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DECLARATION

OF

SOME COMPLEX FLUORIDES

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A THESIS SUBMITTED TO THE

UNIVERSITY OF BOMBAY

FOR THE DEGREE

DOCTOR OF PHILOSOPHY

in

PHYSICAL CHEMISTRY

by

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National Chemical Laboratory

Published work of the Author included in this Thesis

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DECLARATION

The investigations were carried out under the direction of Professor A. B. Biswas. The experimental observations and the interpretations are entirely those of the candidate.

The work has not been submitted, in whole or in part, for any other degree and is not being concurrently submitted for any other degree.

(H. V. Keer)

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(H.V. Keer)

P A R T - I

CHAPTER I

INTRODUCTION

It has long been recognized that the energy state of a substance is one of its most fundamentally important attributes. An understanding of the nature of matter and its interactions can be revealed through a study of interaction energies between particles, and between aggregates of particles of varying degrees of complexity. An outstanding way to determine these energies is by heat capacity measurements over a wide temperature range. Thus an insight into the details of the molecular structure, electronic energy level pattern and mechanism of various types of phase transitions occurring in solids may be obtained. Besides it provides data for useful chemical thermodynamic functions.

The heat capacity, C_x , of a system of N interacting particles under an external constraint 'x' is defined by

$$C_x = (\partial Q / \partial T)_x ,$$

the ratio of the added heat to the corresponding temperature rise of the system. The constraint 'x' may

be either constant pressure or constant volume. The heat capacities of solids are, however, generally measured at constant pressure (C_p), while statistical mechanics leads more naturally to formulae for the constant volume quantity (C_v). The thermodynamic formula

$$C_p - C_v = \frac{9\alpha^2 VT}{\beta}$$

relates C_p to C_v . The quantities α , V , and β represent, respectively, the coefficient of thermal expansion, the specific volume and the compressibility. Whilst this difference, ($C_p - C_v$), is quite small at liquid helium temperatures, it gets progressively more important and a correction must be applied as the temperature is increased.

Measurements of the heat capacity at constant pressure, C_p , of the various phases ($\alpha, \beta, \dots, \gamma$) involved together with the enthalpy increments of such phase transitions, ΔH_1 , occurring reversibly at temperatures, T_1 , permit evaluation of the standard enthalpy increment of a substance by the equation :

$$H_{\text{O}} - H_{\text{O}}^{\circ} = \int_0^{T_1} C_{p,\alpha} dT + \Delta H_1 + \int_{T_1}^{T_2} C_{p,\beta} dT + \Delta H_2 + \dots + \int_{T_n}^T C_{p,\gamma} dT$$

and the standard entropy by the related equation :

$$S^{\circ} = S_{\circ}^{\circ} + \int_0^{T_1} \frac{C_{P,\alpha} dT}{T} + \frac{\Delta H_1}{T_1} + \int_{T_1}^{T_2} \frac{C_{P,\beta} dT}{T} + \frac{\Delta H_2}{T_2} + \dots + \int_{T_n}^T \frac{C_{P,\zeta} dT}{T}$$

These functions may be combined to yield the standard Gibbs energy function for the substance :

$$\left[\frac{F^{\circ} - H_{\circ}^{\circ}}{T} \right] = \left[\frac{H^{\circ} - H_{\circ}^{\circ}}{T} \right] - S^{\circ}$$

Symbolizing a generalized chemical reaction as

$$\sum \delta_i S_i' = 0$$

in which S_i' indicates a mole of the i^{th} substance involved and δ_i is the stoichiometric coefficient (positive for products and negative for reactants) the Gibbs energy increment of the reaction, ΔF° , may be found by summation of the Gibbs energy functions and the enthalpies of formation, ΔH_f° , for the substances involved :

$$\Delta F_T^{\circ} = \sum \delta_i' (G^{\circ})_i = \sum \left[\frac{F^{\circ} - H_{\circ}^{\circ}}{T} \right]_i - \sum \delta_i' (\Delta H_f^{\circ})_i$$

From ΔF_T° the equilibrium constant of the reaction, K , may be readily evaluated from the relation :

$$\Delta F_T^\circ = - RT \ln K .$$

R here represents the gas constant in appropriate units.

THEORIES OF SPECIFIC HEAT

Before the advent of the quantum theory the values of the specific heats of solids were calculated using the classical theorem of the equipartition of energy. It was assumed that each atom or molecule in a solid was able to vibrate about a fixed point and since this vibration can extend in three dimensions the equipartition of energy theorem ascribed an energy of $3kT$ to each atom or molecule, where ' k ' is Boltzmann's constant. This leads to a constancy of the molar specific heat value as $3R = 5.96$ cal./mole.deg. This is the law of Dulong and Petit, which was found to be approximately true for many substances at and above room temperature.

The proposal of Dulong and Petit had been a great scientific advance in the following sense : it had provided a working criterion with which to compare the experimental results and a stimulus for improving calorimetric measurements to ascertain whether the law was in error or otherwise.

The experiments however showed that the specific heat values decreased considerably at low temperatures. The first satisfactory explanation for the decrease was put forward by Einstein¹ on the basis of the quantum theory, that the atoms oscillating at a frequency ν could only have discrete values of energy separated from one another by a quantity $h\nu$, where 'h' is Planck's constant.

Einstein's theory was not entirely satisfactory because of the over-simplified assumption that all the atoms vibrate independently with the same frequency. In fact there must be strong forces between the atoms and they vibrate like coupled oscillators in a crystal. Treatments on these lines were developed by Debye². He postulated a solid to be an elastic continuum. Since a continuum has an infinite number of normal modes, Debye cut the frequency spectrum off at a frequency such that the total number of normal modes was equal to the number of degrees of freedom of the atoms ($3N$) in a solid. The theoretical heat capacities based on his frequency spectrum are in good agreement with experimental results.

An important conclusion of this theory is the prediction of a relation $C_v \propto T^3$ at low temperatures. This asymptotic T^3 law was first observed experimentally by

Nernst and his collaborators many years ago and has been verified for many materials. The results of Pitzer³ and De Sorbo⁴ on diamond are typical of a non-metal.

Several important exceptions to the T^3 law⁵⁻⁷ have been observed. Experimental C_V behaviour of these materials is better fitted by the form $C_V \propto T^2$; which is more appropriate for systems with layer structure, indicating that the binding forces between crystal layers are very weak. Thermodynamic properties are then derived by considering these materials as formed of almost two-dimensional arrays of atoms. Transverse vibrations give the main contribution to thermodynamic quantities. Newell⁸ has made a detailed investigation of weakly interacting layer structures and has reviewed the work of earlier authors. Various other layer structures can be expected to have a ' T^2 ' law for the low temperature heat capacities.

There is also some evidence of a ' T ' law in materials such as selenium and sulphur which are composed of weakly connected atomic chains⁹.

It is to be expected that some improvement should result from the use of a discrete lattice model rather than a continuum one. Unfortunately, the theory becomes much more complicated. No simple treatment for thermodynamic

properties seems to exist, each example being a special case. This discrete model was first analyzed by Born and von Kármán¹⁰. Blackman¹¹ has extended these calculations which are essentially qualitative but seem to throw some light on the behaviour of specific heat at low temperatures.

ANOMALIES IN HEAT CAPACITIES

In some systems, energy appears to change abnormally over only a narrow temperature range. Accordingly, a specific heat anomaly will also be observable in that temperature region. It will occur when there is only a finite number of energy levels for the system. Once the temperature has been raised sufficiently for them all to be equally populated, no further change in energy will occur on raising the temperature. If the spacing of the energy levels is kT' , then a peak in the specific heat - temperature curve will be observable at temperatures of the order of T' . An elucidation of this anomaly has been attempted by many research workers.

anomalies have often been observed in the form of 'λ points' or discontinuities, in binary substitution alloys, ferro- and antiferromagnets, ferroelectrics, hydrogen halides, superconductors and various molecular crystals.

These are generally associated with some kind of order-disorder process. If one wishes to compare the results of a quantitative theory of an anomalous effect with experimental measurements, it is necessary to have an accurate theory of the normal contribution of lattice vibrations to the heat capacities so that the anomalous effect can be obtained by subtraction, provided the temperature is sufficiently high so as to render the electronic contribution negligible.

At this juncture, the structural aspects of co-operative transformations in solids may be briefly reviewed. These can be broadly classified into two subgroups :

- a) transformation from a paraelectric to a ferroelectric or antiferroelectric solid, and
- b) transformation from paramagnetic to ferromagnetic or antiferromagnetic state in crystals.

FERROELECTRIC MATERIALS

In the paraelectric phase, i.e. $T > T_c$, where T_c is the transition temperature (Curie point) individual molecular dipoles in the crystal behave more or less independently. Below T_c the dipole fields co-operate to give a much higher total polarisation in the so-called

ferroelectric field. Since energy is required to destroy this polarisation, this manifests itself as a peak in the heat capacity versus temperature curve. Of some importance are the following relationships :

$$\Delta S = S_0 - S = \frac{2\pi}{C} \Delta P^2$$

and

$$\Delta C_P = C_P - C_{P_0} = \frac{2\pi}{C} T \frac{\partial P^2}{\partial T^2}$$

where S , C_P and S_0 , C_{P_0} represent, respectively, the entropies and heat capacities of the polar and non-polar states, C is the Curie constant and P , the polarisation. These relations enable one to compare results from heat capacity measurements with those obtained from other studies.

The study of ferroelectric substances has gained considerable importance in recent years due to the wide industrial applications of ferroelectrics. Besides, the phenomenon poses several interesting problems in solid state chemistry. Many excellent reviews¹²⁻¹⁴ are available in the literature, which describe the various properties of ferroelectric crystals in detail. We may consider only a few interesting results which have been reported recently.

Hoshino and Pepinsky et al.¹⁵ have studied the dielectric and thermal properties of triglycine sulphate (TGS). They

found that TGS undergoes a second order transition at 48°C with $\Delta S = 0.48$ cal./mole.deg (from heat capacity measurements) and $\Delta S = 0.64$ cal./mole. deg. (from dielectric measurements). The results of both techniques are in fair agreement although the accuracy involved in this comparison is poor, owing to the fairly small transition energy of TGS.

Recently ferroelectricity has been reported¹⁶⁻¹⁸ in potassium ferrocyanide trihydrate, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$. Heat capacity measurements by Nakagawa *et al.*¹⁹ revealed a hump at -25°C with $\Delta S = 0.46$ cal./mole.deg. which agrees well with the theoretical value $R \ln 2$ in the phase transition of the order-disorder type. In order to determine the role played by water molecules in the ferroelectricity of this compound, the author²⁰ measured the heat capacity of anhydrous potassium ferrocyanide in the temperature range $80^{\circ}-300^{\circ}\text{K}$. No anomalous behaviour was detected in the entire range of measurements, indicating that ferroelectricity gets destroyed on loss of water molecules. This conclusion has been confirmed later by the results of X-ray and nuclear magnetic resonance studies²¹.

MAGNETIC MATERIALS

In many crystalline substances there exists a pattern of electronic energy levels such that in the

experimentally accessible range of temperature it is possible to observe a transition from a low temperature, completely ordered form of essentially zero entropy to a high temperature disordered form where there is a nearly random distribution among several electronic states per molecular unit. There is, therefore, in the higher temperature form, a substantial electronic contribution to the entropy of the crystal, of magnitude $R \ln n$ per mole, where 'n' is the number of electronic states per molecular unit. Such a pattern of energy levels is found in substances having unpaired electrons and, in particular, in ionic crystals containing elements with partially filled d or f electronic shells. Because of the magnetic moment accompanying the spin and orbital angular momenta of the electrons, these substances are, in the higher temperature region, paramagnetic. The change from the completely ordered low temperature form to a high temperature form where there is a random distribution among several electronic states may be called a magnetic transition, e.g. ferromagnetic \rightarrow paramagnetic and antiferromagnetic \rightarrow paramagnetic transformations. Since energy is required to destroy the alignment of spin moments, the heat capacity exhibits a peak or hump, with a maximum at a characteristic temperature, called the Curie (ferromagnets) or the Néel (antiferromagnets) point.

Above this temperature, both ferro- and antiferromagnets become paramagnetic and obey the Curie-Weiss law. However, at temperatures below 300°K , the occurrence of antiferromagnetism is the general rule.

Antiferromagnetism is a domain of research which has attracted wide-spread attention in recent years. The concept of antiferromagnetism was first put forward by Néel²² in connection with his study of the paramagnetic susceptibility of metals and alloys of transition elements. He supposed that the atoms of some substances possess magnetic moments and that a negative exchange coupling is operating among them. As a consequence, he guessed that the arrangement of the atomic magnetic moments in the crystal lattice is such that they point upward and downward in an alternating manner when the temperature is sufficiently low.

The interaction energy between different magnetic ions may be formally described as an exchange energy

$$- 2J_{xy} \vec{S}_x \cdot \vec{S}_y$$

where J_{xy} is the exchange integral between the x^{th} and y^{th} atoms and \vec{S}_x and \vec{S}_y are the respective spin angular momenta. A positive J corresponds to a ferromagnetic interaction and a negative J to an antiferromagnetic interaction (lowest

energy for the antiparallel spin alignment of the two atoms). Néel's original theory has been extended by van Vleck²³, Néel himself²⁴, Anderson²⁵, Smart²⁶ and others.

A fundamental problem in antiferromagnetism is the origin of the exchange interactions. Néel²⁴ recognized for antiferromagnetic compounds the importance of superexchange, that is, the exchange coupling between magnetic atoms through the intermediary of a negative non-magnetic ion. This sort of interaction was first considered by Kramers²⁷ and its realistic treatment was given by Anderson²⁸.

Many experimental techniques have been employed to study the magnetic properties, in general, and magnetic transitions occurring at Néel/Curie temperature, in particular. Prominent among these are (1) Neutron diffraction (2) Nuclear magnetic resonance, (3) Magnetic susceptibility and (4) Heat capacity, measurements.

NEUTRON DIFFRACTION

Neutrons are scattered by interactions with the nuclei of atoms constituting a material but in addition they interact also with the magnetic moment vectors of the atoms. If these magnetic vectors are randomly arranged, the magnetic scattering will be coherent, but in an antiferromagnetic material the magnetic vectors are aligned

antiparallel at temperatures below the Néel point ; then, if the resulting magnetic unit cell is different in size from the chemical unit cell, extra diffraction lines will be observed, and the exact pattern of the ordering can be deduced.

Sparks and Komoto²⁹ have reported a powder neutron diffraction study of stoichiometric nickel sulphide, NiS, in the range 85°-770°K. They found a paramagnetic-antiferromagnetic transition at 263°K. In the antiferromagnetic state the moments in a hexagonal layer are coupled ferromagnetically and point in the direction of the c axis. The coupling between adjacent hexagonal layers is antiferromagnetic.

NUCLEAR MAGNETIC RESONANCE

Atomic nuclei of magnetic atoms can serve as delicate and precise probes of the local fields inside magnetic materials. By studying the nuclear resonance frequency and relaxation times in the critical region it is possible to obtain accurate and detailed information³⁰ on the establishment of magnetic order. Broadly speaking, two types of experimental informations are obtained :

(1) The time-averaged sublattice magnetization M is determined as a function of temperature and external magnetic

field. In particular it will be shown that in zero external field the relation

$$M \propto (T_N - T)^{1/3}$$

holds with remarkable accuracy just below T_N , the Néel temperature.

(ii) The behaviour of the NMR line-widths show that large fluctuations in the magnetization take place near T_N .

Heller³¹ has made a detailed experimental study of the F^{19} nuclear resonance in the antiferromagnet MnF_2 near its $T_N = 67.34^\circ K$. The dependence of the time-averaged sublattice magnetizations on temperature and external magnetic field was deduced from the behaviour of the NMR frequencies. In zero external field the reduced sublattice magnetization was found to follow the cube-root law with remarkable precision over the reduced temperature range $0.92 < T/T_N < 0.99993$.

MAGNETIC SUSCEPTIBILITY

At the Néel temperature the magnetic susceptibility exhibits a maximum value. Friedberg et al.³² have measured the magnetic susceptibility of ferrous chloride tetrahydrate, $FeCl_2 \cdot 4H_2O$ in powder and single crystal form. The T_N was found to be about $1^\circ K$.

However, it may be noted that a slight impurity in the specimens is likely to introduce a large error in the accuracy of the measurements.

HEAT CAPACITY

Since energy is required to destroy the order of magnetic spin moments, heat capacity is expected to reveal a peak or hump at the Néel temperature. This technique may be considered as the most reliable in the determination of T_N , since the results are almost indifferent to the presence of traces of ferromagnetic and allied impurities and are affected only to the extent of their percentage. Besides, magnetic susceptibility maximum may lie at a temperature higher than T_N . For example, the Néel temperature of copper fluoride dihydrate, $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, is 10.9°K ^{33,34} and the peak of the magnetic susceptibility has been observed at 26°K ³⁵. Nagai³⁶ has developed a statistical theory of antiferromagnetism in an attempt to explain this peculiar behaviour.

Hadley and Stout³⁷ have reported an anomaly in the heat capacity of MnBr_2 at $2.16 \pm 0.01^\circ\text{K}$, arising from the ordering of the spins of the magⁿanous ions.

Recently a series of compounds of the type KMf_3 , where M is a divalent transition metal ion such as Mn^{+2} ,

Co^{+2} , Ni^{+2} and Cu^{+2} , has been found to exhibit anti-ferromagnetic \rightarrow paramagnetic transitions below the room temperature. These compounds have been studied by various workers employing techniques such as neutron diffraction³⁸, magnetic susceptibility^{39,40} and heat capacity measurements. The results of the last-mentioned technique have been reported by us⁴¹. The Néel temperatures of KMnF_3 , KCoF_3 , KNiF_3 and KCuF_3 were found to be 83.3°K , 109.5°K , 253.5°K and 233.2°K respectively. In order to estimate the magnetic contributions to the heat capacity and entropy, it was necessary to measure the heat capacity of the corresponding isomorphous diamagnetic potassium zinc trifluoride, KZnF_3 . This has been reported in Chapter III and the data obtained was employed to determine the lattice and magnetic contributions.

Since the mechanism of super-exchange is considered to be responsible for the magnetic behaviour of KMF_3 compounds, a study of the effect of random substitution of the magnetic ions with diamagnetic ones would be of considerable interest, especially from the point of view of the lowering of the Néel temperature and its complete disappearance at a critical concentration of paramagnetic ions. Hence heat capacities of three compounds, $\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$ ($x = 0.85, 0.69$ and 0.49) were measured and are reported in Part II.

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CHAPTER II

DESCRIPTION OF THE CRYOSTAT ASSEMBLY

Measurements of heat capacities were started about two hundred years ago and to-day the technique has attained the status of a separate field of research. There is no doubt that the various theories concerned with the properties of lattice, put forward from time to time, have largely contributed to the development of the modern, sophisticated experimental techniques to obtain very accurate data needed for testing these theories.

The very earliest heat capacity measurements were, strictly speaking, specific heat measurements made by the method of mixtures, in which a measured amount of a hot substance and a measured amount of a cold substance (one of which was usually water) were mixed. The initial temperatures of the separate substances and the final temperature of the mixture were observed.

Petit and Dulong¹ determined specific heats by the method of cooling in air from a temperature 5 to 10° above the temperature of the surrounding air. Joule² began in about 1840 and continued for several years the determination

of the mechanical and electrical equivalents of heat. This work was perhaps the most important calorimetric study ever made.

As the years went by, following the work of Petit and Dulong, studies on the variation of heat capacity with temperature became a more and more absorbing phase of calorimetry. Such studies introduced their own problems, of which a most particularly difficult one was that of controlling exchange of energy between the substance under study and its surroundings. A very famous calorimeter devised to overcome this problem was that of Eucken and Nernst^{3,4} for low temperature heat capacity measurements. It had the following features : The heat leak from outside was made extremely small by hanging the sample in an evacuated space in a liquid bath in a Dewar vessel ; warming of the sample was accomplished electrically by a platinum resistance wire ; the same wire resistor could serve for temperature measurement as well as for heating ; the substance itself could be the calorimeter (or if not a suitable material it could be contained in a metal container).

The Nernst-Eucken calorimeter was of the type now known as the isothermal-jacket calorimeter. Accurate heat capacity measurements with it still required measurement of the temperature changes in the sample caused by heat

transfer by radiation and conduction between the sample and the isothermal wall nearby. The difficulty is overcome by insertion of a metal shield between the sample container and the wall of the vessel containing the refrigerating liquid. With this arrangement, adjustment of the temperature of the shield to a constant value near which heat capacity measurements are to be made allows the heat transfer to be much reduced in these regions.

