CuMn_2O_4 , also the improvement is due to the orientation effects.

Further attempts to improve the magnetic properties of barium ferrite were made by doping it with another type of impurity which replaced the magnetic ions as distinct from the earlier impurities which did not go into the lattice but had only some sort of catalytic activity. Replacement of tetrahedral sites by non-magnetic ions should result in an improvement because the Fe^{3+} ions on these sites have their spins directed opposite to the resultant magnetic moment of the unit cell. The diamagnetic ions like Zn^{2+} , Cd^{2+} , Si^{4+} and Ge^{4+} are known to prefer tetrahedral sites, hence they would be a good choice. In fact, attempts were made⁴⁴ to replace Fe^{3+} ions by Zn^{2+} ions, but this did not succeed because the charge was not compensated and some ferric ions were required to change to ferrous ions. In the present work this difficulty was avoided by simultaneously incorporating a divalent and a tetravalent impurity from the above list so that the three requirements (i) zero spin moment, (ii) preference for tetrahedral sites and (iii) average valency $\neq 3$, were all simultaneously met with. The results of magnetic measurements when tetrahedral Fe^{3+} ions were

replaced by Zn^{2+} and Si^{4+} (50:50) are given in table 23.

T A B L E 23

MAGNETIC PROPERTIES OF THE COMPOSITIONS $BaO \cdot (6-x)Fe_2O_3 \cdot xSiO_2 \cdot xZnO$ WITHOUT AND WITH 1.5% BISMUTH OXIDE WHEN x VARIES FROM 0 TO 1.0.

x	$4 \pi I$ gauss	B_r gauss	$B_c^{H_c}$ Oersted	$I_c^{H_c}$ Oersted	density gm/c.c.	Curie Temp. °C.
<u>Compositions without bismuth oxide</u>						
0.0	2900	2000	1400	2200	4.89	455
0.2	3100	2100	1400	2400	5.04	455
0.4	2600	1750	1300	2600	5.09	435
0.7	2150	1400	1100	2900	5.03	433
1.0	1800	1150	900	2400	4.86	430
<u>Compositions with 1.5% bismuth oxide</u>						
0.0	3080	2100	1500	2200	5.00	460
0.2	3425	2300	1400	2200	5.15	460
0.4	2865	1860	1400	2500	5.08	450
0.7	2275	1450	1100	2600	4.98	445
1.0	1575	900	800	2600	4.78	440

The magnetic measurements were made on samples sintered at 1250°C. The results on the above compositions when 1.5% bismuth oxide was added to them are also included in the table. It can be seen that an increase in magnetization does take place as expected on partial replacement of tetrahedral Fe^{3+} ions by non-magnetic ions. However a larger concentration of non-magnetic ions ($BaO \cdot (6-x)Fe_2O_3 \cdot xSiO_2 \cdot xZnO$ with $x > 0.2$) causes a decrease in the Curie temperature, magnetization $4 \pi I$ and the remanence B_r . This is most probably due to a weakening of the superexchange effects on

account of the interruptions in the interaction chain by the presence of non-magnetic ions.

However, in the case of samples of barium ferrite containing five percent borax, although $4\pi I$ shows an increase, σ decrease considerably. H Kojima^{49,50} has studied the effect of addition of B_2O_3 in the system $MO-Fe_2O_3$ ($M = Ba, Sr, Pb$). He found that the magnetic properties of the system improved when small quantities (upto 3%) of B_2O_3 were added. From the present study it is now clear that in reality B^{3+} spoil the intrinsic property of barium ferrite, but this is more than compensated by the increase in density so that $4\pi I$ shows a slight increase. A critical examination of various possible causes for the decrease in σ suggests that it is probably due to B^{3+} ions replacing Fe^{3+} ions substitutionally. No extra x-ray diffraction lines were observed showing that the entire product has the magnetoplumbite structure. B^{3+} ion has the inert gas electron configuration so that its preference for one site or another in a crystal structure is determined mainly by Madelung and Born's energy terms. It can be seen qualitatively that Madelung energy will remain unchanged if B^{3+} and Fe^{3+} ions are interchanged over octahedral and tetrahedral sites because they carry the same charge. The same would hold for Born's repulsive energy term if the octahedral and tetrahedral holes have equal radii. This is expected to be so on the basis of known values in the case of spinel structure where the two holes are nearly of equal dimensions. In this case the location of B^{3+} ions would be determined by the preference of Fe^{3+} ions on the basis of their covalent bond forming properties.

Fe^{3+} ions with d^5 configuration are expected to prefer tetrahedral sites, hence B^{3+} ions would preferentially replace the ions at octahedral sites. A statistical distribution of B^{2+} ions over octahedral sites should lead to about eight percent decrease in σ , while a preferential replacement of only those ions whose magnetic moment point in the right direction would lead to a decrease of about 15%. The observed decrease (13%) indicates that octahedral replacement is very likely but it cannot conclusively establish whether there is any preferential substitution of the second type discussed above.