The metal shield may be made continuously adjustable in temperature, permitting it to be kept at all times at the same temperature as the sample container within. By this procedure the heat transfer to or from the sample can be reduced to a very low value, and may even be made negligible. In a calorimeter having this feature, the surface to which the sample or its container is exposed is no longer isothermal during a heat capacity measurement. As there is essentially no heat transfer, all electrical energy supplied goes to raising the temperature of the sample. Because the process is essentially adiabatic, the shield is called an adiabatic shield and the calorimeter is called an adiabatic calorimeter. With separate heater and thermometer, suitable cryogenic shielding and a manually or automatically controlled adiabatic shield, it is capable

of precision measurements to within about 0.03% between 300 and 100°K and somewhat more at lower temperatures⁵. Recently an adiabatic calorimeter has been devised by West and Ginnings⁶ for operation to 500°C. A distinguishing feature is the multiple radiation shields on the calorimeter proper and adiabatic shield. This calorimeter, with automatic shield-temperature control, has been found to give heat capacities with a range of about 0.01% in a short series of three or more measurements.

Even though an ideal adiabatic calorimeter requires no heat leak between it and its surroundings, it is impossible to achieve this condition in practice. Since our studies were confined to temperatures below 300°K, where heat leaks by radiation were easily calculable, we preferred the use of an isothermal calorimeter for the determination of heat capacities. The details of the construction and operation were similar to those described previously by us⁷. However, there were two major changes :

(i) another calorimeter with laboratory designation 102L and radiation shield were used and

(ii) a platinum resistance thermometer (serial No. 1644177) calibrated and certified by the National Bureau of Standards, U.S.A. was employed to check the calibration chart of the copper-constantan thermocouples, prepared

in this laboratory a few years ago and continuously in use since then for the measurement of temperature.

THE CALORIMETER AND THE RADIATION SHIELD

The calorimeter is a cylindrical copper vessel with a diameter of 4 cm., a height of 6 cm. and a wall thickness of 0.05 cm. A tubing of 1 cm. diameter and 1.5 cm. height is soldered to one of the faces of the cylinder which has at its centre a hole of the same diameter, so as to introduce a sample. A cap sits firmly in the circular trough immediately surrounding this tubing and concentric with the same, so that it can be soldered to make a vacuum-tight seal. Ordinary soft solder is employed as a sealing material. On the centre of the cap, there is a pin-hole through which helium or hydrogen gas can be introduced to increase conduction of heat to a sample. Six copper radial vanes are silver soldered to the bottom surface of the calorimeter so as to facilitate thermal equilibrium (in the calorimeter used previously⁷ the vanes were not incorporated).

Around the calorimeter a thin coating of insulated tar was given and an enamelled copper wire (S.W.G.44) of 0.00813 cm. diameter and of about 240 ohms^{ms} resistance would on it uniformly leaving a space of about 0.5 cm. on either side of the cylindrical part of the calorimeter.

Obviously this copper wire was used as a combined resistance thermometer-heater for measuring temperatures and energy. Since both the calorimeter and the thermometer-heater were made of the same material, strain due to temperature change was minimized. After giving another coating of tar, first silver and then gold were vacuum deposited on the cylindrical surface of the calorimeter. The thickness of the plating was of the order of 10^4 \AA . Very thin gold foils were also attached to the cylindrical surface and since they have very negligible heat capacity, their contribution was considered as very small. All joints in the calorimeter were silver soldered except the cap on the filling tube (which was soft soldered). The weight of the empty calorimeter, including the thermometer-heater, is 137.8 g.

The heavier calorimeter (the previous calorimeter⁷ weighed only 38.1 g) obviously required another radiation shield (the earlier one⁷ weighed only 650 g). The radiation shield presently employed is also made out of a copper sheet and weighs about 1800 g. It served satisfactorily to maintain a good environment of constant temperature. Its dimensions were almost the same as the earlier one⁷, the only difference being in the thickness of the walls. As in the case of the calorimeter, an enamelled copper wire (S.W.G.40) of about 150 ohms resistance was wound on it and gold was vacuum deposited on the entire surface.

N
PLATINUM RESISTANCE THERMOMETRY
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The International Practical Temperature scale is based upon six defining fixed points to which numerical values have been assigned. Values between these fixed points are defined by the indication of specified measuring instruments and the use of specified interpolation formulae to relate these indications to temperature. Between -182.97°C and 630.5°C the instruments are platinum resistance thermometers which have been calibrated at specified defining fixed points to determine the constants in the interpolation formula. Over the range 0° to 630°C the interpolation formula may be put in the form

$$t = \frac{R_t - R_0}{\alpha R_0} + \delta \left(\frac{t}{100} - 1 \right) \frac{t}{100}$$

In this formula, 't' is the temperature in $^{\circ}\text{C}$, ' R_t ' is the resistance at the temperature, 't' and R_0 is the resistance at 0°C . The constants, α and δ , have values which are characteristic of the individual thermometer. The constant α , which is equivalent to $\frac{R_{100} - R_0}{100 R_0}$, is determined from measurements of thermometer resistor at the triple point of water (0.01°C) and the steam point. The value of α must be greater than 0.003920 to satisfy one of the international requirements for a standard thermometer. The

constant δ , is determined from measurements at an additional fixed point, either the boiling point of sulphur, which is a defining fixed point, or the freezing point of zinc, which is recommended in the text of the International Practical Temperature scale as an alternative.

Over the range 0° to -182.97°C , the interpolation formula may be put in the modified form

$$t = \frac{R_t - R_0}{\alpha R_0} + \delta \left(\frac{t}{100} - 1 \right) \frac{t}{100} + \beta \left(\frac{t}{100} - 1 \right) \left(\frac{t}{100} \right)^3$$

The constant β , is also characteristic of the individual thermometer and is determined from an additional measurement at the boiling point of oxygen.

A standard platinum resistance thermometer is constructed so that precise measurements may be made of the resistance of its platinum resistor. The resistor is made of very pure platinum wire, is compact in form, and is contained in a protecting tube. At each end of the resistor is a branch point to which are joined two leads, commonly called 'current' and 'potential' leads. This construction makes it possible to measure the resistance of the resistor alone (i.e. between the branch points) independent of the resistance of the leads.

For accurate determinations of temperature with a platinum thermometer it is necessary to refer to some known and reproducible temperature (fixed point) which should be readily available whenever it is needed. This fixed temperature is most commonly either the ice point, or the triple point of water (0.01°C). Measurement of the resistance of the thermometer in a suitable ice bath will give R_0 directly, while a small correction, very nearly equivalent to 0.01°C , is necessary if a triple point cell is used⁸. The choice between these two fixed points is largely on the basis of the accuracy required. The triple point may be realized within $\pm 0.0002^{\circ}\text{C}$., while the accuracy of realizing the ice-point is typically five to ten times worse. Since temperature determinations depend directly upon R_0 , it should be redetermined frequently enough to assure the user that he has a sufficiently reliable value when measurements are made.

Since only ratios of resistances are required to determine temperature, the units may be absolute ohms, international ohms, or any arbitrary unit ; the calibrated bridge (or potentiometer) must be self-consistent.

Certain precautions must be observed if reliable temperature determinations are to be made with a resistance thermometer: (a) The thermometer coil must be immersed to a depth sufficient to prevent a significant error from

transfer of heat along the thermometer leads and protecting tube. A check of the adequacy of the immersion in each uniform constant temperature bath may be made by varying the depth of immersion of the thermometer and noting whether there is a change in resistance.

(b) When a measuring current flows in the thermometer, some heating of the resistor results ; consequently the same current should be used in making measurements as was used in the calibrations.

(c) Sufficient time must be allowed, after the current is turned on, for equilibrium to be established.

(d) The characteristic constants of a thermometer may change as a result of changes in the dimensions of the wire, strains in the wire, or the subjection of the thermometer to excessive temperatures. It is particularly important that care be taken to protect the thermometer from small mechanical shocks, which strain the wire to produce small changes in the characteristics of the wire in the platinum resistor.

At the time of the construction and calibration of an isothermal low temperature calorimeter a few years ago⁷, no certified platinum resistance thermometer was available to us. Hence we employed copper-constantan thermocouples

for measurement of temperatures. Their use was suggested by Giauque⁹ because of the ease with which they could be handled and their reliable performance over a period of years was established^{10,11}. Fortunately, we could subsequently secure a platinum resistance thermometer (Leeds and Northrup Company, Philadelphia, Pennsylvania, Serial Number 1644177) calibrated at and certified as a satisfactory thermometer by National Bureau of Standards, U.S.A.

Copper-constantan thermocouples were directly compared in the conventional way with this standard thermometer at a few selected fixed points (Table 1). The excellent agreement obtained once again stressed the importance of copper-constantan thermocouples as thermometers at moderately low temperatures.

TABLE - 1

Recalibration Data of Thermocouples

Fixed point	Temperature by platinum resistance thermometer °K	E.M.F. shown by thermo- couple μV	Corres- ponding tempera- ture °K
1. Liquid nitrogen	V.P. 77.18	5524	77.10
2. Liquid oxygen	V.P. 89.06	5317	89.00
3. Carbon-di-sulphide	F.P. 161.56	3652	161.52
4. Toluene	F.P. 178.06	3190	177.98
5. Solid carbon-di-oxide	V.P. 193.92	2730	193.88
6. Carbon-tetrachloride	F.P. 250.26	863	250.20
7. Ice	M.P. 273.15	0	273.15

V.P. = Vapour pressure ; F.P. = Freezing point ; M.P. = Melting point

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CHAPTER III

HEAT CAPACITY OF POTASSIUM ZINC TRIFLUORIDE

In our earlier papers¹⁻³, the results of low temperature heat capacity measurements in the range 80°-300°K on KMnF_3 , KCoF_3 , KNiF_3 and KCuF_3 were presented. Each of these compounds exhibited an anomaly above 80°K in their heat capacity-temperature behaviour associated with the antiferromagnetic ordering of the atomic magnetic moments. However, it was not possible to estimate the magnetic contribution to heat capacity and entropy at that time.

At temperatures above 80°K, the experimental heat capacity may be assumed to consist of only two parts, namely, the lattice and ^{the} magnetic. Hence, if the lattice contribution could be estimated, then the magnetic one can be evaluated by simple subtraction. To estimate the former, Stout⁴ has postulated that the heat capacity of an isomorphous, diamagnetic compound can be used. He evaluated the lattice contributions to heat capacity and entropy of MnF_2 , CoF_2 and NiF_2 using the data on ZnF_2 and corresponding states argument.

Since potassium zinc trifluoride, KZnF_3 , is isomorphous with KMnF_3 , KCoF_3 , etc., the heat capacity of the former may be employed to estimate the lattice and consequently the magnetic contributions in these compounds. In the following, the preparation, identification and heat capacity measurements of KZnF_3 have been described in detail.

PREPARATION AND ANALYSIS

Crystal structure of KZnF_3 has been determined by various workers and the data have been tabulated by Martin et al.⁵ The compound was found to be either cubic, pseudo-cubic, monoclinic or tetragonal. It is probable that the variety of structures observed arises from variations in preparative conditions such as the use of the wet and dry way methods, different ignition temperatures and rates of cooling. The following method was employed for the preparation of our calorimetric sample:

Appropriate quantities of potassium hydrogen fluoride and zinc fluoride, were mixed and the precipitated compound was filtered, washed and dried.

The compound was analysed by X-ray powder diffraction at room temperature, using a 14 cm Debye-Scherrer camera and $\text{Cu-K}\alpha_1$ ($\lambda = 1.54050 \text{ \AA}$) radiation. No extra line due

to any of the components was observed. The compound showed cubic perovskite-like pattern. The calculated lattice constant ($a = 4.049 \text{ \AA}$) agreed well with the data reported in the literature ($a = 4.050 \text{ \AA}$).

HEAT CAPACITY MEASUREMENTS

The mass of the sample loaded into the calorimeter was 67.06 g. The calorimeter was sealed after filling it with the heat exchange gas (hydrogen). Heat capacities were measured in the range 80° - 300° K in the usual way. The ratio of the heat capacity of the sample to that of the filled calorimeter varied from 0.47 at 80° - 200° K to 0.44 at 300° K.

In calculating the heat capacities the defined calorie was taken as equal to 4.184 abs. joules. The ice from distilled water was used as the reference point, 273.15° K. The temperatures T listed are the arithmetic means of the initial and final temperatures. The heat capacities reported are the ratios of increase in enthalpy ΔH to the rise of temperature. ΔT . The several series of measurements made are given in chronological sequence in Table 2 and represented graphically in Fig.1.

In ^{the} first series, the calorimeter was cooled to 105° K and measurements were made upto 180° K. The

TABLE - 2

Heat Capacity of Potassium Zinc Trifluoride
(cal./mole.deg.)

Temp. °K	C _P	Temp. °K	C _P
<u>SERIES - I</u>			
107.91	16.01	166.93	21.91
110.17	16.62	171.81	22.27
112.53	17.10	175.42	22.51
113.27	16.86	177.46	22.95
114.52	17.38	180.09	22.99
117.21	17.29	<u>SERIES-II</u>	
121.41	17.96	82.68	13.14
126.44	18.54	85.22	13.34
130.01	18.68	87.92	13.85
132.74	18.97	93.25	14.32
134.81	19.50	96.16	15.12
140.48	19.98	103.42	15.72
144.69	20.18	107.01	16.14
150.26	20.46	110.35	16.86
154.27	20.94	113.41	16.97
158.67	21.30	116.29	17.29
163.15	21.99	119.67	17.92

Contd...

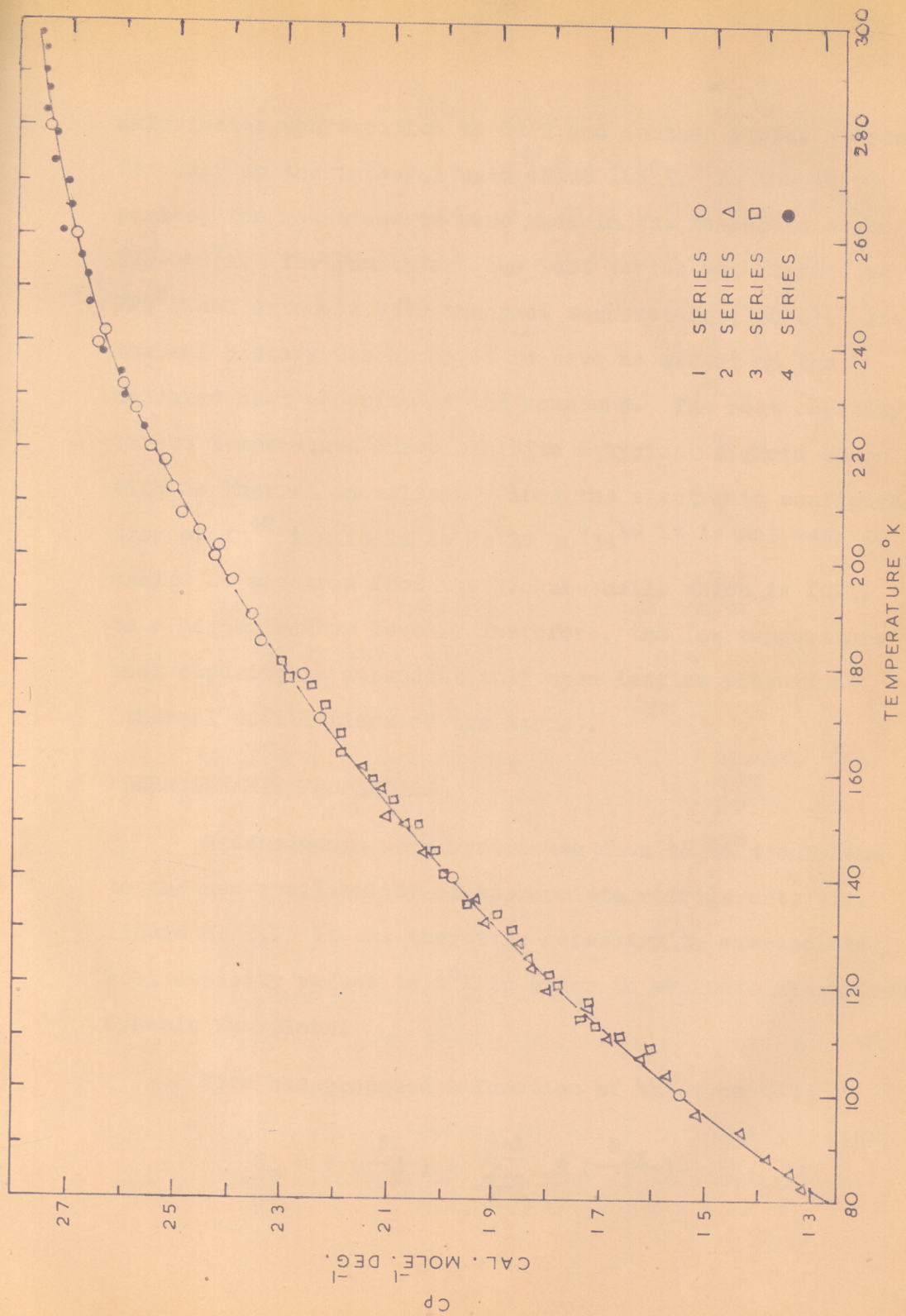


FIG.1. HEAT CAPACITY OF KZnF_3

calorimeter was recooled to 80°K and another series started to cover up the interval upto about 165°K. In the third series, the measurements were made in the temperature range 170°-240°K. The fourth and the last series was started at 220°K and extended upto the room temperature (300°K). The thermal history was observed to have no effect on the measured heat capacity of the compound. The heat capacity versus temperature curve exhibits a typical sigmoid shape, with no thermal anomalies. Since the electronic configuration of Zn⁺² ion is 1s²2s²2p⁶3s²3p⁶3d¹⁰ it is not easy to excite an electron from the 3d sub-shell, which is full, to a higher energy level. Therefore, the low temperature heat capacity is dependent only upon lattice vibrations (thermal oscillations of the atoms).

THERMODYNAMIC PROPERTIES

Measurements were restricted down to 80°K only due to the non-availability of appropriate refrigerants viz. liquid He/H₂. It was therefore necessary to extrapolate heat capacity values to 0°K in order to evaluate the thermodynamic functions.

Born has proposed a function of the type

$$C_V = f\left(\frac{\theta_D}{T}\right) + \sum_{i=1}^{p-1} f\left(\frac{\theta_{Ei}}{T}\right)$$

where $f\left(\frac{\theta_D}{T}\right)$ and $f\left(\frac{\theta_{E1}}{T}\right)$ represent Debye and Einstein functions respectively and 'p' the number of atoms in a molecule of the substance. This type of equation has been shown to represent heat capacities of several substances over a wide temperature range and permit reasonably accurate extrapolation. The following equation was fitted to represent the heat capacity of potassium zinc trifluoride over the entire range of measurements, the accuracy being $\pm 2\%$.

$$C_p \cong D\left(\frac{90}{T}\right) + 2E\left(\frac{270}{T}\right) + 2E\left(\frac{425}{T}\right)$$

The values of thermodynamic functions such as entropy (S_{λ}°), enthalpy ($H^{\circ} - H_0^{\circ}$), and Gibbs free energy $-\left(\frac{F^{\circ} - H_0^{\circ}}{T}\right)$, together with the smoothed values of heat capacity (C_p°) have been listed in Table 3. At 298.15°K, the values of C_p° , S_{λ}° , ($H^{\circ} - H_0^{\circ}$) and $-\left(\frac{F^{\circ} - H_0^{\circ}}{T}\right)$ were 27.58 cal/mole.deg., 37.08 cal/mole.deg., 5362 cal/mole and -19.09 cal/mole.deg. respectively.

The heat capacity values of potassium zinc trifluoride, $KZnF_3$, together with those of other fluorides, viz. $KMnF_3$, $KCoF_3$, $KNiF_3$ and $KCuF_3$ are listed for comparison in Table 4 at regular temperature intervals. It is interesting to note that $KNiF_3$ displays consistently lower heat capacity than $KZnF_3$. The importance of this finding will be discussed in Chapter IV.