Effect of Impurities on Alkali Metal Lanthanum Ferrites:

Sodium lanthanum ferrite samples containing various impurities listed in table 24 were formed as described earlier by reacting them at 1300°C for three hours. The products were examined by x-ray diffraction and the results are given in column 8 of the table. It can be seen that in many cases the resultant product is not the magnetoplumbite phase but merely a mixture of $\alpha\text{-Fe}_2\text{O}_3$ and other oxides. This clearly indicates that either sodium or lanthanum oxide reacts with the impurity oxide in preference to $\alpha\text{-Fe}_2\text{O}_3$, forming a compound more stable than the magnetoplumbite phase. These impurities are thus of no importance for the present study. However, the samples containing Bi_2O_3 showed some interesting properties and were, therefore, studied in some detail. Samples of sodium lanthanum ferrite containing CaO , SrO , PbO , CdO , CoO , NiO , MgO and ZnO showed magnetoplumbite structure. In the last five cases,

T A B L E 24

EFFECT OF IMPURITIES ON SODIUM LANTHANUM FERRITE SINTERED AT
1300° C.

Impurity	$4 \pi I$ gauss	B_r gauss	B^{H_c} Oersted	I^{H_c} Oersted	density gm/cc	σ gauss. cm ³ /gm	* Crystal struc- ture.
nil	2230	1780	1400	2700	4.38	40.5	M
5% SiO ₂	85	70	-	-	4.42	1.5	X
5% TiO ₂	275	225	-	-	4.18	5.2	X
5% Sb ₂ O ₃	545	500	450	2100	3.69	11.7	X
5% As ₂ O ₃	840	790	700	3600	3.26	20.5	X
5% SnO ₂	1040	535	250	450	3.70	21.9	X
5% Al ₂ O ₃	1355	1240	1000	3650	3.53	30.5	X
5% Na ₂ B ₄ O ₇ · 10H ₂ O	1470	1280	1100	3000	3.61	32.3	X
5% ZrO ₂	1525	1205	900	1800	3.63	34.4	X
5% Bi ₂ O ₃	1555	1255	1000	3000	4.96	24.9	X
5% CuO	1790	1370	800	1900	3.78	37.7	X
5% BeO	2005	1610	1100	2000	3.94	40.5	X
5% NiO	2190	1745	900	1800	3.72	46.7	M
5% MgO	2200	1660	800	1900	3.76	46.5	M
5% CdO	2225	1760	1150	2000	4.08	43.4	M
5% ZnO	2270	1710	1050	1900	3.76	48.0	M
5% CoO	2330	1690	1100	2200	4.34	42.7	M
5% CaCO ₃	2595	2020	1200	1800	4.25	48.4	M
5% PbO	2740	2110	1100	1500	4.30	50.5	M
5% SrCO ₃	2870	2250	1400	2000	4.40	51.8	M

* M stands for magnetoplumbite structure and X for a mixture of oxides.

however, the diffraction lines which coincide with those from spinel structure show an enhanced intensity indicating that the impurity oxides are present as ferrites having the spinel structure. SrO, CaO and PbO are known to form stable magnetoplumbite phase, hence the formation of homogeneous product of this structure in case of sodium lanthanum ferrite containing these oxides is as expected.

Effect of Bi_2O_3 : Sodium lanthanum ferrite containing five per cent Bi_2O_3 was examined for its magnetic properties. The saturation magnetization and remanence showed considerable decrease whereas the intrinsic coercivity increased slightly as compared to the pure compound. The product on examination by x-ray diffraction showed that it contained free $\alpha\text{-Fe}_2\text{O}_3$ and only a small proportion of the magnetoplumbite phase, thus showing that the addition of bismuth oxide leads to a partial decomposition of sodium lanthanum ferrite. Since only a small proportion of bismuth oxide is adequate to decompose a large amount of sodium lanthanum ferrite, it is clear that bismuth oxide is reacting preferentially with one of the minor constituents i.e. Na_2O or La_2O_3 of the latter. Therefore, mixtures of $\text{Na}_2\text{CO}_3 + \text{Bi}_2\text{O}_3$ (1:1) and $\text{La}_2\text{O}_3 + \text{Bi}_2\text{O}_3$ (1:1) were heated at 900°C for two hours. X-ray diffraction patterns were taken before and after the reactions and in both the cases they gave the evidence of the formation of new compounds, confirming that these reactions are responsible for the decomposition of sodium lanthanum ferrite and other ferrites containing lanthanum.

A further confirmation of this came from the results of the following experiment. A mixture of Fe_2O_3 , Bi_2O_3 , Na_2CO_3 and La_2O_3 in the ratio 6:0.12:0.5:0.5 was reacted at high temperature. It can be seen that a large excess of both sodium carbonate and lanthanum oxide was taken. The idea was to provide lanthanum and sodium required for the formation of stable compounds with bismuth and still leave behind enough of them to form the magnetoplumbite phase. The results show that in this case the complete formation of the magnetoplumbite phase did, indeed, take place. The σ value of the product after sintering at 1200°C matches with that of the pure sodium lanthanum ferrite as can be seen from table 25.