TABLE - 3

Thermodynamic Functions of Potassium Zinc Trifluoride

Temp. °K	C_p° cal./mole.deg.	$S^{\circ}-S_0^{\circ}$ cal./mole.deg.	$H^{\circ}-H_0^{\circ}$ cal./mole	$-(F^{\circ}-H_0^{\circ})/T$ cal./mole.deg.
80	12.60	(9.64) ⁺	(444.8) ⁺	(4.080) ⁺
85	13.38	10.42	510.0	4.419
90	14.08	11.21	578.8	4.779
95	14.76	11.99	650.8	5.140
100	15.36	12.76	726.2	5.498
105	16.02	13.53	804.6	5.867
110	16.62	14.29	886.2	6.234
115	17.20	15.04	970.8	6.597
120	17.76	15.78	1058	6.964
125	18.28	16.52	1148	7.337
130	18.78	17.24	1241	7.695
135	19.32	17.96	1336	8.063
140	19.80	18.67	1434	8.430
145	20.24	19.38	1535	8.790
150	20.72	20.07	1637	9.160
155	21.16	20.76	1742	9.520
160	21.58	21.44	1849	9.890

Contd...

Temp. °K	C_p° cal./mole.deg.	$S^{\circ} - S_0^{\circ}$ cal./mole.deg.	$H^{\circ} - H_0^{\circ}$ cal./mole.	$-(F^{\circ} - H_0^{\circ})/T$ cal./mole.deg.
165	21.96	22.11	1958	10.24
170	22.32	22.77	2069	10.60
175	22.66	23.42	2181	10.95
180	23.02	24.07	2295	11.32
185	23.32	24.70	2411	11.67
190	23.68	25.33	2528	12.03
195	24.02	25.95	2648	12.37
200	24.32	26.57	2768	12.73
205	24.60	27.17	2891	13.07
210	24.88	27.77	3014	13.42
215	25.18	28.36	3139	13.76
220	25.48	28.94	3266	14.09
225	25.76	29.52	3394	14.43
230	26.02	30.09	3523	14.77
235	26.20	30.65	3654	15.10
240	26.38	31.20	3785	15.43
245	26.52	31.75	3917	15.76
250	26.68	32.28	4050	16.08
255	26.81	32.81	4184	16.40
260	26.96	33.33	4318	16.72

Contd...

Temp. °K	C_p° cal./mole.deg.	$S^{\circ} - S_0^{\circ}$ cal./mole.deg.	$H^{\circ} - H_0^{\circ}$ cal./mole.	$-(F^{\circ} - H_0^{\circ})/T$ cal./mole.deg.
265	27.12	33.85	4453	17.04
270	27.20	34.36	4589	17.36
275	27.28	34.86	4725	17.68
280	27.41	35.35	4862	17.99
285	27.44	35.86	4999	18.32
290	27.48	36.31	5137	18.60
295	27.54	36.78	5275	18.90
300	27.60	37.25	5413	19.21
273.15	(27.25)	(34.67)	(4675)	(17.55)
298.15	(27.58)	(37.08)	(5362)	(19.09)

+ Extrapolated

TABLE -4

Heat Capacity of KMF_3 Compounds (Cal./mole.deg.)

Compound	C_p				T_N °K
	100°K	150°K	200°K	298.15°K	
$KMnF_3$	15.75 ⁺	20.21	23.49	27.50	83.3
$KCoF_3$	18.31 ⁺	21.89	25.18	28.84	109.5
$KNiF_3$	14.80	20.05	23.50	27.30	253.5
$KCuF_3$	13.60	20.00	25.38	28.47	233.2
$KZnF_3$ ⁺⁺	15.36	20.72	24.32	27.58	-

+ Transition region

++ Present work.

COMPARISON OF MF_2 AND KMF_3 SERIES

The divalent cation series, Mn^{+2} , Fe^{+2} , Co^{+2} and Ni^{+2} appears in three sets of compounds : MF_2 , KMF_3 and MO . However, we shall confine ourselves to the comparison of MF_2 and KMF_3 series. In both cases, the magnetic interaction increases monotonically through the series and in each case the Ni^{+2} - Ni^{+2} interaction is particularly large compared to the other compounds of the series. The results on these cubic perovskites and difluorides provide us with the rare opportunity of comparing exchange interactions in systems which have the same cations and the same anions in different geometrical arrangements. The interaction in the perovskites is larger than in the corresponding difluorides by factors ranging from 1.2 to 3.5. This result might tentatively be attributed to the larger M-F-M angle in the perovskites, since the super-exchange interaction is angle-dependent and is stronger for larger angles. Incidentally it is the largest for 180° .

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CHAPTER IV

LATTICE HEAT CAPACITY AND ENTROPY OF
MAGNETIC COMPOUNDS

Generally three terms contribute to the specific heat of a magnetic substance : a lattice term, an electronic term and a magnetic term. Thus the magnetic one can be obtained by subtracting the contributions arising from the lattice and electronic terms. At temperatures above 20°K , the electronic term is negligible and may reasonably be ignored. Then the experimental heat capacity will consist only of the other two parts, namely, the lattice and the magnetic. The magnetic specific heat values lead to quantities which can be compared with the theoretically derived values and with the other types of results of magnetic measurements.

One quantity of interest is the area under a magnetic specific heat curve. This is equal to the energy ΔH required to take the spin system from the state of approximately complete magnetic order at $T \ll T_c$ to the state of approximately complete magnetic disorder at $T \gg T_c$. Another

quantity of interest is the total entropy gain in going from the ordered to the disordered state. This can be easily calculated from the magnetic specific heat curve. Simple considerations show that the theoretical entropy increase in going from a completely ordered to disordered spin state is equal to $R \ln (2S + 1)$ where S is the spin per atom. Hence, a necessary although not sufficient condition for the validity of a separated magnetic specific heat curve is that the associated total magnetic entropy gain approximates to $R \ln (2S + 1)$. The estimation of both these quantities, namely, magnetic specific heat and entropy, depends upon the estimation of lattice and electronic contributions.

The contributions arising from the lattice waves can be represented by

$$C_p = (1 + \alpha GT) f \left(\frac{\theta_D}{T} \right)$$

where $f \left(\frac{\theta_D}{T} \right)$ represents the usual Debye function, α is the coefficient of volume expansion and G the Gruneisen constant. The constant θ_D can be obtained by matching the theoretical specific heat in a temperature region where the magnetic contribution is negligible. In fact θ_D is fitted at temperatures either much below or far above the transition temperature.

Most antiferromagnets are favourable in having no electronic specific heat; however, the lattice specific heat may no longer be describable by one simple Debye function. As shown by Hofmann et al.¹ the specific heat of a large number of binary salts can be described by two Debye parameters, one Debye temperature for each type of atom in the binary compound. In other words the specific heat of a binary compound $R_n X_m$ can be represented by the relationship :

$$C_V = nf (\theta_R/T) + mf (\theta_X/T)$$

where θ_R and θ_X refer to the Debye temperatures associated with R and X, respectively. The values of these two parameters can be found by matching the experimental specific heat or the entropy to the theoretical values at temperatures widely different from the critical temperature; when matching the entropy at $T \gg T_c$ magnetic contribution is obviously defined to be $R \ln (2S + 1)$. This 'two Debye constant' procedure gives an excellent description (accuracy $\pm 1\%$) of the specific heat of some diamagnetic salts (e.g. ZnF_2). However, it cannot be used for salts with more than two types atoms in the molecule or for those binary salts which have a layer type structure, e.g. $MnCl_2$.

Jennings and Hansen² have recently extended this procedure to layer type structures by using an additional parameter 'a' so that,

$$C_V = af(\theta_R/T) + (n + m - a) f(\theta_X/T)$$

This expression could reproduce the experimental values of the lattice heat capacity of $MnCl_2^3$, within 1/4 % over the entire range.

Osborne and Westrum^{4,5} assumed that the lattice contribution to the heat capacities of UO_2 and NpO_2 equals the heat capacity of the isomorphous diamagnetic ThO_2 and that the heat capacity of ThF_4 represents the lattice contribution in UF_4 . From their heat capacity measurements of NiF_2 and ZnF_2 , Stout⁶ found that the observed heat capacity of NiF_2 was considerably less than that of the isomorphous diamagnetic ZnF_2 . Since the formula weights of the isomorphous⁷ MnF_2 , FeF_2 , CoF_2 , NiF_2 , and ZnF_2 are not widely different, Stout assumed that the vibrational contributions to the entropy and heat capacity of these halides obey a law of corresponding states. Then the lattice entropy $S(\text{lat.}) = \Phi(T/\theta)$, and the lattice heat capacity, $C_p(\text{lat.}) = (-\frac{T}{\theta}) \Phi'(T/\theta)$, where Φ is the same function for all five compounds and θ is a characteristic temperature different for each compound.

If $S(\text{MF}_2, T)$ represents the entropy of an anti-ferromagnetic fluoride, denoted generally by MF_2 , at temperature T , then $S^*(\text{MF}_2, T) = S(\text{MF}_2, T) - R \ln(2S + 1)$ is equal to the lattice contribution to the entropy of MF_2 provided the magnetic entropy is fully excited. When the magnetic entropy is less than $R \ln(2S + 1)$ then $S^*(\text{MF}_2, T)$ would be lower than the true, lattice entropy of MF_2 . One can find the temperature T' where $S(\text{ZnF}_2, T')$ is equal to $S^*(\text{MF}_2, T)$. The ratio $\frac{T'}{T} = \frac{\theta(\text{ZnF}_2)}{\theta(\text{MF}_2)}$ is denoted by $r(\text{MF}_2, S)$. Similarly one finds a temperature T'' where ZnF_2 has the same heat capacity as does MF_2 at temperature T and denotes the ratio T''/T by $r(\text{MF}_2, C_p)$. If the principle of corresponding states were exactly followed one would expect to find that at the higher temperatures $r(\text{MF}_2, S)$ and $r(\text{MF}_2, C_p)$ were equal to one another and were both temperature independent. These values are then extrapolated to low temperatures and are useful in separating the magnetic contribution to the entropy and heat capacity from the lattice contributions. One finds the total entropy $S(\text{MF}_2, T)$ at a temperature T from the experimental heat capacity data. The lattice contribution $[= S(\text{ZnF}_2, rT)]$ is subtracted from $S(\text{MF}_2, T)$ to give magnetic entropy of MF_2 at temperature T . The lattice contribution to the heat capacity is obtained from

the thermodynamic relation

$$\begin{aligned}
 C_p(\text{lat.}, T) &= T \frac{dS(\text{lat.}, T)}{dT} \\
 &= T \left\{ \frac{d[S(\text{ZnF}_2, rT)]}{d(rT)} \right\} \times \frac{d(rT)}{dT} \\
 &= C_p(\text{ZnF}_2, rT) \left[1 + \frac{d \ln r}{d \ln T} \right]
 \end{aligned}$$

In all these derivations, it was assumed that the contribution of the lattice and of the magnetic system are independent of one another and that there is no interaction between them. Such an interaction is reflected in the anomalies in the coefficient of expansion⁸ and X-ray structures⁹⁻¹¹ found in MnO, FeO, CoO, and NiO. However, the dimensional changes found in the oxides were small and the Néel temperatures were also comparatively high.

The principle of corresponding states is less accurate at the higher temperatures and that the deviations from this principle are more pronounced in $r(\text{MF}_2, C_p)$ than in $r(\text{MF}_2, S)$. The expected error in $r(\text{MF}_2, C_p)$, arising from the experimental inaccuracy in the heat capacity measurements, increases considerably at higher temperatures. This is partly because the heat capacity measurements themselves are not very precise in the temperature of matching the heat

capacity values, but also because, since dC_p/dT decreases at the higher temperatures, a given fractional error in C_p produces a larger error in r (MF_2 , C_p).

As reported earlier¹²⁻¹⁴, $KMnF_3$, $KCoF_3$, $KNiF_3$ and $KCuF_3$ exhibit anomalies in heat capacity associated with the antiferromagnetic ordering. These compounds, together with diamagnetic $KZnF_3$ form an isomorphous series of compounds. The heat capacity and thermodynamic properties of $KZnF_3$ have already been described in Chapter III. These data have been employed to estimate the magnetic heat capacity and entropy of KMF_3 compounds and the details of the results have been described in the next chapter.

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CHAPTER V

ESTIMATION OF THE MAGNETIC HEAT CAPACITY
AND ENTROPY OF KMF_3 COMPOUNDS

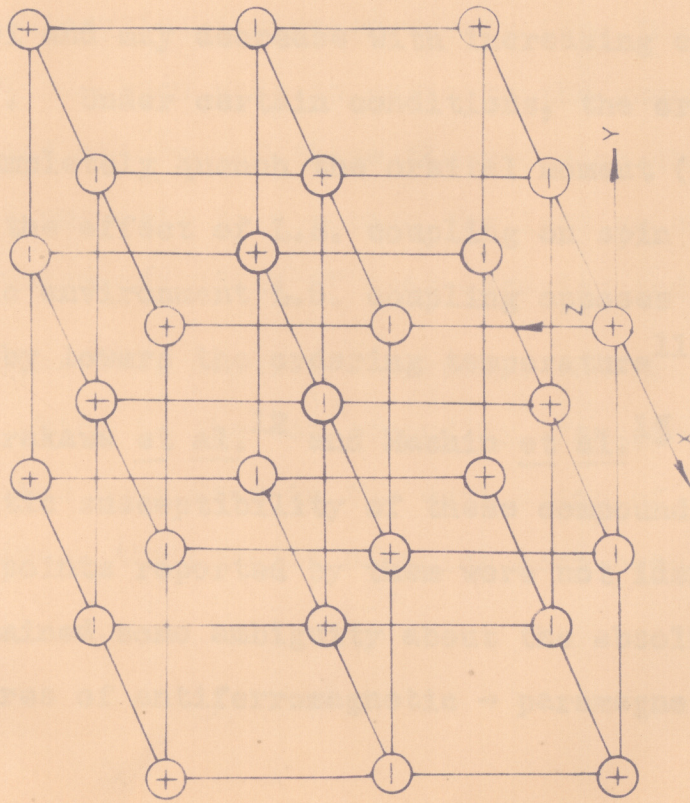
Recently the compounds with perovskite-like structures are becoming very important as they show many interesting solid state properties. KMF_3 , where M denotes a divalent 3d transition group ion such as Mn^{+2} , Co^{+2} , Ni^{+2} and Cu^{+2} , is one such series that has aroused considerable interest among research workers.

The crystal structures of these antiferromagnetic compounds have been investigated and are summarized by Martin et al.¹ However, all these works were done with powders and hence the results were rather ambiguous. Okazaki and others²⁻⁵ subsequently carried out X-ray analysis using single crystals. The general conclusion was that these compounds crystallize in the cubic perovskite structure at room temperature, excepting $KCuF_3$, which crystallizes as a tetragonal modification of the perovskite-like structure. The magnetic (M^{+2}) ions are arranged more or less in a simple cubic lattice. The F^- ions lie in between the M^{+2} ions. Hence one may expect

plenty of information about the exchange and anisotropy mechanisms in these compounds. Neutron diffraction studies by Scatturin et al.⁶ have revealed that the magnetic structures of these double fluorides are characterised by the so-called A and G type arrangements. The A-type structure, which consists of ferromagnetic (001) sheets coupled antiferromagnetically along the (001) direction, is found in KCrF_3 . In the G-type structure, the magnetic ion is coupled antiferromagnetically to its six nearest neighbours. This structure is found in KMnF_3 , $\text{KFe}_A^{\text{F}_3}$ and KNiF_3 (Fig.2).

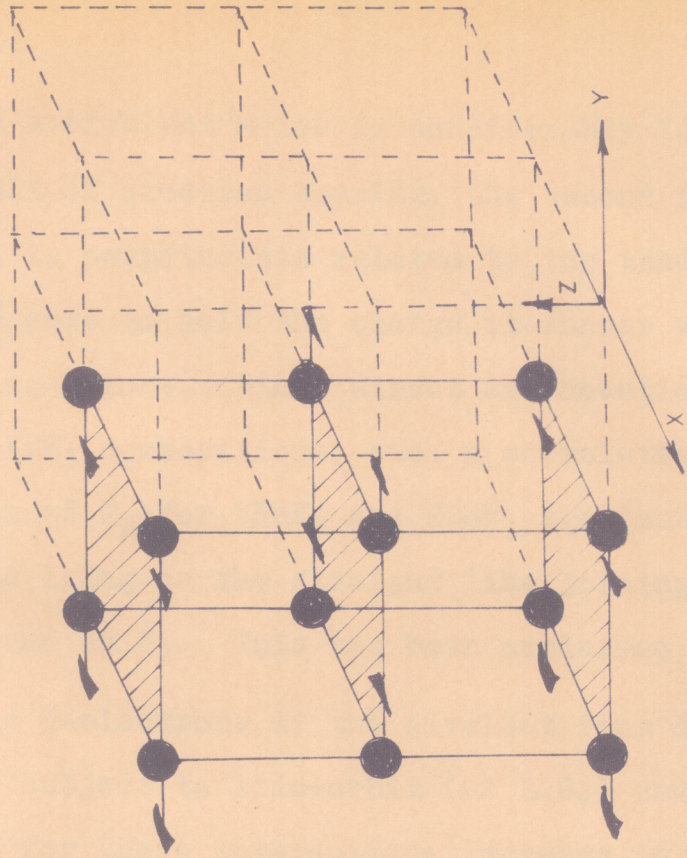
The arrangement of the moments in the double fluorides is the one expected on the basis of an indirect exchange mechanism. The interactions are supposed to take place via the non-magnetic F^- anions, and the electronic configuration of the cations as well as the crystal structure determine the particular type of magnetic ordering. Hence the same interaction mechanism, which accounted for the magnetic structure of trivalent transition metal perovskites^{7,8} and related trifluorides, is seen to explain the divalent transition metal double fluorides, provided one takes into consideration the change in the electronic structure.

Van Uitert⁹ has correlated the Néel temperatures of KMf_3 compounds/with the ionization potential required to form the free M^{+2} ion (I_{p_2}). Although the positive



G-TYPE MAGNETIC STRUCTURE

⊕ Mn^{+2} , Fe^{+2} , Co^{+2} , Ni^{+2}



A-TYPE MAGNETIC STRUCTURE

● Cr^{+2} , MOMENT IN (001) PLANE,
ARBITRARY DIRECTION

FIG. 2. A AND G TYPE MAGNETIC STRUCTURES IN 3d TRANSITION METAL DOUBLE FLUORIDES

charge on a divalent M-ion is considerably less than two as a result of electron sharing, the second ionization potential is nevertheless related to the tendency for the M-ion core to hold the charge it shares with the surrounding anions. Since direct interactions do not occur in KMf_3 compositions, such a correlation is tenable. The values of T_N for KFeF_3 and KCoF_3 are found to be lower than those lying on the straight line joining the Néel points of KMnF_3 and KMIF_3 . This has been explained as follows :

The d-electrons of the divalent ions of the iron group are subject to spin-orbit (or L.S.) coupling. The constants for these interactions increase in the order Mn, Fe, Co, Ni and may decrease with increasing covalency in bonding¹⁰. Under certain conditions, the crystal field can almost completely quench the orbital moment (L) and thereby minimize the effect of L.S. coupling on spin alignment. In a cubic environment L.S. coupling opposes spin alignment and thereby lowers the ordering temperature¹¹.

Hirakawa et al.¹² and Machin et al.¹³ have determined the magnetic susceptibility of these compounds. However, the Néel points reported by them were not identical and there remained some ambiguity about the absolute values of temperatures of antiferromagnetic \rightarrow paramagnetic transitions.

For example, the values of Néel temperature of KCuF_3 , were reported as 243°K and 215°K respectively.

It is well known, however, that susceptibility measurements are likely to give incorrect results if traces of ferromagnetic impurities are present. On the other hand, the calorimetric technique is relatively more precise, and less subject to being masked by impurities. With this advantage in view, Deenadas *et al.*¹⁴⁻¹⁶ studied the heat capacity-temperature behaviour of these double fluorides. The Néel temperatures for KMnF_3 , KCoF_3 , KNiF_3 and KCuF_3 were found to be 83.3° , 109.5° , 253.5° and 233.2°K respectively. These values are somewhat lower than those reported from magnetic susceptibility measurements (see Table 5). Besides, no attempt had been made to estimate the magnetic heat capacity and entropy of these fluorides at that time, as it was not possible to separate the lattice contributions from the measured totals of heat capacity and entropy.