T A B L E 25

EFFECT OF EXCESS OF SODIUM AND LANTHANUM OXIDES ON THE MAGNETIC PROPERTIES OF SODIUM LANTHANUM FERRITE CONTAINING BISMUTH OXIDE

Composition	$4\pi I$ gauss	density gm/c.c.	σ gauss.cm ³ /gm.
Pure sodium lanthanum ferrite	2420	4.80	40.0
Sodium lanthanum ferrite containing 5% Bi_2O_3	1635	4.95	26.2
Sodium lanthanum ferrite containing Bi_2O_3 and excess of La_2O_3 and Na_2CO_3	2495	4.91	40.4

In addition to the decomposition caused by Bi_2O_3 , the thermal decomposition at 900°C and its recombination at temperatures above 1100°C is also observed as in the case of pure sodium

lanthanum ferrite. However, in the present case the repeated alternate heating between 900°C and 1100-1300°C did not lead to the formation of inactive Fe₂O₃ as was observed in the case of pure compound. Therefore, even after a number of cycles, the original value was obtained on heating at 1300°C.

Effect of PbO, SrO and CaO: These impurities go into solid solution with sodium lanthanum ferrite giving homogeneous magnetoplumbite phases which have saturation magnetizations higher than the pure compound. Curie temperatures of these were determined and an increase was observed only in the case of strontium doped compound where it was raised by 20°C. In other cases it remained unchanged within the experimental errors. It appears that the addition of these impurities raises the value of σ to what is obtained in the case of pure barium ferrite when sintered under corresponding conditions. The samples containing Pb²⁺ and Sr²⁺ have values higher than those containing Ca²⁺ as is also observed for barium ferrite. Ca²⁺ ions partially replace Ba²⁺, however, this replacement causes a deterioration of the properties of barium ferrite as shown by Rutkowska⁵¹ and Kozlowski and Ziolkowski⁴⁵. Although the resulting compound was of one phase and still possessed the characteristics of a permanent magnet, its magnetic properties were inferior to that of the pure compound.

The results suggest that the pure sodium lanthanum ferrite, although found to consist of homogeneous magnetoplumbite phase by x-ray diffraction, might contain some impurity of β -

alumina structure. This is isomorphous with magnetoplumbite and hence can remain unidentified by x-ray diffraction if present in small amounts. However, this phase is antiferromagnetic so that it would decrease the bulk magnetic moment of the samples. Addition of CaO, SrO and PbO would change this antiferromagnetic phase to the magnetoplumbite phase, which in solid solution or as a free phase would increase the saturation magnetization to the required value for a cent percent magnetoplumbite phase.

CHAPTER III

III. 4 : Magnetic Properties of the
System BaO - Fe₂O₃ - Bi₂O₃ ... 102

MAGNETIC PROPERTIES OF THE SYSTEM BaO - Fe₂O₃ - Bi₂O₃

In the last chapter we had discussed the effect of certain impurities on the properties of hard ferrites. It was found that 5% bismuth oxide has a very favourable effect on the magnetic properties of barium ferrite. It was, therefore, decided to extend this investigation to other compositions containing different proportions of bismuth oxide. Study of the ternary system BaO - Fe₂O₃ - Bi₂O₃ had already been made by Sugimoto and Takei⁵⁴ with the aid of x-ray diffraction analysis and microscopic examinations. They found that the single phase region was restricted to a very small area in the vicinity of Ba_{0.6}Fe₂O₃ (see fig. 5). It was decided to restrict our investigations to this single phase region only. Seven representative compositions were chosen and detailed studies of magnetic properties were made.

These compositions were formed in the usual way by mixing all the oxides (or carbonates) in the appropriate proportions and reacting them at elevated temperatures. After reaction all the compositions gave a homogeneous single phase as revealed by the x-ray results. The results of the magnetic measurements on the pellets pressed out of these compositions under a pressure of 3000 lbs/sq.cm., after grinding them for 15 hours in a ball mill, are given in table 25.

It can be seen that in all these compositions $4 \pi I_s$, B_r and $B_c^{H_c}$ increase with the sintering temperature and attain the maximum values at about 1100-1200°C. The initial increase

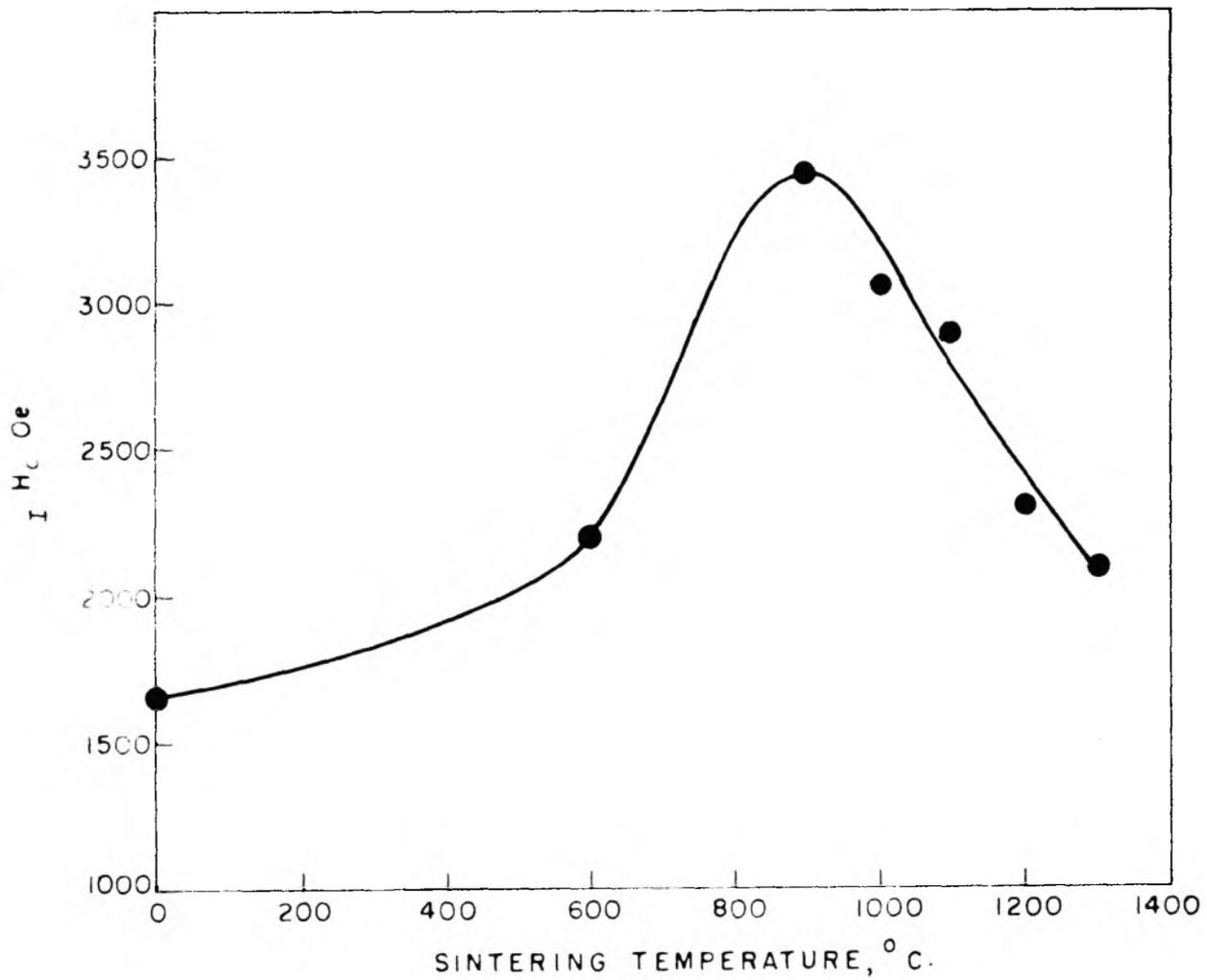


Fig.19 VARIATION OF INTRINSIC COERCIVITY OF COMPOSITION $14 \text{ BaO} \cdot 84 \text{ Fe}_2\text{O}_3 \cdot 2 \text{ Bi}_2\text{O}_3$ WITH SINTERING TEMPERATURE

in the saturation magnetization and the remanence is due to the increase in density i.e. more magnetic material per unit volume and the removal of the surface defects produced during the ball milling of the samples as reported earlier. On sintering the pellets at 1300°C and beyond there is a fall in both the saturation magnetization and the remanence. This again is probably due to the loss of oxygen at high temperatures as discussed in chapter IV. The behaviour of intrinsic coercivity with the sintering temperature is also parallel to that observed in the case of alkali metal lanthanum ferrites. The H_c first increases with the sintering temperature, comes to a maximum value at approximately 900°C and then falls progressively with higher sintering temperatures. The typical results for the composition $14BaO.84Fe_2O_3.2Bi_2O_3$ are shown in figure 19. The maxima in this case lies at a much lower temperature as compared to that in the case of sodium and potassium lanthanum ferrites where it is observed around 1200°C. This is due to the fact that these compositions sinter to high densities at much lower temperatures than the latter compositions. The decrease in the intrinsic coercivity beyond 900°C sintering is due to the increase in the particle size which leads to the formation of domain walls and hence easier changes in the magnetization of the sample. The increase around 700°C can be due to the partial decomposition of the magnetoplumbite phase as had been observed in the case of sodium and potassium lanthanum ferrites. However, as reported earlier, this is not conclusive as no decomposition around this temperature has been detected by x-ray or magnetic

T A B L E 26

MAGNETIC PROPERTIES OF COMPOSITIONS FROM THE SINGLE
PHASE REGION OF THE PHASE DIAGRAM OF THE SYSTEM BaO-Fe₂O₃-Bi₂O₃.