As has been mentioned already, the heat capacity data on KZnF_3 , which is the corresponding diamagnetic isomorphous compound, has been used in the estimation of the magnetic contributions, the details of which have been presented below:-

TABLE - 5

Néel Temperatures of KMF_3 Compounds

Compound	Specific heat	T_N °K	
		Magnetic susceptibility Ref.(a)	Magnetic susceptibility Ref.(b)
$KMnF_3$	83.3	88	80
$KCoF_3$	109.5	114	135
$KNiF_3$	253.5	275	280
$KCuF_3$	233.2	243	215

Ref.(a) K. Hirakawa, K. Hirakawa and T. Hashimoto,
J.Phys.Soc.Japan, 15 2063 (1960)

Ref.(b) D.J. Machin, R.L. Martin and R.S. Nyholm,
J.Chem.Soc., 1490 (1963).

POTASSIUM MANGANESE TRIFLUORIDE (KMnF_3)

Preliminary X-ray measurements of KMnF_3 by Beekman et al.¹⁷ showed that the room temperature ideal cubic perovskite structure persists down to 184°K , where a distortion to a tetragonal pseudocell with $c/a > 1$ sets in. At the Néel temperature ($T_N = 88^\circ\text{K}$) a second change occurs when $c/a < 1$. In both temperature regions the true crystallographic cell contains four molecules of KMnF_3 . Okazaki et al.¹⁸ have reported lattice parameters at room temperature and 77°K . They report a monoclinic pseudocell at the lower temperature, a phase that Beckman and Knox⁴ subsequently found in the temperature region 88°K to 105°K , provided the crystal is warmed from the antiferromagnetic region. This intermediate phase does not seem to occur with decreasing temperature.

Torsion measurements by Heeger et al.¹⁹ have shown the existence of a second magnetic transition at 81.5°K , not far below the Néel temperature of 88°K . Below 81.5°K the crystal has a weak ferromagnetic moment caused by a canting of the spins. Neutron diffraction investigations at 4.2°K indicate⁶ that the ordered magnetic structure is of the G-type that is, the manganese atoms form a simple cubic arrangement with all nearest neighbours coupled anti-ferromagnetically. (Fig.2).

Deenadas et al.¹⁴ have determined the heat capacities over the temperature range 78°-300°K. They reported two peaks, a sharp one at 83.3°K, associated with the Néel temperature and a smaller one at 179.0°K, attributed to a structural change.

It may be noted that these heat capacity measurements were restricted to 78°K on the lower side of the anomaly. In order to apply the corresponding states principle (described in Chapter IV) it is necessary to estimate the entropy due to the magnetic ordering below 78°K. For that purpose a Debye-Einstein type of function, namely $C_p = D \left(\frac{97}{T} \right) + 2E \left(\frac{208}{T} \right) + 2E \left(\frac{211}{T} \right)$ was fitted to the rising part of the transition and the same trend of heat capacity was assumed to follow at temperatures below 78°K. In an attempt to estimate the lattice heat capacity, Deenadas et al.¹⁴ had fitted a function $C_p = D \left(\frac{97}{T} \right) + 2E \left(\frac{225}{T} \right) + 2E \left(\frac{568}{T} \right)$ to the experimental data over the temperature range 120-170°K. The same Debye parameter has been used, indicating that the magnetic contribution may be assumed to become negligible at very low temperatures.

The value of r (KMnF_3, S) was estimated in the usual way by matching the entropy curves in the temperature region 120°-160°K. The extrapolation of this value of r (=1.08) to

lower temperatures is likely to show a variation of the order of 1%. This may be considered as negligible and the constant value $r = 1.08$ was used in the calculations. The magnetic entropy attained at 80°K and 110°K was 3.06 and 3.66 cal./mole.deg., respectively. Theoretically, Mn^{+2} ions ($3d^5$) with spin $5/2$ are expected to give a magnetic entropy contribution of $R \ln (2s+1) = R \ln 6$ i.e. 3.56 cal./mole.deg. Even though the value at 110°K is slightly higher than the theoretically expected one, it may be explained as due to the uncertainty in the extrapolated values of heat capacity below 78°K .

Similarly, the lattice heat capacity was evaluated by using the equation

$$C_p = D \left(\frac{97}{T} \right) + 2E \left(\frac{225}{T} \right) + 2E \left(\frac{568}{T} \right)$$

derived previously¹⁴. By subtracting from the experimentally measured values and the extrapolated ones below 80°K , the magnetic heat capacity was evaluated (Fig.3). The value of the exchange constant, $-|J|/K$, derived from the relation $\Delta H = NZS^2 |J|$, where ΔH is the energy of transition, N the Avogadro's number, Z the number of nearest magnetic neighbours and S the spin, was in good agreement with that derived from magnetic susceptibility measurements (Table 6).

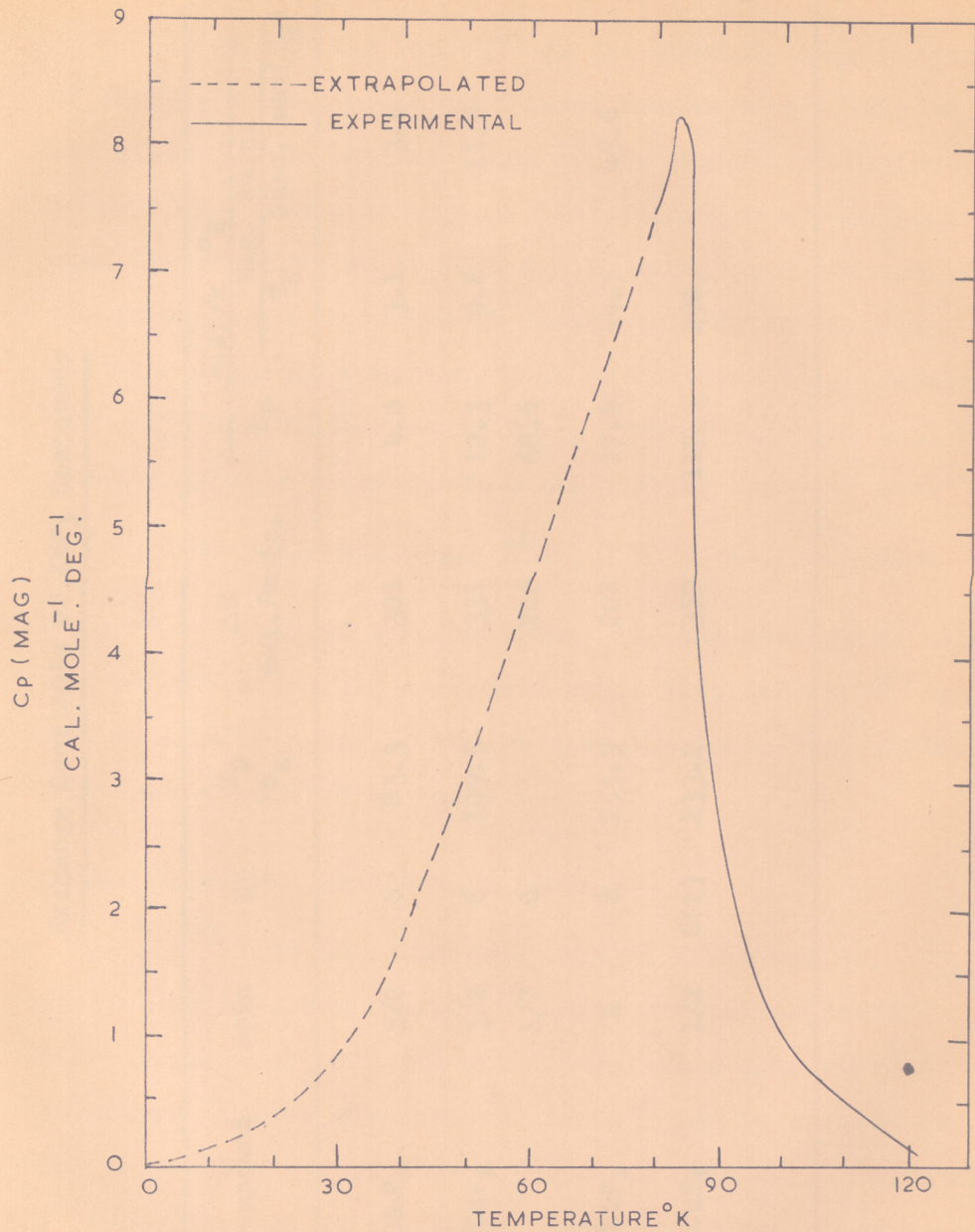


FIG. 3. MAGNETIC HEAT CAPACITY OF KMnF_3 ($S = 5/2$)

TABLE - 6

Exchange Constants of KMF_3 Compounds

Compound	Spin	Z	T_N °K	ΔH cal./mole.	C_P	$\frac{- J /k}{T_N}$ °K Mag. susc. Susc. max(T_N)
$KMnF_3$	5/2	6	83.3	301	4.0	3.1 3.6
$KCoF_3$	3/2	6	109.5	331	12.3	9.6 11.8
	1/2	6		206	68.6	
$KNiF_3$	1	6	253.5	208	17.4	44.5 45.6
$KCuF_3$	1/2	6(?)	233.2	350	117	190

32
37

In an earlier report¹⁴ on the thermodynamic properties of KMnF_3 , we had noted that those values were likely to be low since no account was taken of the magnetic contribution below 80°K . Since an approximate estimation of the heat capacity of KMnF_3 below 80°K can be made, as discussed in the foregoing paragraphs, it is possible to re-evaluate the thermodynamic functions such as entropy (S°), enthalpy ($H^\circ - H^\circ_0$) and Gibbs free energy ($\frac{F^\circ - H^\circ_0}{T}$), which will be relatively more accurate than the earlier reported ones¹⁴. ($S^\circ = 38.02$ cal./mole.deg.; $H^\circ - H^\circ_0 = 5399$ cal./mole. and $\frac{F^\circ - H^\circ_0}{T} = -19.92$ cal./mole.deg.). The respective values at 298.15°K are 41.77 cal./mole.deg., 5614 cal./mole, and -22.94 cal./mole.deg., The revised thermodynamic functions have been presented in Table 7.

POTASSIUM COBALT TRIFLUORIDE (KCoF_3)

Co^{+2} ions in octahedral crystal field are of particular interest because of their unusual magnetic behaviour. KCoF_3 has the cubic perovskite-like crystal structure at room temperature. A Co^{+2} ion is located at the body-centred position of the cubic unit cell, while six F^- ions, located at the face-centred positions, form a regular octahedron around the corners. Each Co^{+2} ion is surrounded

TABLE - 7

Revised Thermodynamic Functions of Potassium
Manganese Trifluoride

Temp. °K	$S^{\circ} - S_{0}^{\circ}$ cal./mole.deg.	$H^{\circ} - H_{0}^{\circ}$ cal./mole.	$-(F^{\circ} - H_{0}^{\circ})/T$ cal./mole.deg.
80	(13.70) [†]	(685.7) [†]	(5.3) [†]
85	15.03	795.2	5.67
90	16.05	883.6	6.23
95	16.90	963.2	6.76
100	17.71	1042	7.29
105	18.49	1122	7.80
110	19.26	1204	8.32
115	20.01	1288	8.81
120	20.76	1376	9.29
125	21.50	1467	9.77
130	22.22	1559	10.23
135	22.93	1653	10.68
140	23.64	1749	11.15
145	24.33	1851	11.57
150	25.02	1948	12.03
155	25.69	2050	12.46
160	26.35	2153	12.89

Contd...

Temp. °K	$S^{\circ} - S_0^{\circ}$ cal./mole.deg.	$H^{\circ} - H_0^{\circ}$ cal./mole.	$-(F^{\circ} - H_0^{\circ})/T$ cal./mole.deg.
165	27.00	2259	13.31
170	27.66	2373	13.70
175	28.33	2486	14.12
180	29.04	2611	14.53
185	29.71	2733	14.93
190	30.34	2851	15.33
195	30.94	2969	15.71
200	31.54	3084	16.12
205	32.12	3202	16.50
210	32.70	3322	16.88
215	33.26	3442	17.24
220	33.83	3563	17.64
225	34.38	3687	18.00
230	34.92	3809	18.36
235	35.46	3936	18.71
240	35.99	4063	19.07
245	36.52	4191	19.42
250	37.04	4319	19.76
255	37.56	4450	20.10
260	38.07	4581	20.45

Contd...

Temp. °K	$S^{\circ} - S_0^{\circ}$ cal./mole.deg.	$H^{\circ} - H_0^{\circ}$ cal./mole.	$-(F^{\circ} - H_0^{\circ})/T$ cal./mole.deg.
265	38.57	4714	20.78
270	39.07	4846	21.12
275	39.57	4982	21.46
280	40.06	5116	21.79
285	40.53	5254	22.09
290	41.01	5389	22.43
295	41.48	5527	22.74
300	41.95	5666	23.06
(273.15)	(39.38)	(4934)	(21.32)
(298.15)	(41.77)	(5614)	(22.94)

+ Extrapolated

by an octahedron of six F^- ions, while each F^- ion is collinear with its two nearest neighbour Co^{+2} ions.

Magnetic susceptibility measurements by Hirakawa et al.¹² and Machin et al.¹³ have shown that $KCoF_3$ undergoes an antiferromagnetic transition at low temperatures. The Néel points reported by them were $114^\circ K$ and $135^\circ K$ respectively. Scatturin et al.⁶ performed the neutron diffraction measurements on powdered samples at $4.2^\circ K$. However, since the configurational symmetry of the magnetic structure is cubic²⁰, it was not possible to find the spin directions relative to the crystallographic directions. Hirakawa et al.²¹ investigated the magnetic anisotropy of single crystals $KCoF_3$ by the torque magnetometer in the temperature range from 78° to $300^\circ K$. The Néel temperature observed was $119^\circ K$. Thermal conductivity measurements by Suemueⁿ and Ikawa²² have exhibited an anomalous decrease near the Néel temperature of $114^\circ K$. This was explained as due to the incoherent scattering of phonons caused by the phonon-magnon interactions. Since $KCoF_3$ distorts below the transition temperature, the twin boundaries may contribute as the scatterers of phonons in these temperature regions. Optical measurements by Hawkes et al.²³ have shown that there is very little short-range order at and above the Néel temperature (of $114^\circ K$)

in KCoF_3 . It was suggested that the strong phonon-magnetic ion coupling was responsible for the result. Nuclear magnetic resonance of ^{19}F in powdered and single crystal KCoF_3 has been studied independently by Tsang²⁴ and Shulman and Knox²⁵ respectively. Both give almost identical results. Tsang observed that the resonance signal weakened considerably as temperature was lowered from 133° to 125°K . No resonance was observed at $T = 112^\circ\text{K}$. These data suggest that the Néel temperature of KCoF_3 may be either $\sim 112^\circ\text{K}$ or $\sim 135^\circ\text{K}$. In an attempt to settle this controversy Deenadas *et al.*¹⁵ determined the heat capacity of KCoF_3 in the temperature region 78° - 300°K . A sharp λ -type anomaly was observed at 109.5°K . Normal behaviour was observed at $T \sim 135^\circ\text{K}$.

KCoF_3 is a special case of Co^{+2} ion in a 'weak' octahedral crystal field. The situation of Co^{+2} in weak octahedral crystal field and in the absence of exchange has been extensively discussed by Low^{26,27}. It may be noted, however, that the exact spin quantum number of Co^{+2} is difficult to estimate, although resorts to $S = \frac{1}{2}$ ²³ and $S = \frac{3}{2}$ ²⁸ have been made. At sufficiently high temperatures, the situation might be much more complex. However, for simplicity, S equal to $1/2$ as well as $3/2$ have been considered for evaluating the magnetic contribution.

KCoF_3 ($S = 1/2$) :

The value of r (KCoF_3, S), evaluated by matching the entropy curves around 300°K , where the magnetic entropy is believed to have been fully excited, was found to be 1.03. The lattice and magnetic contribution to the entropy, estimated using this value of r ($= 1.03$) have been presented in Table 8. It can be seen that only half of the total theoretical entropy i.e. $R \ln 2 = 1.38$ cal./mole.deg. has been attained at the Néel temperature and hence a considerable short-range order persists above the transition temperature. Similar results have been observed in CoCl_2 by Stout²⁹. However, it may be noted that CoCl_2 forms a layer lattice of the CdCl_2 type^{30,31} while KCoF_3 is simple cubic.

At this juncture, it may be interesting to compare the results of the corresponding states method with those obtained by Deenadas³² using a Debye-Einstein function, to represent the lattice heat capacity. At 115°K he obtained a value of 0.84 cal./mole.deg. for the magnetic contribution compared to 0.73 cal./mole.deg. from the corresponding states principle. This may apparently indicate that the total expected entropy might be $R \ln 2$, as found in the cases of CoCl_2 and CoF_2 by Stout³². However, it is probable that the lattice heat capacity of KCoF_3 has been over-estimated, especially in the temperature regions below the Néel temperature.

TABLE - 8

Magnetic Entropy of KCoF₃ (S=1/2)

Temp. °K	S(lattice) cal./mole.deg.	S(mag.) cal./mole.deg.	$\frac{S(\text{mag.})}{R \ln(2S + 1)}$
80	10.01	0.10	0.07
90	11.63	0.12	0.09
100	13.22	0.27	0.20
110	14.78	0.64	0.47
120	16.31	0.81	0.59
130	17.80	0.87	0.53
140	19.27	0.92	0.67
150	20.69	0.98	0.71
160	22.08	1.03	0.75
170	23.43	1.09	0.79
180	24.75	1.13	0.82
190	26.04	1.15	0.83
200	27.29	1.19	0.86
210	28.51	1.21	0.88
220	29.70	1.22	0.88
230	30.86	1.23	0.89
240	31.98	1.25	0.91
250	33.07	1.27	0.92

KCoF_3 ($S = 3/2$) :

The constant value of r , obtained in a similar way as above, came out to be 0.98. The results have been listed in Table 9. It is again found that only half of the total theoretical entropy i.e. $R \ln 4 = 2.76$ cal./mole.deg. has been attained at the Néel temperature.

The lattice heat capacity, energy of transition, entropy and the exchange constant in both ($S = 1/2$ and $3/2$) cases have been evaluated. (see Figs. 4,5 and Tables 6,8 and 9). It can be seen that the value of the exchange constant corresponding to $S = 3/2$ is in good agreement with that obtained from magnetic susceptibility measurements. Thus $S = 3/2$ seems preferable to $S = 1/2$.