The pellets were sintered at various temperatures after reacting the materials at 1000°C for 3 hours followed by ball milling for 15 hours and pressing under a pressure of 3000 lbs/sq.cm.

Composition	Property	"as-pressed"	Sintering temperature					
			600°C	900°C	1000°C	1100°C	1200°C	1300°C
14BaO.83Fe ₂ O ₃ .3Bi ₂ O ₃	4 π I _s	1780	1800	2630	2975	3150	3150	3100
	B _r	1420	1450	2030	2250	2410	2450	2400
	B ^H _c	1000	1150	1800	2000	1900	1700	1600
	I ^H _c	1650	2100	3300	3200	2550	2300	2100
	Density	3.18	3.19	4.64	5.08	5.16	5.17	5.17
15BaO.83Fe ₂ O ₃ .2Bi ₂ O ₃	4 π I _s	1820	1930	2590	2915	3170	3120	3080
	B _r	1476	1560	1980	2220	2450	2400	2360
	B ^H _c	1050	1200	1800	1900	2000	2000	1800
	I ^H _c	1800	2350	3550	3300	3000	3000	2600
	Density	3.18	3.19	4.37	4.91	5.11	5.13	5.14
16BaO.83Fe ₂ O ₃ .Bi ₂ O ₃	4 π I _s	1750	1850	2500	2950	3200	3150	3100
	B _r	1360	1420	1930	2250	2500	2450	2400
	B ^H _c	1000	1150	1800	1900	2000	2000	2000
	I ^H _c	1850	2450	3500	3300	3200	3150	3100
	Density	3.04	3.07	4.11	4.61	5.04	5.08	5.10

Contd...

Composition	Property	"as-pressed"	Sintering temperature					
			600°C	900°C	1000°C	1100°C	1200°C	1300°C
14Ba0.84Fe ₂ O ₃ ·2Bi ₂ O ₃	4 \wedge I _s	1860	1900	2700	3140	3250	3250	3200
	B _r	1330	1360	2060	2365	2550	2480	2450
	B ^H _c	900	1000	1750	2000	2100	1850	1650
	I ^H _c	1650	2200	3450	3050	2900	2300	2100
	Density	3.16	3.17	4.37	4.96	5.12	5.15	5.15
15Ba0.84Fe ₂ O ₃ ·Bi ₂ O ₃	4 \wedge I _s	1760	1860	2600	3025	3225	3250	3150
	B _r	1420	1500	2025	2300	2500	2500	2400
	B ^H _c	1050	1250	1700	2000	2000	1900	1750
	I ^H _c	1850	2400	3750	3300	3000	2900	2700
	Density	3.14	3.18	4.35	4.89	5.10	5.19	5.20
14Ba0.85Fe ₂ O ₃ ·Bi ₂ O ₃	4 \wedge I _s	1800	1860	2440	2900	3200	3300	3300
	B _r	1390	1480	1940	2250	2500	2550	2350
	B ^H _c	1000	1200	1700	1900	2000	1750	1150
	I ^H _c	1700	2100	3500	3050	2700	2100	1500
	Density	3.12	3.18	4.03	4.58	5.02	5.15	5.15
14.3BaO. 85.7Fe ₂ O ₃	4 \wedge I _s	1350	1400	1630	1925	2350	2700	3100
	B _r	1000	1100	1300	1440	1750	1950	1980
	B ^H _c	800	950	1100	1150	1250	1200	900
	I ^H _c	2350	2700	3000	3000	2750	2000	1200
	Density	2.82	2.84	2.99	3.34	3.90	4.31	4.65

measurements.

It can be seen from table 26 that the best magnetic properties are obtained from the composition $14\text{BaO} \cdot 84\text{Fe}_2\text{O}_3 \cdot 2\text{Bi}_2\text{O}_3$ when sintering is done at 1100°C . A detailed investigation of the effect of reaction temperature, reaction time and pressure applied during pressing was, therefore, made for this composition.

Reaction Temperature: From tabel 27 it can be seen that the reaction temperature has a pronounced effect on the magnetic properties. Measurements were made after ball milling the reacted samples for fifteen hours, pressing under a pressure of 3000 lbs/sq.cm. and finally sintering the pellets for 30 minutes. $4 \pi I_s$ and B_r improve progressively on increase in the reaction temperature upto 1200°C beyond which it remains unchanged. The intrinsic coercivity falls with increase in the reaction temperature. This is an interesting result and is probably due to the fact that the mass on reacting at higher temperatures becomes very hard. The resultant particles after grinding for a certain length of time would be bigger than those obtained under corresponding conditions from samples reacted at lower temperatures.

Reaction Time: The reaction time appears to have only a slight detrimental effect if it is more than a few hours. This is probably because of the loss of bismuth oxide which evaporates on prolonged heating. The results obtained from samples reacted at 1000°C for various durations and sintered at 1100°C are given in table 28.

T A B L E 27

EFFECT OF REACTION TEMPERATURE ON COMPOSITION $14\text{BaO}\cdot 0.84\text{Fe}_2\text{O}_3\cdot 2\text{Bi}_2\text{O}_3$

Samples reacted for 4 hours were ground for 15 hours, pressed under a pressure of 3000 lbs/sq.cm. and sintered at 1100°C .

Reaction temp. $^\circ\text{C}$	$4 \pi I_s$ gauss	B_r gauss	B^H_c oersted	I^H_c oersted	$(BH)_{\max} \times 10^6$ gauss oersted
800	2690	1900	1500	3200	1.0
900	2950	2250	1650	3000	1.1
1000	3150	2420	1800	2950	1.2
1100	3250	2460	1800	2700	1.2
1200	3280	2420	1700	2500	1.1
1300	3280	2370	1550	2300	1.0

T A B L E 28

EFFECT OF REACTION TIME AT 1000°C . PELLETS WERE PRESSED UNDER 3000 lbs/sq.cm. AFTER GRINDING FOR 15 hours & FINALLY SINTERED AT 1100°C .

Reaction time hrs.	$4 \pi I_s$ gauss	B_r gauss	B^H_c oersted	I^H_c oersted	$(BH)_{\max} \times 10^{-6}$ gauss oersted
$\frac{1}{2}$	2980	2300	1850	3250	1.1
1	3050	2340	1850	3100	1.1
2	3100	2400	1850	3050	1.2
4	3150	2420	1800	2950	1.2
8	3150	2400	1750	2900	1.1
16	3180	2400	1700	2800	1.1

T A B L E 29

EFFECT OF PRESSURE APPLIED DURING PRESSING ON SAMPLES OF
 $14\text{BaO} \cdot 84\text{Fe}_2\text{O}_3 \cdot 2\text{Bi}_2\text{O}_3$ REACTED AT 1000°C , GROUND FOR 15 HOURS
 AND SINTERED AT 1100°C .

Applied pressure lbs/sq.cm.	$4 \pi I_s$ gauss	B_r gauss	B^H_c oersted	I^H_c oersted	k	$(BH)_{\max} \times 10^{-6}$ gauss oersted
"with hand only"	2950	2150	1700	2750	0.25	0.9
750	3050	2300	1800	2750	0.25	1.0
1500	3100	2430	1800	2750	0.26	1.1
3000	3200	2500	1800	2750	0.28	1.2
4500	3200	2520	1800	2750	0.28	1.2
7500	3200	2540	1800	2750	0.28	1.2
15000	3200	2540	1800	2750	0.28	1.2

Applied Pressure: The results of magnetic measurements carried out to study the effect of pressure applied during pellet formation are summarized in table 29. The measurements were made on samples reacted at 1000°C, ground for 15 hours, pressed under various pressures and finally sintered at 1100°C for 30 minutes. It can be seen that the magnetic properties improve slightly with increasing pressure upto 1500-3000 lbs/sq.cm. beyond which the increase in pressure has practically no effect. The fullness factor k , which is a measure of the degree of orientation of the material, increases from 0.25 to 0.28 for the pellets pressed under a pressure of 3000 lbs/sq.cm. and beyond. This indicates that at this pressure some orientation is introduced during pressing which will be helpful in increasing the orientation on sintering at elevated temperatures and, therefore, the $(BXH)_{\max}$ improves.

From these results it is clear that the reaction at 1000°C for 2 hours followed by ball milling for 15 hours, pressing into pellets under a pressure of 3000 lbs/sq.cm. and finally sintering at 1100°C for 30 minutes are the optimum conditions suitable to get the best permanent magnetic properties of the composition $14BaO \cdot 84Fe_2O_3 \cdot 2Bi_2O_3$.

S U M M A R Y

S U M M A R Y

Magnetic and structural properties of some hexagonal ferrites have been investigated. Two new ferromagnetic compounds of the chemical composition $\text{Ag}_{\frac{1}{2}}\text{La}_{\frac{1}{2}}\text{Fe}_{12}\text{O}_{19}$ and $\text{Tl}_{\frac{1}{2}}\text{La}_{\frac{1}{2}}\text{Fe}_{12}\text{O}_{19}$ have been synthesized by solid state reactions between the component oxides at temperatures 1100° to 1350°C . Their crystal structures have been determined by x-ray powder diffraction technique and are found to be isomorphous with magnetoplumbite. The unit cell is hexagonal and the cell constants are $c = 22.85\text{\AA}^{\circ}$, $a = 5.85\text{\AA}^{\circ}$ for silver lanthanum ferrite. The unoriented sample of the former, when sintered at 1300°C , has the remanence $B_r = 1600$ gauss coercivity $B_{Hc}^H = 1100$ Oe and $I_{Hc}^H = 2450$ Oe and Curie point $T_c = 435^{\circ}\text{C}$. The values of these magnetic constants for thallium lanthanum ferrite are found to be close to those of the silver compound. Heating the silver compound with Bi_2O_3 or Al_2O_3 decomposes it to α - Fe_2O_3 , free silver and a double oxide of lanthanum and bismuth or aluminium, thus leading to a marked deterioration in its magnetic properties.