POTASSIUM NICKEL TRIFLUORIDE, KNiF_3

Crystal structure of KNiF_3 has been worked out by Okazaki and Suemune⁵. KNiF_3 possesses the ideal perovskite structure at room temperature except for some considerable elongation of F^- ions. This elongation has been analyzed by Okazaki and Suemune⁵ based on each of the following assumptions : (i) anisotropic thermal vibrations of F^- ions due to the tetragonal symmetry of their positions, (ii) isotropic thermal vibrations of F^- ions which occupy

TABLE - 9

Magnetic Entropy of KCoF_3 ($S=3/2$)

Temp. °K	S(lattice) cal./mole.deg.	S(mag.) cal./mole.deg.	$\frac{S(\text{mag.})}{R \ln (2S + 1)}$
90	10.93	0.82	0.30
100	12.45	1.04	0.38
110	13.96	1.47	0.54
120	15.42	1.70	0.61
130	16.87	1.80	0.65
140	18.27	1.92	0.69
150	19.66	2.01	0.73
160	21.00	2.10	0.76
170	22.32	2.20	0.80
180	23.60	2.28	0.83
190	24.85	2.34	0.85
200	26.07	2.41	0.87
210	27.27	2.45	0.89
220	28.43	2.49	0.90
230	29.57	2.52	0.92
240	30.67	2.56	0.93
250	31.75	2.59	0.94

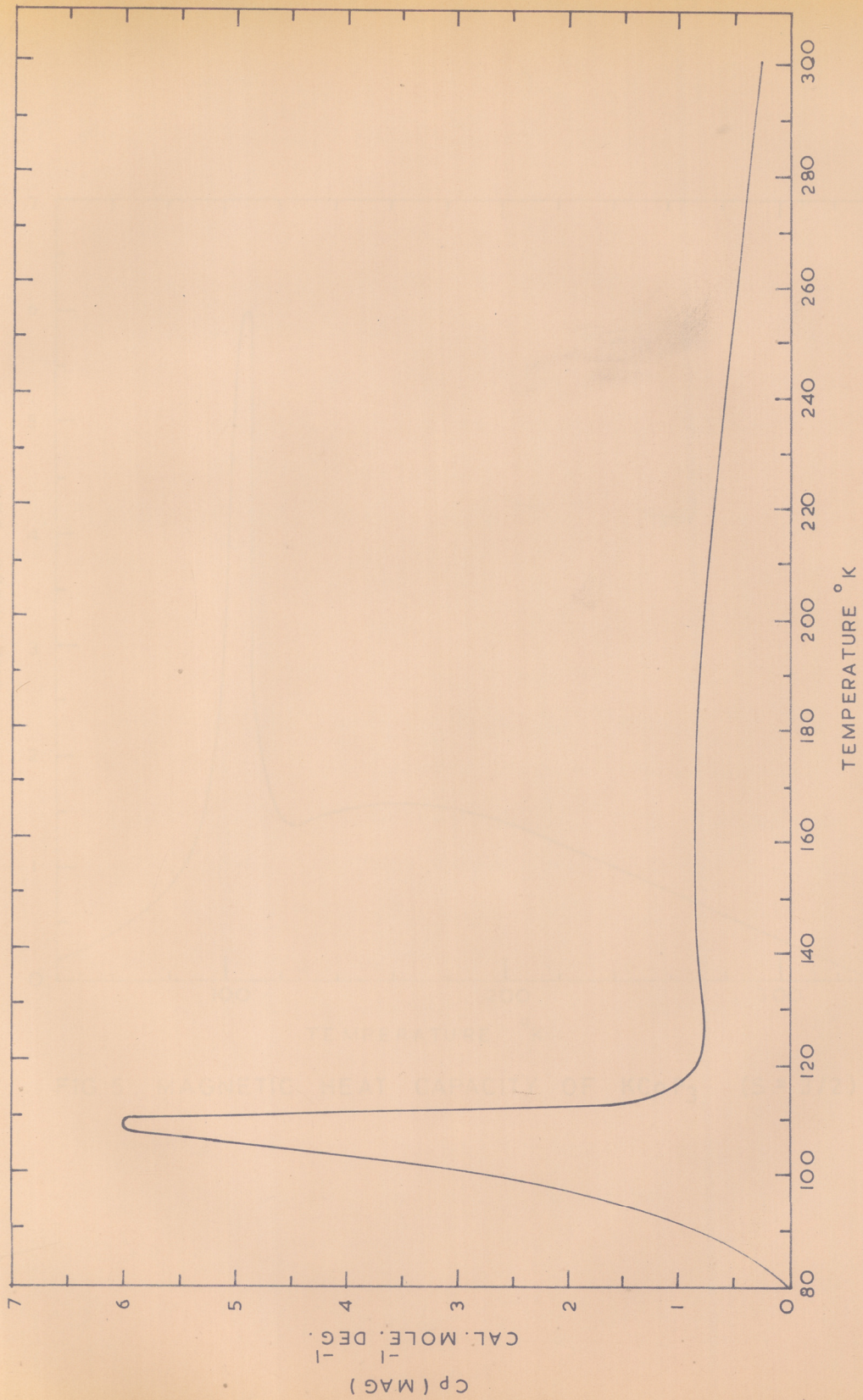


FIG. 4. MAGNETIC HEAT CAPACITY OF KCoF_3 ($S=1/2$)

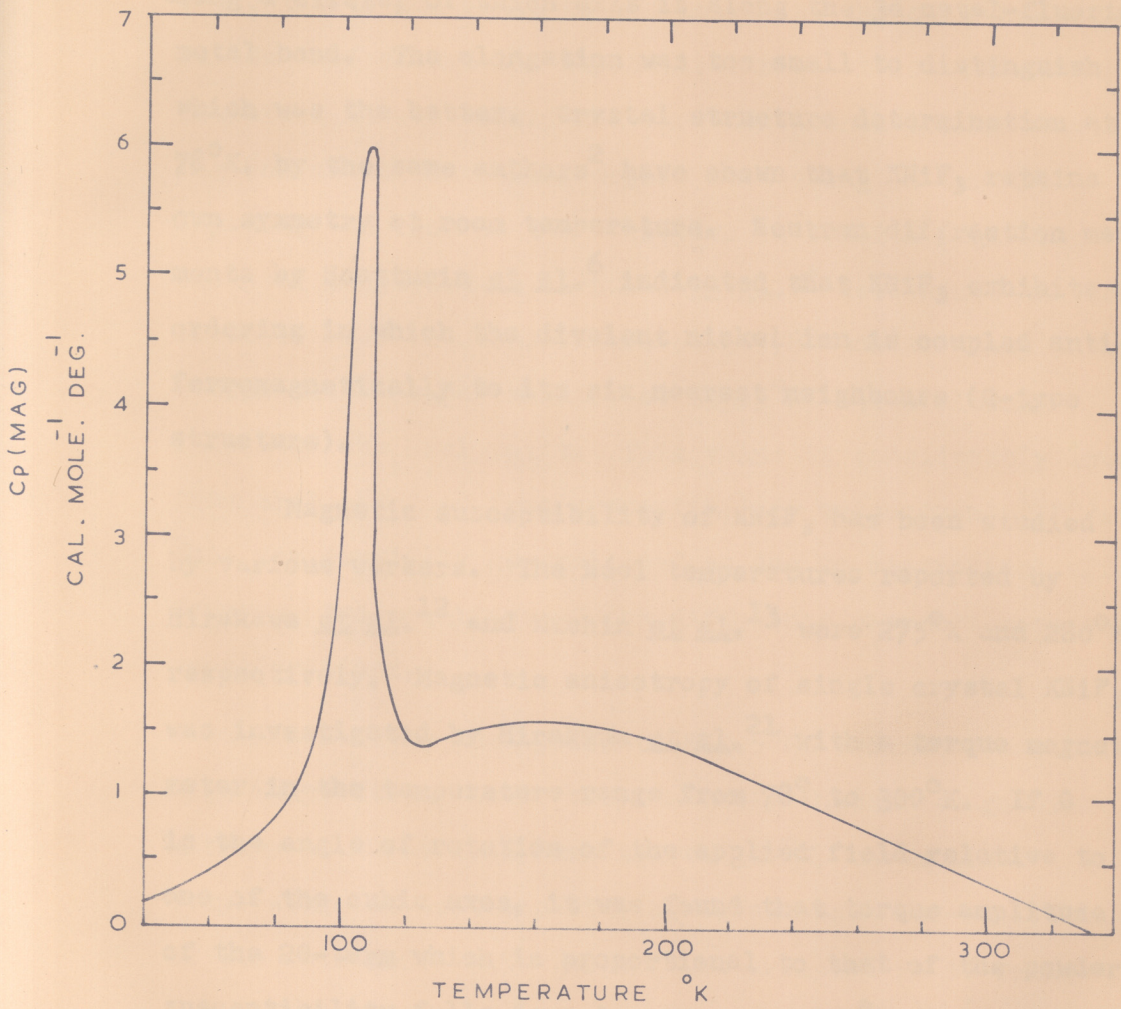


FIG. 5. MAGNETIC HEAT CAPACITY OF $KCoF_3$ ($S = 3/2$)

such positions as being distributed with uniform probability along a circle, of which axis is along the 3d metal-fluorine-3d metal bond. The elongation was too small to distinguish, which was the better. Crystal structure determination at 78°K. by the same authors² have shown that KNiF₃ retains its own symmetry at room temperature. Neutron diffraction measurements by Scatturin et al.⁶ indicated that KNiF₃ exhibits an ordering in which the divalent nickel ion is coupled antiferromagnetically to its six nearest neighbours (G-type structure).

Magnetic susceptibility of KNiF₃ has been studied by various workers. The Néel temperatures reported by Hirakawa et al.¹² and Machin et al.¹³ were 275°K and 280°K, respectively. Magnetic anisotropy of single crystal KNiF₃ was investigated by Hirakawa et al.²¹ with a torque magnetometer in the temperature range from 78° to 300°K. If θ is the angle of rotation of the applied field relative to one of the cubic axes, it was found that torque amplitude of the 2 θ -term which is proportional to that of the powder susceptibility falls down to zero near 253°K. However, the thermal conductivity of single crystals of KNiF₃, determined by Suemune and Ikawa²² in the temperature range 15°-300°K, failed to exhibit any anomaly at about the Néel temperature

($\sim 275^\circ\text{K}$). The temperature dependence of the thermal conductivity was found to be similar to those of the alkali halides and showed the exponential rise at low temperatures. Therefore it was considered that the phonon-phonon scattering dominated the phonon-magnon scattering in the KNiF_3 crystal. In view of the variation in results regarding the Néel temperature, Deenadas *et al.*¹⁵ determined the heat capacity over the temperature range $78^\circ\text{-}300^\circ\text{K}$. They observed a typical ' λ -type' anomaly at 253.5°K , which clearly indicates the Néel point. This value is considerably lower than that obtained from susceptibility measurements^{12,13}. This may partially be explained as due to statistical effects. However, the magnitude of the difference warrants more careful considerations.

Since the Néel point ($= 253.5^\circ\text{K}$) occurs at a relatively high temperature, it is very unlikely that the magnetic entropy would be fully excited at 300°K , the maximum temperature of heat capacity measurements. Non-availability of the data above this temperature prompted us to follow the following procedure:-

Since the magnetic dipoles would most likely be completely disordered at about $400^\circ\text{-}600^\circ\text{K}$, the value of $r(\text{KNiF}_3, S)$ at these temperature would be very suitable.

Even though heat capacities of both KNiF_3 and KZnF_3 are not known, the total entropy values above 300°K can be evaluated by using the Debye-Einstein functions fitted to the low temperature heat capacities of these salts employed for the purpose of extrapolation below 80°K . The functions used for KNiF_3 and KZnF_3 were $D\left(\frac{97}{T}\right) + 2E\left(\frac{225}{T}\right) + 2E\left(\frac{568}{T}\right)$ and $D\left(\frac{90}{T}\right) + 2E\left(\frac{270}{T}\right) + 2E\left(\frac{425}{T}\right)$ respectively. The value of r thus obtained was 0.92. The results have been presented in Table 10 and Fig.6.

The magnetic heat capacity and exchange constant calculations show poor agreement with other techniques (Table 6) even after making an allowance of about 2% in the heat capacity values in the temperature region $120^\circ\text{-}240^\circ\text{K}$. However, this is not surprising in view of the drastic assumptions made in obtaining the same. Besides, the corresponding states method is known to yield less accurate results at relatively high temperatures.

POTASSIUM COPPER TRIFLUORIDE, KCuF_3

Crystal structure has been determined by Okazaki and Suemune by X-ray analysis³. At room temperature the crystals were found to be tetragonal, $a = \sqrt{2} a_0 = 5.855$ and $c = 2c_0 = 7.852 \text{ \AA}$; with four formula units (KCuF_3) in the unit cell,

TABLE - 10Magnetic Entropy of KNiF_3 ($S = 1$)

Temp. °K	S(lattice) cal./mole.deg.	S(mag.) cal./mole.deg.	S(mag.)
			Rln (2S + 1)
100	11.52	1.39	0.64
110	12.94	1.43	0.66
120	14.35	1.50	0.69
130	15.72	1.56	0.71
140	17.07	1.60	0.74
150	18.39	1.63	0.75
160	19.68	1.66	0.76
170	20.95	1.68	0.77
180	22.19	1.70	0.78
190	23.39	1.73	0.79
200	24.57	1.75	0.80
210	25.73	1.75	0.80
220	26.86	1.76	0.81
230	27.96	1.79	0.82
240	29.03	1.83	0.84
250	30.09	1.93	0.88
260	31.11	2.06	0.94
270	32.11	2.07	0.95
280	33.08	2.07	0.95
290	34.03	2.07	0.95
300	34.96	2.07	0.95

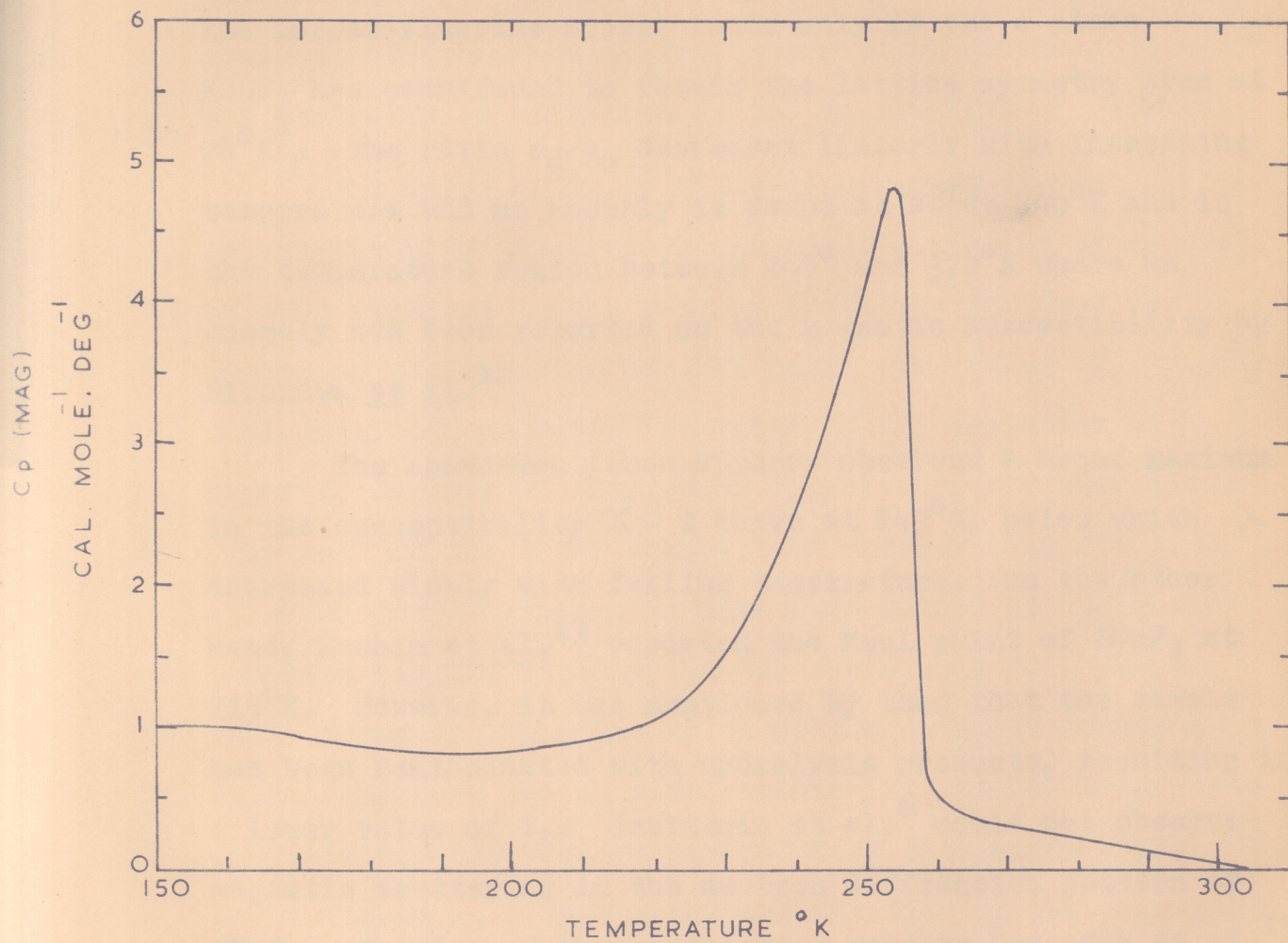


FIG.6. MAGNETIC HEAT CAPACITY OF KNiF_3 ($S=1$)

where a_0 and c_0 designate the lattice constants of the fundamental pseudo-perovskite structure. This superstructure is due to a displacement of fluorine ions along the copper-fluorine-copper bonds only in the c plane. $KCuF_3$ has been found to retain the lattice symmetry even at $78^\circ K$.² The ratio c_0/a_0 decreases linearly with increasing temperature and no anomaly is found at about $240^\circ K$ and in the temperature region between 240° and $370^\circ K$ where an anomaly has been reported on the magnetic susceptibility by Hirakawa *et al.*¹²

The above-mentioned authors observed a broad maximum in the susceptibility $\chi - T$ curve at $243^\circ K$, below which χ decreased slowly with falling temperature. On the other hand, Machin *et al.*¹³ reported the Néel point of $KCuF_3$ at $215^\circ K$. However, it was mentioned by them that the sample had been contaminated with hydrolysis products, resulting in a lower value of T_N . Scatturin *et al.*⁶ could not observe magnetic scattering in the neutron diffraction pattern of $KCuF_3$. In view of the conflicting results Deenadas *et al.*¹⁵ determined the heat capacity in the temperature range $78^\circ - 300^\circ K$. A hump in the heat capacity versus temperature curve with a maximum at $233.2^\circ K$ was observed. This temperature ($= 233.2^\circ K$) was considered as the Néel point, which supports susceptibility studies by Hirakawa *et al.*¹² and Machin *et al.*¹³ The

results of the former authors can be taken as more reliable since the C_p - maximum lies at a relatively higher temperature and the sample was not very pure in the work of the latter authors. The lower value of T_N obtained from C_p measurements compared to that reported by Hirakawa *et al.*¹² may partially be explained as due to statistical effects.

The value of T_N ($= 233.2^\circ\text{K}$) of KCuF_3 lies at a relatively high temperature and hence a similar procedure as that employed in the case of KNiF_3 was followed for obtaining the magnetic contribution. The value of $r(\text{KCuF}_3, S)$ thus obtained was 0.90. In Table 11 the variation of magnetic entropy of KCuF_3 with temperature has been listed. Only half of the total theoretical entropy ($R \ln 2 = 1.38$ cal./mole.deg.) appears to have been gained at T_N , while the rest (of the entropy) in the subsequent 70°K short-range order region. The value of the exchange constant calculated from the C_p measurements (Fig.7) has been given in Table 6. However, it may be noted that since KCuF_3 crystallizes in a tetragonal modification of the perovskite structure, the application of the corresponding states method would be valid, only if it could be assumed that the tetragonal distortion from cubic symmetry is negligible.

TABLE - 11Magnetic Entropy of KCuF_3 ($S = 1/2$)

Temp. °K	S(lattice) cal./mole.deg.	S(mag.) cal./mole.deg.	S(mag.) $R \ln (2S + 1)$
200	24.07	0.08	0.06
210	25.20	0.22	0.16
220	26.32	0.38	0.27
230	27.41	0.61	0.44
240	28.48	0.83	0.60
250	29.52	0.94	0.68
260	30.54	0.99	0.72
270	31.53	1.03	0.75
280	32.49	1.08	0.78
290	33.43	1.13	0.82
300	34.36	1.16	0.84

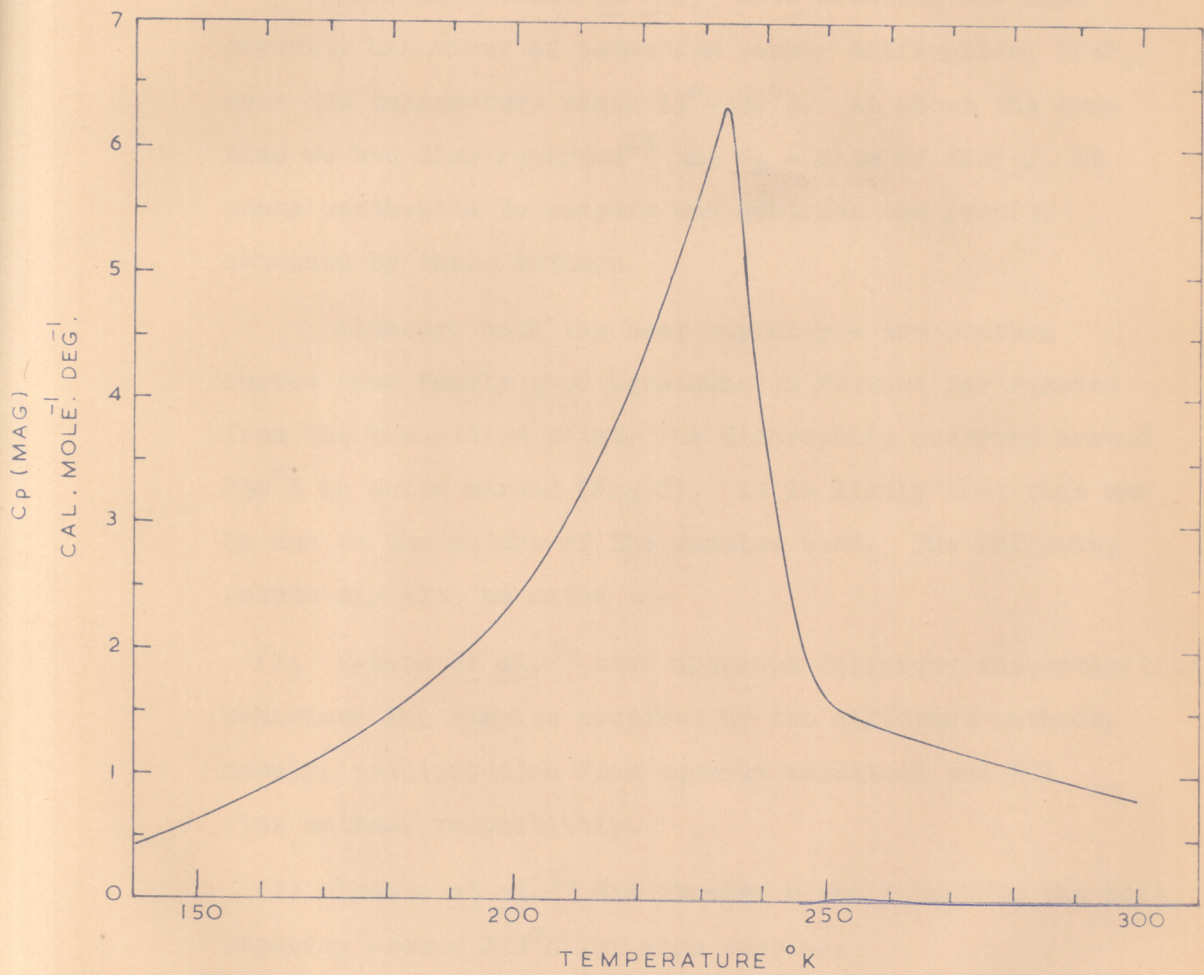


FIG. 7. MAGNETIC HEAT CAPACITY OF KCuF_3 ($S=1/2$)

HEAT CAPACITY OF POTASSIUM COPPER TRIFLUORIDE

Recently Kadota et al.³⁴ have measured the heat capacity behaviour of potassium copper trifluoride, KCuF_3 , over the temperature range $15^\circ\text{-}300^\circ\text{K}$. At about the same time we had also reported¹⁵ the C_p - data of KCuF_3 . It seems worthwhile to compare and contrast the results obtained by these authors.

Although both the heat capacity - temperature curves show fairly good agreement in regions far removed from the transition point, the discrepancy observed around 230°K is quite marked (Fig.8). It is likely that this may be due to the nature of the samples used. The following points may also be noted : -

(1) Kadota et al.³⁴ have observed different susceptibility behaviour for samples prepared by two different methods, namely, precipitation from aqueous solutions and KCl flux method, respectively.

(2) Kadota et al.³⁴ did observe a small peak in the heat capacity around 220°K for some samples.

Whether the different behaviour of samples employed by Kadota et al.³⁴ and Deenadas et al.¹⁵ originate from the presence of minute traces that are not detected by X-ray

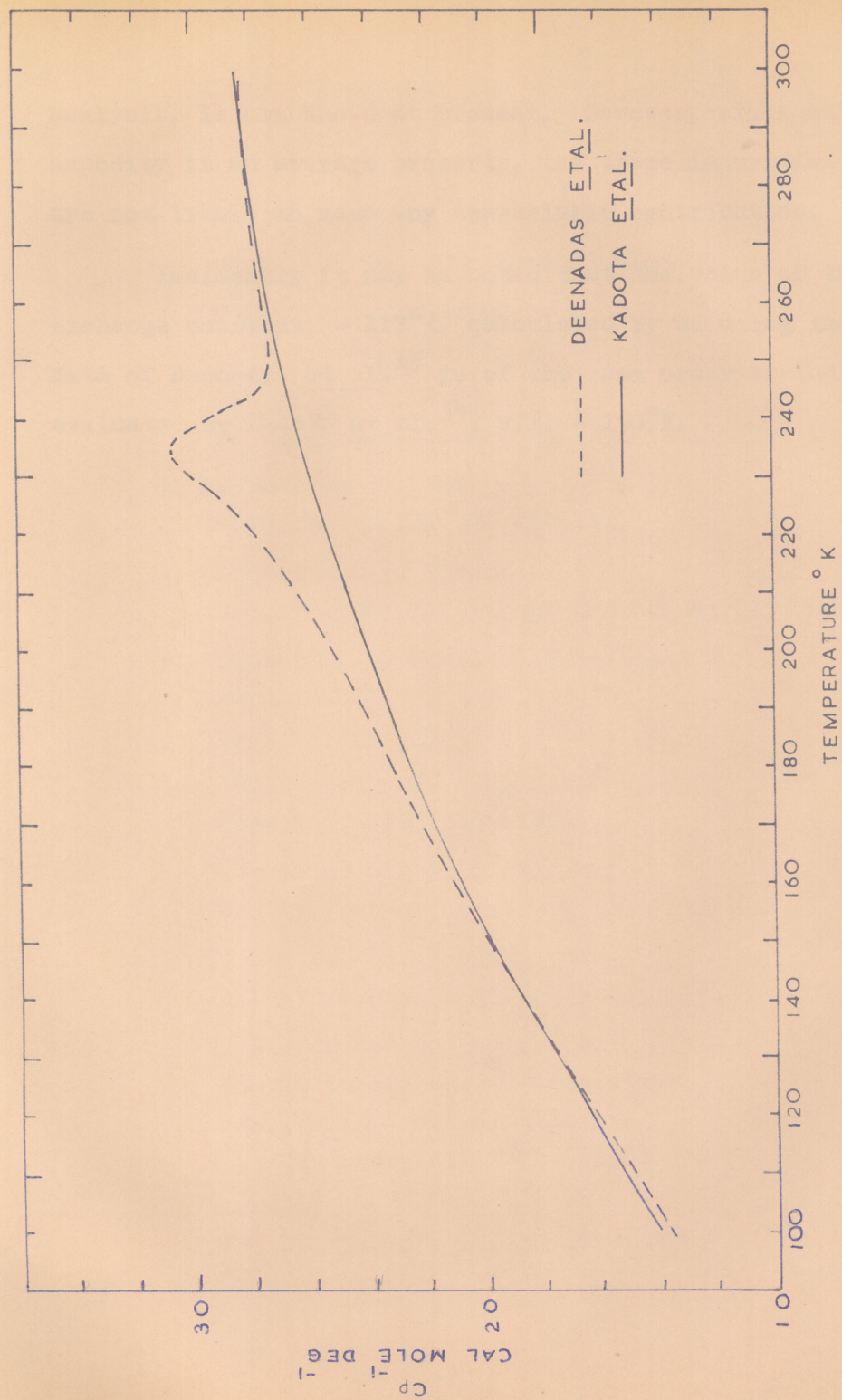


FIG. 8 HEAT CAPACITY OF KCuF_3

analysis, is not known at present. However, since heat capacity is an average property, the trace impurities are not likely to make any appreciable contribution.

Incidentally it may be noted that the value of the exchange constant, -117°K , calculated by us using the data of Deenadas et al.¹⁵ is of the same order as that evaluated by Kadota et al.³⁴, viz. -190°K .

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PART - II

CHAPTER VI

DILUTE MAGNETIC MATERIALS

In the study of the origin of ferromagnetism or of antiferromagnetism, it is of fundamental importance to know the nature of the interaction between magnetic atoms and the value of the magnetic moments of such atoms. One of the most powerful procedures for this purpose is to study the magnetic properties of a magnetically dilute system, that is a system in which a small fraction of magnetic atoms is added to a non-magnetic matrix or vice versa. Since only the magnetic atoms have magnetic moments in such a case, we can obtain the magnetic moment of magnetic atoms and their dependence upon the concentration from the measurement of the paramagnetic susceptibility. Also, from the behaviour of the transition from paramagnetism to ferro- or antiferromagnetism and its dependence upon concentration, we can obtain information concerning the nature of the interaction between magnetic atoms. Such a situation can be realized experimentally by preparing appropriate metallic alloys or solid solutions with

non-metallic compounds. Perhaps the most interesting point to consider is the way in which the transition temperature depends on the composition of the system. If the molecular field approximation is used to solve this problem the predicted result is a simple linear variation of transition temperature with concentration of the magnetic component i.e.

$$T_c(p) = p T_c$$

where 'p' is the concentration of magnetic atoms in the system and T_c is the transition temperature when no diluent is present. However, the molecular field method is equivalent to the assumption of an infinitely long-range interaction which is independent of distance. This assumption is not very realistic for many magnetic systems, where the interaction is believed to be a rapidly diminishing function of distance ; in such cases, a model in which each atom interacts with only a few sets of nearest neighbours would seem to be a better approximation. For simplicity, let us consider the case in which each atom interacts only with its 'Z' nearest neighbours. Then, for $p \ll 1$, most magnetic atoms have no magnetic nearest neighbours and long-range order cannot occur ; thus the molecular field theory obviously gives wrong results in this

region. Instead there must be some critical concentration p_0 such that for $p > p_0$, there is a transition temperature which decreases with decreasing 'p' and which vanishes at $p = p_0$; for $p < p_0$, no ordering occurs.

From the foregoing discussion, it is evident that the results obtained will depend upon the model chosen to describe the interaction; furthermore, the ensuing statistical problem is a complicated one which must be solved by some sort of approximation, and the quantitative results will depend to some extent upon the nature of the approximation. Various theories of dilute magnetic systems have been postulated by many workers and it is worthwhile to give a brief outline of them.

Considering the Ising model of a two dimensional ferromagnetic crystal containing defects, Elcock¹ showed that the combinatorial method developed by Kac and Ward² was particularly appropriate to the investigation of the defect crystal. It was found that the co-operative behaviour of the infinite perfect crystal is not destroyed in the defect crystal. The specific heat singularity persists, though at a progressively lower temperature as the density of defects is increased, until a high density of

defects is reached. The value of this limiting density of defects above which the co-operative behaviour is destroyed was found to be 0.4142.

Sato et al.³ used the Ising model with nearest neighbour interaction only and employed the Takagi-Kikuchi method of solution^{4,5}. It was shown that a Curie or a Néel temperature does not appear until a finite concentration of magnetic atoms is obtained if the atomic distribution is random. This concentration depends on the coordination number of the lattice and on the range of interaction, but not on the strength of the interaction. For a system with antiferromagnetic interaction, it was found that the inverse susceptibility shows a complicated temperature-dependence varying with concentration and that the existence of a maximum in the susceptibility does not necessarily mean the onset of antiferromagnetism.

Brout⁶ used the Ising model with arbitrary range of interaction and showed how his method could be generalized to the Heisenberg case for spin $1/2$. He obtained his results by generalization and combination of the cluster expansion method of condensation theory⁷ and Kirkwood's treatment⁸ of the order-disorder problem.

De Gennes et al.⁹ used a model which is equivalent to the Ising model with nearest-neighbour interactions ; their calculation involves finding the critical concentration below which the magnetic atoms occur only in isolated groups and not linked with each other.

It may be noted that Brout's treatment⁶ is somewhat more general and sophisticated than those of Sato et al.³ and de Gennes et al.⁹, but his results are valid only in a limited range i.e., for extreme dilution. For points on which they overlap with each other, these treatments give qualitatively similar results ; for example, for spin 1/2 and nearest neighbour interactions only, each method predicts that p_0 is of the order of 1/2. Each treatment includes the implicit assumption that the moments of the magnetic atoms and their interactions are not changed by the presence of the diluent ; such an assumption is probably better for a solid solution of ionic compounds than for metallic alloys.

Smart¹⁰ presented a method which was conceptually similar to that of Sato et al.³. He used the classical Heisenberg model with nearest neighbour interactions only and the Bethe-Peiers-Weiss (BPW) method of solution. His treatment avoided one of the principal objections to the method of Sato et al.³, namely, that the use of the Ising

model is not very realistic for magnetic problems. However, his results were similar, both qualitatively and quantitatively, to those of Sato et al.³ despite the explicit difference between the two methods. Both methods give the same value of p_0 , namely,

$$p_0 = (Z - 1)^{-1}$$

The variation of T_c with p for $p > p_0$ has almost the same quantitative behaviour. The principal difference lies in the region near p_0 where Sato's method predicts a more precipitous decline of the transition temperature than does Smart's method. Charap¹¹ claimed that Smart had exaggerated the interaction between a cluster and its surroundings by retaining the uniform magnetic field and that the calculation was improved by allowing the molecular field to vary from site to site on the first shell of a cluster, thereby taking into account the fact that this interaction is sensitive to the relative location of magnetic atoms in the first shell of the cluster and in the surrounding layer. For three-dimensional lattices, the critical concentration was found to vary nearly equal to $2/Z$. However Lyons¹² showed that Charap's calculations were in error and proved that fluctuations of a general kind in the

molecular field have no effect upon the BPW method. Rushbrooke and Morgan¹³ studied the lowering of the Curie temperature of a ferromagnetic substance by random dilution with non-magnetic elements on the basis of Heisenberg and Ising models with nearest neighbour interactions. It was proved that the critical concentration is the same for all models and regardless of the spin value concerned. It only depends on the lattice structure. Recently Devey¹⁴ has used the Heisenberg model to determine the variation of magnetic susceptibilities of dilute magnetic alloys in the vicinity of the Curie point. It was found that, in general, the exponent 'n' in the expression $(\frac{1}{\chi})^n = p' (T - T_c)$, where p' is a constant, T the temperature, T_c the Curie point, and χ , the magnetic susceptibility, decreases as the proportion of diluent increases.

Elliott¹⁵ used the constant coupling approximation to obtain the thermodynamic properties of a Heisenberg ferromagnet of general spin above T_c : The variation of these properties with concentration of these magnetic atoms in an alloy were also given. However, results for antiferromagnets were also included in less detail. Assuming nearest-neighbour interactions only, Elliott et al.¹⁶ showed that in ferromagnetic crystals the critical concentration is a topological property of the lattice and is the same in the

Heisenberg and Ising models and is independent of the value of the spin. The theorem did not apply to antiferromagnets.

Elliott and Heap¹⁷ evaluated the variation of the critical temperature of a magnetic crystal as a function of dilution by a method which expands the susceptibility in a power series in concentration and extrapolates to find the radius of convergence. The method was applied to simple ferromagnetic Bravais lattices using the Ising and Heisenberg models with spin 1/2 and extended to antiferromagnets. Results were obtained for the MnF_2 lattice for comparison with experiment.

Experimental measurements to test the above theories have been made by various workers. Baker et al.^{18,19} measured the Néel temperatures of mixed crystals of $(\text{Mn/Zn})\text{F}_2$ and $(\text{Co/Zn})\text{F}_2$ of various compositions by finding the temperature T_c at which the nuclear magnetic resonance of the F^{19} nuclei disappears on cooling from room temperature. The results were in qualitative agreement with the theoretical curve of Sato et al.³ Elliott and Heap¹⁷ obtained fair agreement with the experimental points and critical concentration by including the effect of exchange with two types of neighbours. Recently Horai and Saiki²⁰ have observed the electron spin resonance of the mixed crystals $\text{KMn}_x\text{Mg}_{1-x}\text{F}_3$ and obtained qualitative agreement with the theory of Sato et al.³

Machin et al.²¹ have measured the magnetic susceptibilities of the antiferromagnetic compounds, KMnF_3 , and the solid solutions $\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$. They observed a progressive lowering of the Néel temperature of the system, $\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$ with concentration $x > x_0$. In a programme of studies on the thermodynamic properties of solids, we have reported²² the heat capacities of KMnF_3 , KCoF_3 , KNiF_3 and KCuF_3 . The Néel temperatures observed were consistently lower than those reported by Machin et al.²¹ from susceptibility measurements. Especially for KNiF_3 , our heat capacity data yielded $T_N = 253.5^\circ\text{K}$ while, Machin et al.²¹ obtained a value of 280°K . The former value is believed to be more reliable since the susceptibility maximum is likely to occur at a temperature higher than the true Néel temperature. Hence it was considered worthwhile to determine the heat capacities of the solid solutions $\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$ to obtain more data on the variation of the Néel temperature with the concentration in order to test some of the existing theories. In the following Chapter, the data on $\text{KNi}_{0.85}\text{Zn}_{0.15}\text{F}_3$, $\text{KNi}_{0.69}\text{Zn}_{0.31}\text{F}_3$ and $\text{KNi}_{0.49}\text{Zn}_{0.51}\text{F}_3$ have been presented in detail.

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CHAPTER VII

HEAT CAPACITIES AND THERMODYNAMIC PROPERTIES OF $\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$ COMPOUNDS

In the previous Chapter, we have described the importance of the determination of heat capacities of solid solutions, $\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$ viz., obtaining data on the variation of Néel temperature with the concentration of paramagnetic ions for testing the existing theories of dilute magnetism. In the following we shall describe in detail the preparation, analysis, heat capacities and thermodynamic properties of $\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$ compounds.

The samples of solid solutions, $\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$, for calorimetric investigation, were prepared using the method employed by Machin *et al.*¹ The procedure has been described below :

A saturated solution of nickel fluoride was prepared by dissolving freshly precipitated nickel carbonate

Reference:

1. D.J. Machin, R.L. Martin, and R.S. Nyholm, *J.Chem.Soc.*, 1490 (1963).

in the calculated amount of dilute hydrofluoric acid. This solution was mixed with an appropriate amount of zinc fluoride solution. This mixture and a separate saturated solution of potassium fluoride were heated, mixed and then again rapidly heated. The precipitate was immediately filtered off, washed with cold water, then acetone and dried at 120°C in air. The zinc compound evidently formed more readily since a much greater proportion of nickel was present in the reaction mixture than was found in the product. The essential precautions observed were (i) to keep the quantity of free acid to a minimum, (ii) to use saturated solutions, and (iii) not to prolong boiling of the solution.

Analysis of the X-ray powder photographs indicated that the solid solutions, $\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$, possessed cubic perovskite structure at room temperature. The lattice parameters of the solid solutions were found to vary linearly with the change of composition within the experimental error.

Since the estimation of nickel in the solid solutions was considered as most accurate compared to the other elements present it was carried out employing the conventional dimethylglyoxime method. The value of 'x' thus obtained was in good agreement with that from X-ray analysis. (Table 12). However, the former value was believed to be more accurate in determining the composition of the solid solutions.

Table - 12

Analytical Data for $\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$ Compounds

Chemical Analysis		X-ray
Ni (%) found	x	x
32.1	0.85	0.83
25.9	0.69	0.70
18.2	0.49	0.50

HEAT CAPACITY MEASUREMENTS

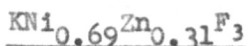
$\text{KNi}_{0.85}\text{Zn}_{0.15}\text{F}_3$:

The calorimeter was loaded with 58.74 g. of the sample. After filling with hydrogen (exchange) gas to facilitate thermal equilibrium, the calorimeter was sealed with soft-solder. Assembly of the different parts of the cryostat was made in the usual way and a low pressure of the order of 10^{-6} mm. Hg obtained.

The calorimeter was cooled to the liquid nitrogen temperature (78°K) and heat capacities were measured upto 200°K . In the second series, measurements were started at

about 190°K and extended upto the room temperature. A hump in the heat capacity-temperature curve with a maximum at 239.2°K was observed. The third series was started at about 90°K and carried to 185°K to study the low temperature side of the anomaly. In the fourth series, the measurements were made between 190°-275°K to get an accurate picture of the behaviour of heat capacity in the neighbourhood of the transition temperature. No dependence on the thermal history of the sample was observed.

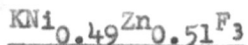
In the calculation of heat capacities, a defined caloric \equiv 4.184 absolute joules was used. The ice-point (\equiv 273.15°K) was taken as the reference temperature.



The mass of the sample used for calorimetric investigations was 57.17 g.

The calorimeter was cooled to 78°K and heat capacities determined upto 150°K. In the second series, the measurements were started at about 140°K and carried upto 235°K, when a hump was noticed with a maximum at 190.0°K. The third series was carried out in the temperature range between 210°-300°K. The calorimeter was recooled to the lowest temperature, 78°K, and measurements continued through

the transition region upto 230°K. No thermal history was observed.