The variation of saturation magnetization and coercivity of sodium and potassium lanthanum ferrites ($\text{Na}_{\frac{1}{2}}\text{La}_{\frac{1}{2}}\text{Fe}_{12}\text{O}_{19}$) has been studied as a function of sintering temperature. In the temperature range of 900 to 1000°C these compounds are found to decompose causing an abrupt decrease in the room temperature saturation magnetization. With further increase in sintering temperature, i.e. in the range 1100°C to 1300°C , the saturation magnetization increases due to progressive increase in the

proportion of the magnetoplumbite phase and the bulk density of the pellets. From 1350°C it starts decreasing again due to a partial loss of oxygen. The decomposition at 900-1000°C is negligible in unground or sintered samples and increases with the time of grinding, suggesting it to be dependent on the particle size of the magnetic phase. The coercivity increases on sintering at 850-1050°C and decreases on sintering at higher temperatures. The first increase is attributed to a decrease in the average particle size of the magnetic phase due to its partial decomposition at 950°C, and the subsequent decrease to the increased particle size due to sintering. The increase in coercivity with decrease in particle size and vice versa is consistent with the fact that demagnetization in bigger particles can take place through domain wall motion which is absent in single domain particles. The kinetics of formation of these ferrites at different temperatures and the effect of the addition of bismuth oxide on the magnetic properties have also been studied.

The effect of a number of impurity ions (Bi^{3+} , Pb^{2+} , Zn^{2+} , Cu^{2+} , Mn^{2+} , Ni^{2+} , etc.) on the saturation magnetization remanence, coercivity and Curie temperature of many sintered polycrystalline ferrites (sodium lanthanum ferrite, potassium lanthanum ferrite, silver lanthanum ferrite and barium ferrite) has been studied. In many cases substantial changes have been observed. The mechanism of these changes has been investigated in detail. The improvement brought about by certain additives has been found to be due to (1) impurity phase changing the sintering characteristics of the magnetic phase whereby a more

dense product is obtained at a lower sintering temperature, (ii) the rate of crystal growth is enhanced in presence of the impurity phase and the size of the crystallites having the right orientation grows at the cost of the wrong ones. On the other hand the deterioration in magnetic properties brought about by certain other additives has been established to be due to the competitive removal of one of the phases taking part in the solid state reaction and thus decreasing the ultimate yield of the magnetic phase.

Magnetic properties of the compounds in the single phase region of the phase diagram of the ternary system $\text{BaO} - \text{Fe}_2\text{O}_3 - \text{Bi}_2\text{O}_3$ have also been investigated.

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REFERENCES

1. G. Aminoff, Geol. Foren. Forhandl. Stockholm, 47, 283 (1925).
2. V. Adelskold, Arkiv Kemi, Min. Geol., 12A, No.29, 1 (1937).
3. S. Wallmark and A. Westgren, Arkiv. f. Kemi. etc. (Sueda), Bd 12B, No.35 (1937).
4. R. Blix, Geol. Foren. Forhandl. Stockholm, 59, 300 (1937).
5. J.J. Went, G.W. Rathenau, E.W. Gorter and G.W. van Oosterhout, Phys. Rev., 86, 424-5 (1952) and Philips Tech. Rev., 13, 194-208 (1952)
6. G.W. Rathenau and J.L. Snoek, Philips. Res. Rept., 1, 239 (1946).
7. E.W. Gorter, Ph.D. Thesis "Saturation Magnetization and Crystal Chemistry of Ferrimagnetic Oxides", University of Lyden (1954).
8. W.E. Henry, Phys. Rev., 112, 326-7 (1958).
9. R.M. Bozorth and V. Kramer, J. Phys. Radium, 20, 393-401 (1959).
10. R. Pauthenet and G. Rimet, Compt. rend., 249, 1875-7 (1959).
11. R.N. Summergrad and E. Banks, Phys. Chem. Solids, 2, 312-17 (1957).
12. E.H. Frie, M. Schieber and S. Shtrikman, Phys. Rev., 1118, 657 (1960).
13. G. Heimke, J. Appl. Phys., 31, 2715-2725 (1960).
14. A. Aharoni and M. Schieber, Phys. Rev., 123, 807 (1961).
15. H.B.G. Casimir et al, J. Phys. Radium., 20, 360-73 (1959).
16. G. Villers, Compt. rend., 248, 2973-5 (1959).
17. W. Sucksmith and J.E. Thompson, Proc. Roy. Soc., 225, 362 (1954).
18. K.J. Sixtus, K.J. Kronenberg and R.K. Tenzer, J. Appl. Phys., 27, 1051 (1956).

19. R.F. Pearson, Proc. Phys. Soc. (London) 70B, 441 (1957).
20. L.F. Bates, Endeavour, 16, 151-60 (1957).
21. M. Paulus, Compt. rend., 245, 2227-30 (1957).
22. C. Kooy, Philips Tech. Rev., 19, 286-9 (1958).
23. D.J. Craik and P.M. Griffiths, Proc. Phys. Soc. (London) 73, 1-13 (1959).
24. J. Smit and H.P.J. Wijn, "Ferrites", Philips Technical Library, Eindhoven (1959).
25. H. Kojima, et al, J. Phys. Soc. (Japan), 16, 1483 (1961).
26. L.H. Brixner, J. Am. Chem. Soc., 81, 3841-43 (1959).
27. R.A. Hunter, Fourth Progress Report, Signal Corps. Project, No.32-2005D.
28. H. Fahlenbrach, Elektrotech. Z., 74, 388-89 (1953).
29. H. Fahlenbrach and W. Heister, Arch. Eisenhüttenw, 24, 523-8 (1953) and Tech. Mitt. Krupp., 12, 47-51 (1954).
30. A.L. Stuijts, G.W. Rathenau and E.W. Gorter, J. Appl. Phys., 23, 1282 (1952).
31. A.L. Stuijts, G.W. Rathenau and G.H. Weber, Philips Tech. Rev., 16, 141-7 (1954).
32. I. Gordon, Am. Ceram. Soc. Bull., 35, 173-5 (1956).
33. B. Kubola and C. Okazaki, J. Phys. Soc. (Japan), 10, 723-4 (1955).
34. J. Suchet, Bull. Soc. france. Ceram., No.33, 33-43 (1956).
35. A.L. Stuijts, Trans. Brit. Ceram. Soc., 55, 57-74 (1956).
and Chem. Weekbald, 52, 49-55 (1956).
36. Y. Goto and T. Takada, J. Am. Ceramic Soc., 43, 150-3 (1960).
37. V. Gottardi, Attie mem. accad. patavina Sci., lettere ed. arti, 68, 16 pp. (1956).
38. H. Stablein, Tech. Mitt. Krupp., 15, 165-8 (1957).
39. G. Heimke, Naturwissenschaften., 11, 260-1 (1958).

40. V. Ivasau, M. Rozenberg and L. Caarlan, *Electrotechnica* (Bucharest), 8, No.6, 210-14 (1960).
41. H. Kojima, *Sci. Repts. Research Inst., Tohoku Univ.*, Ser 7, 507-14 (1955).
42. C. Guillaud and G. Villers, *Compt. rend.*, 242, 2817-20 (1956).
43. L.G. van Uitert, *J. Appl. Phys.*, 28, 317-19 (1957).
44. A.H. Mones and E. Banks., *Phys. Chem. Solids*, 4, 217-22 (1958).
45. L. Kozlowski and Z. Ziolkowski, *Prace. Inst. Hutnicz*, 10, 305-31 (1958).
46. F. Bertaut, A. Deschamps and R. Pauthenet, *Compt. rend.*, 246, 2594-7 (1958).
47. F. Bertaut, A. Deschamps and R. Pauthenet, *J. Phys. Radium.*, 20, 404-8 (1958).
48. C. Brisi and A. Burdese, *Atti. accad. Sci. Torino, Classe Sci. fis. mat. e nat.*, 87, 57-62 (1952-53).
49. H. Kojima, *Sci. Repts. Res. Inst., Tohoku University*, Ser A,8, 540-6 (1956).
50. H. Kojima, *Sci. Repts. Res. Inst., Tohoku University*, Ser A,10, 175-82 (1958).
51. H. Rutkowska, *Prace. Inst. Ministerstwa Hutnictwa*, 9, 303-8 (1957).
52. P.B. Braun, *Philips Res. Repts.*, 12, 491-548 (1957).
53. F. Pawlek and K. Reichel, *Arch. Eisenhüttenw*, 28, 241-4 (1957).
54. T. Takei and M. Sugimoto, *Repts. Sci. Research Inst., (Japan)*, 31, 191-5 (1955).
55. T. Okamura, H. Kojima and S. Watanabe, *Science Repts., Res. Inst., Tohoku University*, Ser A, 7, 411-424 (1955).
56. M. Sugimoto and T. Takei, *Sci. Papers Inst. Phys. Chem. Res. (Japan)* 54, No.2 (1960).
57. A. Deschamps and F. Bertaut, *Compt. rend.*, 244, 3069-72 (1957).
58. S. Brunauer, P.H. Emmett and E. Teller, *J. Am. Chem. Soc.*, 60, 309 (1938).

59. S.J. Gregg, "Surface Chemistry of Solids", Chapman and Hall (London) 300 (1961).
60. D. Dollimore and D. Nicholson, J. Chem. Soc., 960, (1962).
61. E.J.W. Verwey, P.W. Haaijman and F.C. Romeijn, J. Chem. Phys., 15, 181 (1947).
62. A. Aharoni and M. Schieber, J. Appl. Phys., 32, 1851 (1961).
63. S.C. Abrahams and S.C. Geller, Acta Cryst., 11, 437 (1958).
64. R.S. Rott, J. Res. N.B.S., 58, 75 (1957).
65. M. Yuzuri, Y. Kang and Y. Goto, J. Phys. Soc.(Japan), 17, (B-1), 253 (1962).