The calorimeter was filled with 59.26 g. of the sample and sealed in the usual way.

Measurements were started at the lowest temperature (78°K) and continued to about 21.5°K. In the next series, the calorimeter was cooled to 210°K and heat capacity determinations made till around 300°K. The third series was started at 80°K and carried upto 195°K. The last series was made between 220°-300°K. No peak in the heat capacity was observed in the entire temperature range of measurements.

The results have been represented graphically in Figs.9,10,11 and listed in Tables 13,14 and 15.

THERMODYNAMIC PROPERTIES OF $\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$ COMPOUNDS

The extrapolation of the experimental heat capacities to 0°K was made to assess the values of the Debye temperatures. Then a sufficient number of Einstein specific heat terms were added to the Debye term so that the total number of specific heat terms equaled the number of atoms in the chemical formula of the respective compounds. Using this

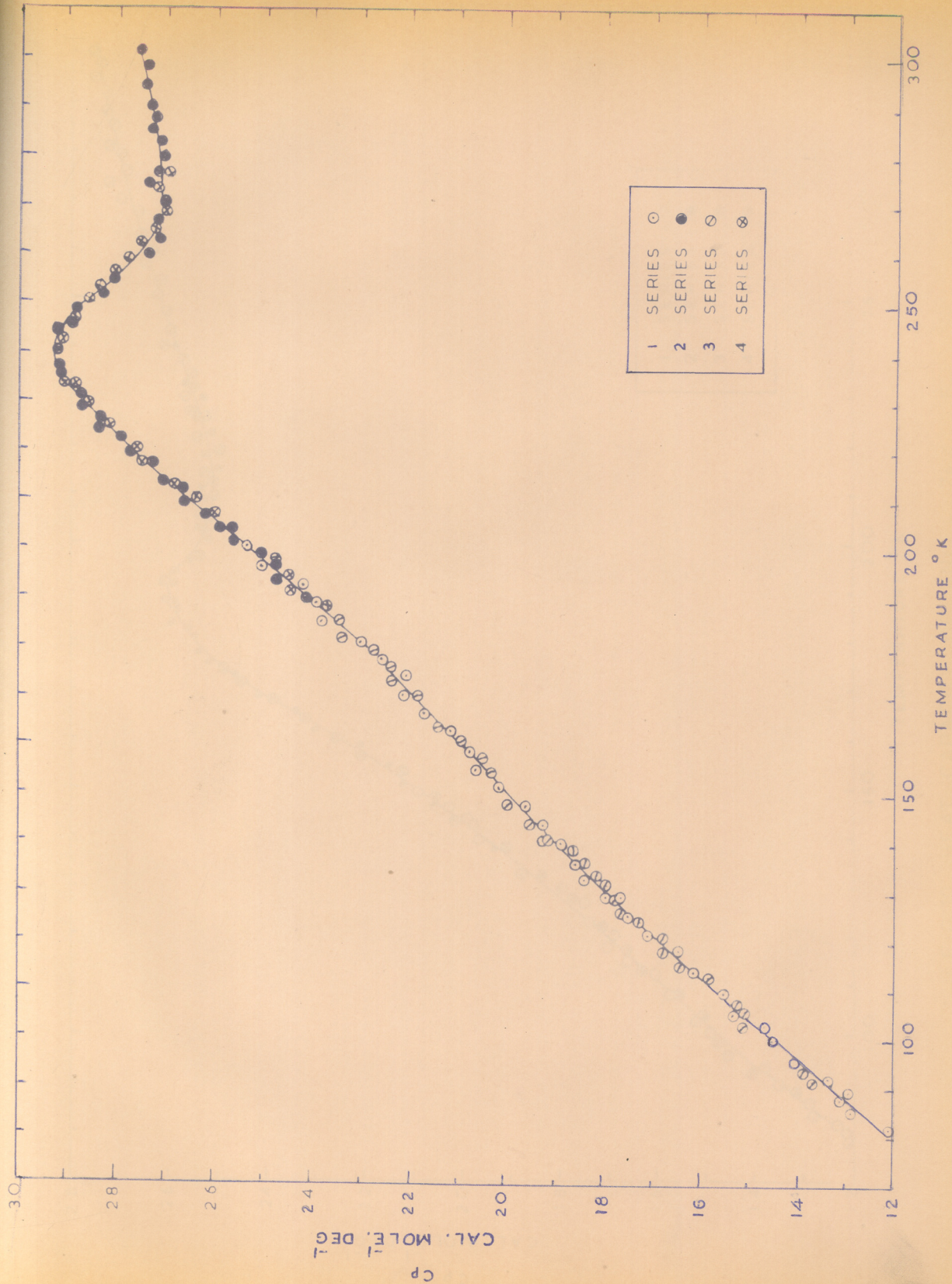


FIG.9 HEAT CAPACITY OF $\text{KNi}_{0.85}\text{Zn}_{0.15}\text{F}_3$

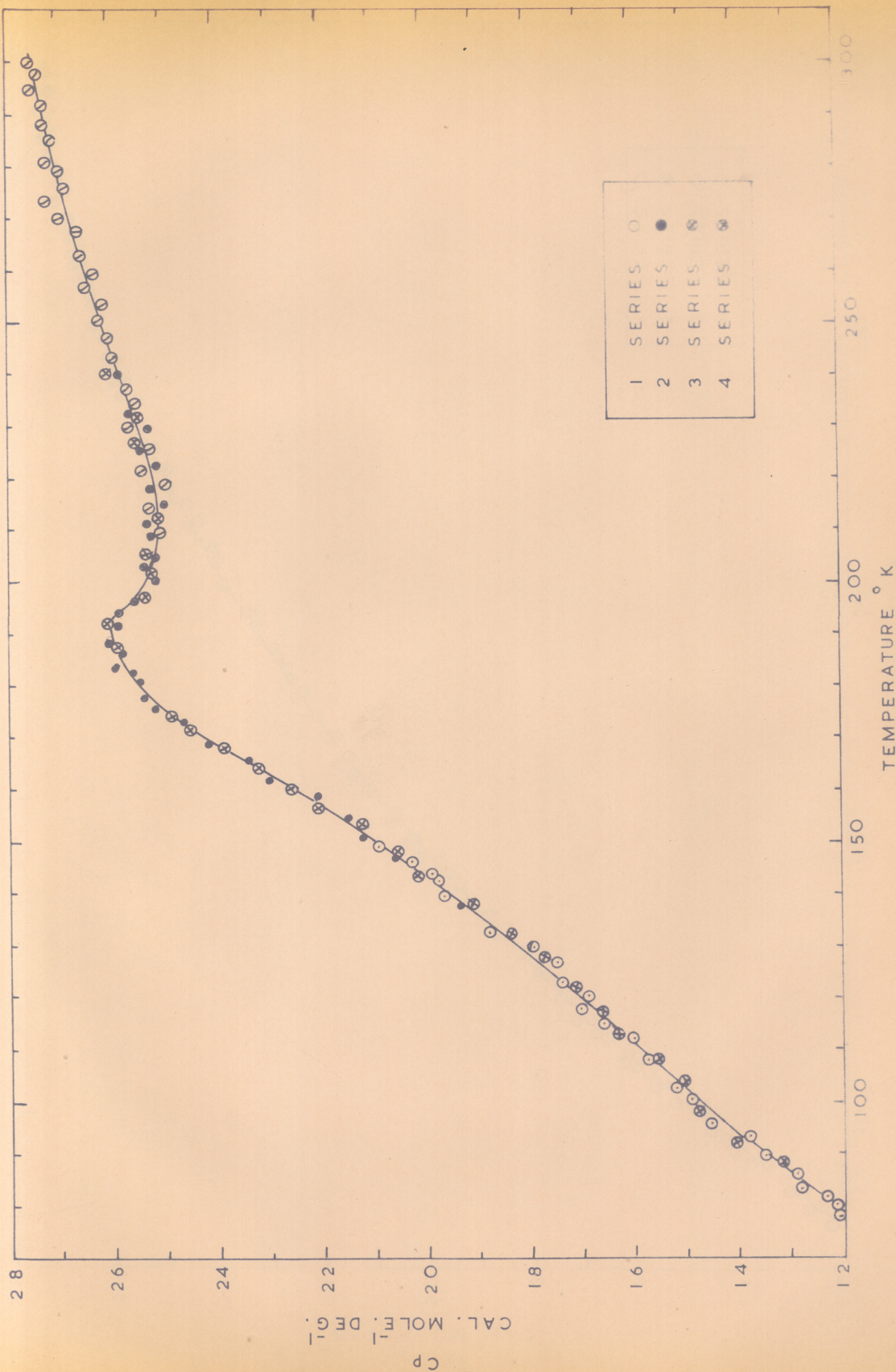


FIG 10 HEAT CAPACITY OF $\text{KNi}_{0.69}\text{Zn}_{0.31}\text{F}_3$

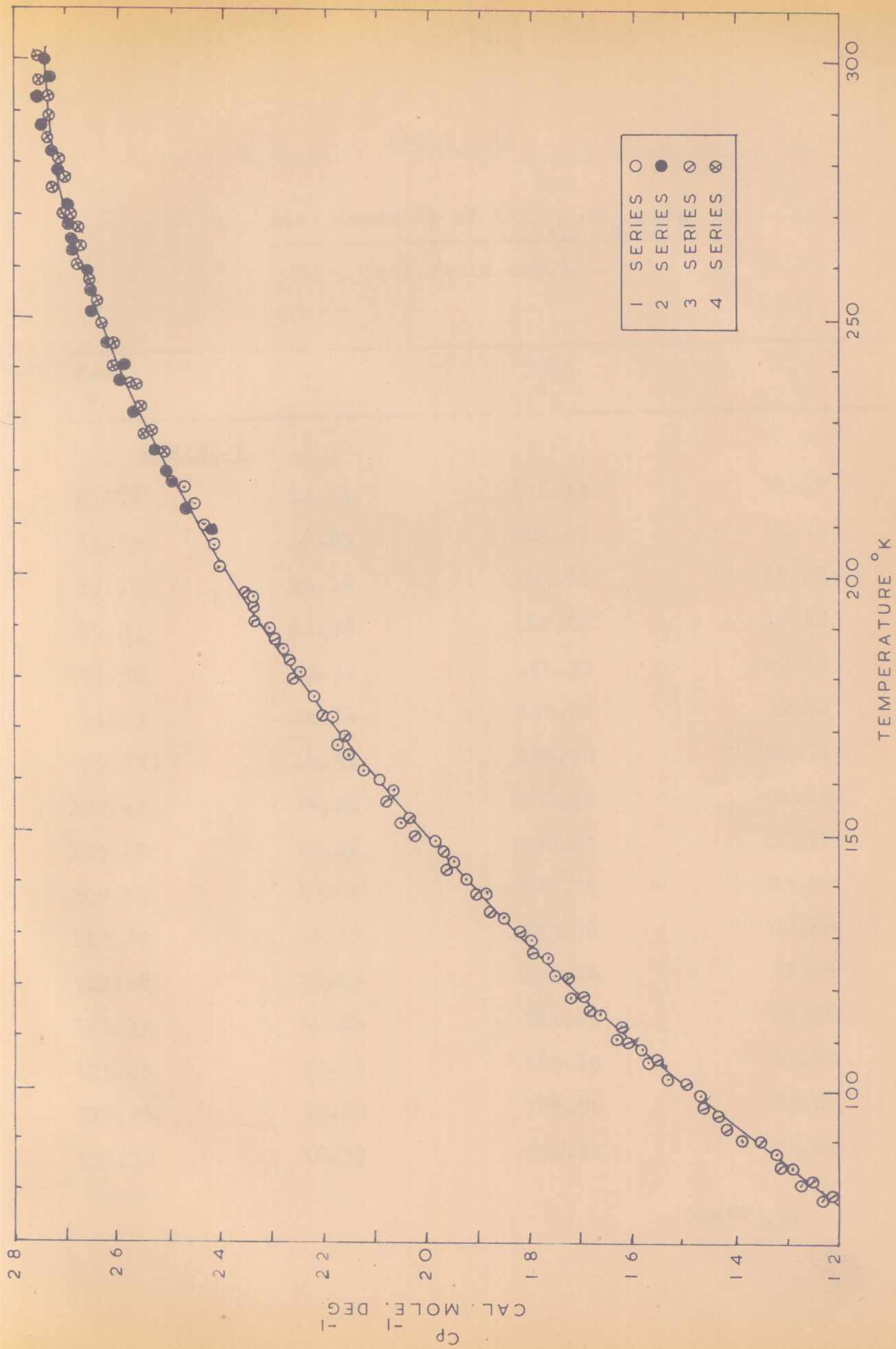


FIG. 11. HEAT CAPACITY OF $\text{KNi}_{0.49}\text{Zn}_{0.51}\text{F}_3$

TABLE - 13

Heat Capacity of $\text{KNi}_{0.85}\text{Zn}_{0.15}\text{F}_3$
 (cal./mole.deg.)

Temp. °K	C _P	Temp. °K	C _P
<u>SERIES-1</u>			
81.82	12.11	136.13	18.62
85.52	12.85	140.01	18.85
87.77	13.10	143.81	19.23
89.63	12.98	147.65	19.58
92.55	13.35	151.30	20.16
96.53	14.04	154.82	20.62
99.95	14.51	158.74	20.71
102.45	14.66	162.55	21.16
105.62	15.29	166.27	21.70
109.43	15.49	170.06	22.12
113.89	16.10	173.78	22.10
117.68	16.42	177.44	22.55
121.37	17.04	181.26	22.96
125.05	17.43	185.10	23.80
128.96	17.60	188.96	23.88
132.32	18.37	192.52	24.25

Contd....

Temp. °K	C _p	Temp. °K	C _p
196.31	25.02	236.33	29.15
200.02	25.30	239.25	29.30
	<u>SERIES-II</u>	242.17	29.22
189.30	24.10	245.08	28.93
193.49	24.72	248.00	28.85
196.75	24.75	251.52	28.27
199.26	25.02	254.37	28.05
201.69	25.60	259.48	27.40
204.23	25.65	263.00	27.12
207.14	26.19	266.26	27.20
209.50	26.60	269.92	26.98
211.97	26.68	273.41	27.33
213.33	27.04	275.90	27.12
217.05	27.28	278.95	27.06
219.48	27.70	282.12	27.10
221.90	27.91	284.66	27.26
224.26	28.32	287.21	27.20
226.31	28.35	289.66	27.25
228.34	28.72	293.34	27.41
230.69	28.70	297.55	27.36
233.46	29.02	300.35	27.50
	19.45		

Contd...

Temp. °K	C _p	Temp. °K	C _p
<u>SERIES-III</u>			
91.58	13.65	148.05	19.95
94.30	13.82	154.32	20.30
96.92	14.00	157.44	20.52
99.65	14.32	160.51	20.90
103.10	15.05	163.60	21.46
105.39	15.08	169.85	21.85
107.52	15.20	172.94	22.32
109.38	15.62	175.85	22.40
112.58	15.82	179.06	22.75
115.63	16.34	182.17	23.40
118.10	16.70	185.25	23.45
120.66	16.75	<u>SERIES-IV</u>	
123.80	17.20	188.30	23.70
126.42	17.65	191.42	24.42
129.00	17.90	194.57	24.45
131.21	17.91	197.66	24.80
133.38	18.09	200.74	25.31
136.33	18.37	203.88	25.95
138.67	18.60	206.95	26.00
141.33	19.22	210.01	26.40
144.72	19.45	213.22	26.82

Contd...

Temp. °K	C _p	Temp. °K	C _p
216.89	27.50	243.21	29.10
220.15	27.58	246.56	28.85
224.89	28.18	250.14	28.55
227.09	28.50	253.18	28.30
229.00	28.54	255.83	28.02
230.62	28.80	258.48	27.78
233.06	28.86	261.48	27.46
235.02	29.10	264.66	27.20
238.43	29.30	267.50	27.00
240.66	29.22	272.92	27.20

TABLE - 14

Heat Capacity of $\text{KNi}_{0.69}\text{Zn}_{0.31}\text{F}_3$
(cal./mole.deg.)

Temp. °K	C _P	Temp. °K	C _P
<u>SERIES-I</u>			
78.96	12.11	126.58	17.49
80.94	12.10	130.01	17.98
92.71	12.32	133.10	18.81
84.16	12.79	136.86	19.02
86.81	12.88	140.22	19.69
89.83	13.50	143.80	19.95
93.25	13.81	146.66	20.32
96.06	14.49	149.43	20.96
98.67	14.28	<u>SERIES-II</u>	
100.56	14.90	138.25	19.41
103.10	15.22	143.14	19.75
108.50	15.75	147.18	20.61
112.19	16.01	150.81	21.25
115.04	16.62	154.61	21.52
117.89	16.99	158.60	22.15
120.52	16.91	162.25	23.06
123.16	17.42	165.26	23.39

Contd....

Temp. °K	C _P	Temp. °K	C _P
168.95	24.20	<u>SERIES-III</u>	
172.28	24.65	209.82	25.10
175.30	25.21	214.00	25.28
177.68	25.40	217.32	25.07
180.48	25.48	221.62	25.42
183.61	25.96	225.74	25.28
186.60	25.84	229.52	25.65
189.21	26.13	234.01	25.52
191.65	25.97	237.08	25.73
193.87	25.92	240.11	26.10
197.45	25.60	242.92	26.02
199.92	25.25	246.27	26.05
202.56	25.43	249.94	26.29
205.12	25.19	253.04	26.24
208.41	25.31	255.87	26.52
211.65	25.35	259.21	26.39
214.83	25.06	262.95	26.60
218.01	25.30	267.02	26.65
221.95	25.16	269.95	27.02
225.02	25.50	273.55	27.25
229.13	25.39	275.47	26.92
233.11	25.72	277.38	27.00

Contd...

Temp. °K	C _p	Temp. °K	C _p
281.14	27.26	153.02	21.22
284.62	27.17	156.38	22.10
288.05	27.30	160.51	22.62
291.23	27.28	164.20	23.22
294.33	27.50	168.02	23.90
297.49	27.40	171.55	24.52
299.96	27.52	173.95	24.89
<u>SERIES-IV</u>		178.85	25.35
89.12	13.16	182.52	25.66
93.01	14.02	187.45	25.95
98.50	14.75	192.36	26.10
104.03	15.00	197.20	25.43
108.51	15.52	201.55	25.25
113.20	16.30	206.10	25.40
117.50	16.62	212.50	25.18
122.00	17.10	219.00	25.00
127.89	17.77	226.52	25.59
132.50	18.35	231.90	25.56
138.62	19.16		
143.60	20.20		
148.50	20.55		

TABLE - 15

Heat Capacity of $\text{KNi}_{0.49}\text{Zn}_{0.51}\text{F}_3$
 (cal./mole.deg.)

Temp. °K	C _P	Temp. °K	C _P
<u>SERIES-1</u>			
79.09	12.25	138.58	18.86
82.21	12.70	140.60	19.25
85.14	12.92	143.81	19.50
87.56	13.20	148.08	19.86
90.61	13.88	152.42	20.45
95.05	14.32	157.38	20.66
98.80	14.65	162.22	21.22
102.15	15.30	167.45	21.74
105.25	15.68	172.36	21.85
108.10	15.82	177.11	22.20
110.74	16.30	181.62	22.44
114.82	16.65	185.85	22.80
118.08	17.20	190.17	23.12
122.10	17.50	195.79	23.40
125.77	17.65	201.87	24.08
129.58	17.97	205.91	24.20
133.62	18.50	209.94	24.35

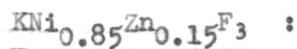
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Temp. °K	C _p	Temp. °K	C _p
213.94	24.58	292.78	27.50
217.28	24.73	296.45	27.36
149.50	<u>SERIES-II</u> 24.28	300.12	27.46
209.10	24.20		<u>SERIES-III</u> 26.45
213.11	24.69	79.52	12.10
217.95	25.02	82.60	12.50
224.22	25.30	85.15	13.14
231.71	25.72	89.83	13.53
237.51	25.95	92.61	14.16
240.87	25.90	96.55	14.60
245.43	26.29	101.32	14.95
250.88	26.50	105.61	15.52
255.00	26.58	109.42	16.10
258.96	26.60	112.69	16.27
262.56	26.92	115.63	16.83
265.12	<u>SERIES-IV</u> 26.95	118.39	16.95
268.02	27.00	122.00	17.30
271.43	26.98	126.43	17.95
278.05	27.20	130.62	18.18
282.14	27.32	134.55	18.74
287.06	27.45	138.52	19.00

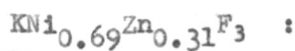
Contd...

Temp. °K	C _P	Temp. °K	C _P
142.37	19.63	240.88	26.10
146.12	19.70	244.86	26.12
149.50	20.28	248.70	26.32
152.76	20.32	252.53	26.45
155.86	20.80	256.34	26.60
160.20	20.91	260.03	26.82
164.83	21.50	263.55	26.70
169.02	21.62	267.05	26.78
173.04	22.02	270.55	27.02
180.15	22.60	273.90	27.30
183.72	22.65	277.10	27.05
187.38	22.94	280.75	27.14
190.77	23.40	284.72	27.36
194.07	23.40	288.74	27.30
197.25	23.55	293.19	27.30
	<u>SERIES-IV</u>	296.07	27.50
220.18	25.10	300.35	27.52
223.58	25.12		
226.42	25.50		
228.12	25.32		
232.51	25.55		
236.83	25.76		

method we were able to fit satisfactorily the specific-heat data over the usual temperature ranges. The results have been given below:

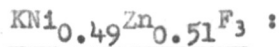


$$D\left(\frac{96}{T}\right) + 2E\left(\frac{260}{T}\right) + 2E\left(\frac{505}{T}\right) \quad (80^\circ\text{-}130^\circ\text{K} ; \pm 1\%)$$



$$D\left(\frac{95}{T}\right) + 2E\left(\frac{260}{T}\right) + 2E\left(\frac{480}{T}\right) \quad (80^\circ\text{-}300^\circ\text{K} ; \pm 1\%)$$

Transition region excluded.



$$D\left(\frac{93}{T}\right) + 2E\left(\frac{265}{T}\right) + 2E\left(\frac{480}{T}\right) \quad (80^\circ\text{-}200^\circ\text{K} ; \pm 0.5\%)$$

Using these functions the thermodynamic properties were evaluated and are listed in Tables 16, 17 and 18.

TABLE - 16

Thermodynamic Functions of $\text{KNi}_{0.85}\text{Zn}_{0.15}\text{F}_3$

Temp. °K	C_p° cal./mole.deg.	$S^\circ - S_0^\circ$ cal./mole.deg.	$H^\circ - H_0^\circ$ cal./mole.	$-(F^\circ - H_0^\circ)/T$ cal./mole.deg.
80	12.05	(9.25) ⁺	(431.7) ⁺	3.85
85	12.70	10.00	493.2	4.20
90	13.37	10.74	558.2	4.54
95	13.98	11.48	626.7	4.88
100	14.55	12.21	698.0	5.23
105	15.15	12.94	772.0	5.59
110	15.70	13.65	848.9	5.93
115	16.28	14.36	929.0	6.28
120	16.75	15.07	1011	6.65
125	17.27	15.76	1096	6.99
130	17.80	16.45	1184	7.34
135	18.42	17.14	1274	7.70
140	18.97	17.82	1368	8.05
145	19.47	18.49	1464	8.40
150	19.95	19.16	1563	8.74
155	20.45	19.82	1664	9.08
160	20.90	20.48	1768	9.43

Contd..

Temp. °K	C_p^0 cal./mole.deg.	$S^0 - S_0^0$ cal./mole.deg.	$H^0 - H_0^0$ cal./mole.	$-(F^0 - H_0^0)/T$ cal./mole.deg.
165	21.33	21.12	1873	9.77
170	21.82	21.77	1981	10.12
175	22.36	22.41	2092	10.46
180	22.97	23.05	2206	10.79
185	23.56	23.69	2322	11.14
190	24.07	24.32	2441	11.48
195	24.75	24.96	2563	11.82
200	25.24	25.59	2688	12.15
205	25.82	26.22	2815	12.49
210	26.45	26.85	2946	12.82
215	27.12	27.48	3080	13.15
220	27.70	28.11	3217	13.49
225	28.26	28.74	3357	13.83
230	28.75	29.37	3500	14.15
235	29.14	29.99	3644	14.48
240	29.31	30.61	3791	14.81
245	29.05	31.21	3936	15.15
250	28.52	31.79	4080	15.47
255	27.95	32.35	4221	15.80
260	27.54	32.90	4360	16.13

Contd...

Temp. °K	C_p° cal./mole.deg.	$S^{\circ} - S_0^{\circ}$ cal./mole.deg.	$H^{\circ} - H_0^{\circ}$ cal./mole	$-(F^{\circ} - H_0^{\circ})/T$ cal./mole.deg.
265	27.20	33.42	4497	16.45
270	26.98	33.92	4632	16.76
275	27.00	34.42	4767	17.08
280	27.10	34.91	4902	17.40
285	27.25	35.39	5038	17.71
290	27.30	35.86	5174	18.02
295	27.40	36.33	5311	18.32
300	27.50	36.80	5449	18.64
273.15	(26.99)	(34.23)	(4717)	(16.96)
298.15	(27.46)	(36.62)	(5398)	(18.52)

+ Extrapolated.

TABLE - 17

Thermodynamic Functions of $\text{KNi}_{0.69}\text{Zn}_{0.31}\text{F}_3$

Temp. °K	C_p° cal./mole.deg.	$S^\circ - S_0^\circ$ cal./mole.deg.	$H^\circ - H_0^\circ$ cal./mole	$-(F^\circ - H_0^\circ)/T$ cal./mole.deg.
80	12.10	(9.35) [†]	(436.5) [†]	3.89
85	12.82	10.11	498.6	4.25
90	13.50	10.86	564.2	4.59
95	14.12	11.61	633.3	4.94
100	14.70	12.35	705.2	5.30
105	15.31	13.09	780.3	5.66
110	15.90	13.82	858.3	6.02
115	16.51	14.54	939.2	6.37
120	17.05	15.25	1023	6.73
125	17.62	15.96	1109	7.09
130	18.21	16.66	1199	7.43
135	18.85	17.36	1291	7.80
140	19.50	18.06	1387	8.15
145	20.25	18.76	1486	8.51
150	20.97	19.46	1589	8.87
155	21.72	20.16	1696	9.22
160	22.51	20.86	1807	9.57

Contd...

Temp. °K	C_p^0 cal./mole.deg.	$S^0 - S_0^0$ cal./mole.deg.	$H^0 - H_0^0$ cal./mole	$-(F^0 - H_0^0)/T$ cal./mole.deg.
165	23.40	21.57	1922	9.92
170	24.32	22.28	2041	10.28
175	25.04	22.99	2165	10.62
180	25.60	23.71	2291	10.98
185	26.05	24.42	2420	11.34
190	26.14	25.11	2550	11.69
195	25.75	25.79	2680	12.05
200	25.44	26.44	2808	12.40
205	25.27	27.06	2935	12.74
210	25.20 <small>(25.15)</small>	27.67 <small>(27.45)</small>	3061 <small>(3031)</small>	13.10 <small>(12.88)</small>
215	25.27 <small>(25.15)</small>	28.26 <small>(28.08)</small>	3187 <small>(3152)</small>	13.43 <small>(13.23)</small>
220	25.28	28.85	3314	13.79
225	25.40	29.42	3441	14.12
230	25.55	29.98	3568	14.46
235	25.70	30.53	3696	14.81
240	25.85 <small>+ Extrapolated</small>	31.07	3825	15.13
245	26.04	31.61	3955	15.47
250	26.23	32.14	4085	15.80
255	26.35	32.66	4217	16.12
260	26.55	33.17	4349	16.44

Contd....

Temp. °K	C_p° cal./mole.deg.	$S^\circ - S_0^\circ$ cal./mole.deg.	$H^\circ - H_0^\circ$ cal./mole	$-(F^\circ - H_0^\circ)/T$ cal./mole.deg.
265	26.70	33.68	4482	16.77
270	26.87	34.18	4616	17.08
275	27.00	34.68	4751	17.40
280	27.11	35.16	4886	17.71
285	27.24	35.65	5022	18.03
290	27.30	36.12	5158	18.34
295	27.42	36.59	5295	18.64
300	27.47	37.05	5433	18.94
273.15	(26.95)	(34.49)	(4701)	(17.28)
298.15	(27.45)	(36.88)	(5382)	(18.83)

+ Extrapolated

TABLE - 18

Thermodynamic Functions of $\text{KNi}_{0.49}\text{Zn}_{0.51}\text{F}_3$

Temp. °K	C_p^0 cal./mole.deg.	$S^0 - S_0^0$ cal./mole.deg.	$H^0 - H_0^0$ cal./mole	$-(F^0 - H_0^0)/T$ cal./mole.deg.
80	12.30	(9.39) [†]	(433.8) [†]	3.97
85	13.00	10.16	497.3	4.31
90	13.65	10.92	563.8	4.66
95	14.36	11.68	633.8	5.01
100	14.95	12.43	707.3	5.36
105	15.58	13.18	783.6	5.72
110	16.16	13.91	863.1	6.06
115	16.68	14.64	945.0	6.42
120	17.20	15.37	1030	6.79
125	17.79	16.08	1117	7.15
130	18.27	16.79	1207	7.51
135	18.82	17.49	1300	7.86
140	19.33	18.18	1395	8.22
145	19.77	18.87	1493	8.57
150	20.15	19.55	1593	8.93
155	20.62	20.22	1695	9.29
160	21.04	20.88	1799	9.63

Contd....

Temp. °K	C_P^0 cal./mole.deg.	$S^0 - S_0^0$ cal./mole.deg.	$H^0 - H_0^0$ cal./mole	$-(F^0 - H_0^0)/T$ cal./mole.deg.
165	21.48	21.53	1906	9.98
170	21.82	22.18	2014	10.33
175	22.15	22.82	2124	10.69
180	22.50	23.44	2236	11.01
185	22.86	24.07	2350	11.36
190	23.20	24.68	2465	11.71
195	23.64	25.29	2582	12.05
200	23.84	25.89	2701	12.39
205	24.17	26.48	2821	12.72
210	24.45	27.07	2943	13.05
215	(24.69)	(27.65)	(3065)	(13.39)
220	(25.00)	(28.22)	(3190)	(13.72)
225	25.26	28.79	3315	14.06
230	25.50	29.34	3442	14.37
235	25.73	29.90	3570	14.71
240	25.94	30.44	3699	15.03
245	26.16	30.98	3829	15.35
250	26.32	31.51	3961	15.67
255	26.53	32.03	4093	15.98
260	26.72	32.55	4226	16.30

Contd....

Temp. °K	C_p^0 cal./mole.deg.	$S^0 - S_0^0$ cal./mole.deg.	$H^0 - H_0^0$ cal./mole	$-(F^0 - H_0^0)/T$ cal./mole.deg.
265	26.90	33.06	4360	16.61
270	27.04	33.56	4495	16.92
275	27.12	34.06	4630	17.22
280	27.20	34.55	4766	17.53
285	27.30	35.03	4903	17.82
290	27.35	35.51	5039	18.13
295	27.40	35.98	5176	18.43
300	27.45	36.44	5314	18.73
273.15	(27.09)	(33.87)	(4580)	(17.11)
298.15	(27.43)	(36.27)	(5263)	(18.62)

the same value of
+ Extrapolated

CHAPTER VIII

DISCUSSION OF RESULTS

In the foregoing Chapter we have presented the heat capacity data of the compounds $\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$ where $x = 0.85, 0.69$ and 0.49 . Machin et al.¹ have reported the susceptibility of such compounds with various values of x , ranging from 0.1 to 1 . Their compounds with $x = 0.845, 0.682$ and 0.484 correspond closely to those whose heat capacities have been described in the previous Chapter. Before we compare and discuss the results obtained from the susceptibility and heat capacity measurements, it would be worthwhile to note some of the important observations which Machin et al.¹ have made :

'The magnetic properties of several preparations with the same value of α ($= x$) have been shown to be identical, suggesting that substitution by zinc ions in the KNiF_3 lattice is a random process. It is convenient to divide the results into three groups for discussion : (i) the range $1 = \alpha > 0.7$, (ii) a transition region $\sim 0.7 > \alpha > 0.5$, and (iii) the remaining compounds $0.5 > \alpha > 0.1$.

If one plots (effective magnetic moment) μ_{eff} against α at single temperatures, the resulting curves show three regions with differing $\mu_{\text{eff.}}/\alpha$ slopes, corresponding to these ranges of α .

We have seen that the antiferromagnetism of potassium trifluoronickelate (II) is due to super-exchange interaction which operates throughout the three-dimensional Ni-F-Ni-F array in the lattice. Random replacement of nickel by zinc in this system may thus be expected to weaken the interaction by decreasing the length of an interacting chain, and thus leading to progressive lowering of the Néel point as more zinc ions are added. This trend is observed in the region (i), the Néel point steadily decreasing as α decreases, from 280°K when $\alpha = 1$ to about 220°K when α has fallen to 0.7. As α decreases in region (i), the maximum in the susceptibility becomes rapidly shallower, degenerating to an inflexion before disappearing completely in region (ii). As the interaction becomes progressively weaker, the magnetic moment increases steadily towards the expected value for an octahedral nickel (II) compound, 3.1-3.3 B.M. However, by the time that the Néel point has disappeared, μ_{eff} has increased only to 2.3 B.M., indicating that a considerable magnetic interaction is still

in operation. One might expect a steady fall in the Néel point to continue as α was further decreased, but in region (ii) this is not so and no maximum in the susceptibility is observed. In this second region, however, if replacement of nickel ions has been random, there will no longer be even pairs of nickel ions separated by a single fluoride ion, and the smallest repeating unit in the structure will be of the type Ni-F-Zn-F-Ni-F, and the original type of interaction cannot occur. There is evidence, however, for long range interactions since an antiferromagnetic material often does not obey the Curie-Weiss law until several hundred degrees above its Néel temperature, where in principle the system is completely randomised. We thus regard region (ii) as a transition region between region (i) where the strong nearest-neighbour interactions give rise to high Néel points and region (iii) in which only comparatively weak, long-range interactions occur, sufficient to reduce μ_{eff} considerably but giving rise to Néel points below 80°K, the limit of our observations (and probably well below this temperature). In region (iii) the steady rise in μ_{eff} as α is decreased reflects the progressive weakening of these interactions in the same way as in region (i), until, for $\alpha = 0.226$, the high-temperature susceptibility obeys the Curie-Weiss law,

the Weiss constant, θ , being 168°K in this case. θ falls to only 84°K when $\alpha = 0.109$, and μ_{eff} has risen to 3.08 B.M., indicating that any residual interaction is very weak. The steady increase in μ_{eff} over the whole composition range studied makes it unlikely that the disappearance of the Néel point is due to the existence of a solubility limit in the system since, if this were the case, μ_{eff} should remain constant at its value at the solubility limit.

Our first compound with $x = 0.85$ corresponds to the mean of the extreme values of the region (i). The second with $x = 0.69$ to the border-line of region (i) and (ii) and the third with $x = 0.49$ to the border-line of regions (ii) and (iii).

$\text{KNi}_{0.85}\text{Zn}_{0.15}\text{F}_3$

The heat capacity rises monotonically from 80°K to 200°K ; it then increases gradually to a maximum of 29.30 cal./mole.deg. at 239.2°K , beyond which it falls slowly, reaching a value of 27.46 cal./mole.deg. at 298.15°K . The temperature 239.2°K clearly indicates the

Néel point, which is lower than that reported by Machin *et al.*¹ for $x = 0.845$ by about 15°K . Similar situation had arisen in the case of potassium nickel trifluoride, KNiF_3 . The above-mentioned authors reported the Néel temperature of

280°K, which was higher than that reported by Deenadas et al.² from heat capacity measurements, namely, 253.5°K. The discrepancy in both these cases may partly be explained as due to statistical effects, the theory of which has been discussed by Nagai³. He showed that the susceptibility maximum usually occurs at a temperature higher than the Néel point. On the other hand, the heat capacity maximum corresponds accurately to the Néel temperature (T_N) and is often regarded as the most precise tool for detection of such transition points. Besides, a slight impurity in the sample would introduce a large error in the susceptibility though not in the heat capacity measurements. However since Machin et al.¹ had taken elaborate precautions in the preparation and analysis of their samples, the possibility of the presence of impurities affecting their susceptibility results may be safely ruled out. Nevertheless it is believed that the discrepancy in the values of T_N from susceptibility and heat capacity measurements may not be entirely due to statistical effects. The probable reasons are not known at present.

It may also be noted that the shape of the heat capacity-temperature curve is not so steep in the neighbourhood of T_N as might normally be expected. There are clear indications of the predominance of the short-range order.

The lower T_N of $\text{KNi}_{0.85}\text{Zn}_{0.15}\text{F}_3$, 239.2°K compared to that of KNiF_3 , 253.5°K indicates that the magnetic interaction has been weakened by random replacement of paramagnetic nickel by diamagnetic zinc ions, which causes a decrease in the length of the interacting chain.

$\text{KNi}_{0.69}\text{Zn}_{0.31}\text{F}_3$:

The heat capacity rises smoothly from 80°K to 150°K ; it then increases gradually with a maximum of 26.14 cal./mole.deg. at 190.0°K beyond which it falls slowly, reaching a value of 27.45 cal./mole.deg. at 298.15°K . Even in this case the Néel point, 190.0°K , is lower than that obtained from susceptibility studies¹. Explanation similar to that offered for $\text{KNi}_{0.85}\text{Zn}_{0.15}\text{F}_3$ may be given for the discrepancy. Further, decrease in the magnetic interaction is observed. Increasing short-range order is also evident from the broadening of the specific heat curve near T_N .

$\text{KNi}_{0.49}\text{Zn}_{0.51}\text{F}_3$

The heat capacity fails to exhibit any anomalous behaviour in the entire temperature range of measurements (80° - 300°K). This result is in agreement with the prediction of the various theories of 'dilute' magnetism. These

theories state that on gradually substituting paramagnetic ions by diamagnetic ones, a lowering of T_N would be obtained, until we reach a certain critical concentration of paramagnetic ions, below which no co-operative phenomenon occurs. It is evident that the critical concentration p_0 , in the system, $\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$ is more than 0.49. It must, however, be less than 0.69, in which case the Néel point occurs at 190.0°K . It means that $0.49 < p_0 < 0.69$. Machin *et al.*¹ found $0.60 < p_0 < 0.68$ from their susceptibility measurements, which gives good agreement between our heat capacity and the magnetic susceptibility studies. Besides the conclusions of the latter (studies) are thereby confirmed.

MAGNETIC HEAT CAPACITY AND ENTROPY OF $\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$ ($x = 0.85$ and 0.69) COMPOUNDS

As mentioned before in Chapter IV, a number of approximate methods have been followed by various workers, to estimate the lattice heat capacity and entropy. Two of the common methods are : (i) a combination of Debye-Einstein functions and (ii) corresponding states principle. In what follows is a description of the application of these methods to $\text{KNi}_{0.85}\text{Zn}_{0.15}\text{F}_3$ and $\text{KNi}_{0.69}\text{Zn}_{0.31}\text{F}_3$ for the evaluation of the normal lattice contribution and consequently the magnetic heat capacity and entropy.

(1) Debye-Einstein Function Method :

Since our heat capacity measurements were restricted to 78°K on the low temperature side, for want of proper refrigerants, it necessitated the extrapolation (of heat capacity) below this temperature, in order to derive the thermodynamic properties of the compounds studied here. This was accomplished by fitting the experimental heat capacity curve with a combination of appropriate Debye and Einstein functions. These functions for $\text{KNi}_{0.85}\text{Zn}_{0.15}\text{F}_3$ and $\text{KNi}_{0.69}\text{Zn}_{0.31}\text{F}_3$ were

$$D\left(\frac{96}{T}\right) + 2E\left(\frac{260}{T}\right) + 2E\left(\frac{505}{T}\right)$$

and

$$D\left(\frac{95}{T}\right) + 2E\left(\frac{260}{T}\right) + 2E\left(\frac{480}{T}\right)$$

respectively. Since the Néel temperatures of these compounds are comparatively high, viz., 239.2°K and 190.0°K, these functions, which were more closely fitted to the low temperature side of the measured heat capacities, could be assumed to represent the lattice heat capacity when extended upto 300°K. The magnetic heat capacities obtained by subtraction of the lattice contributions from the measured totals have been represented graphically in Fig.12 and 13 respectively.

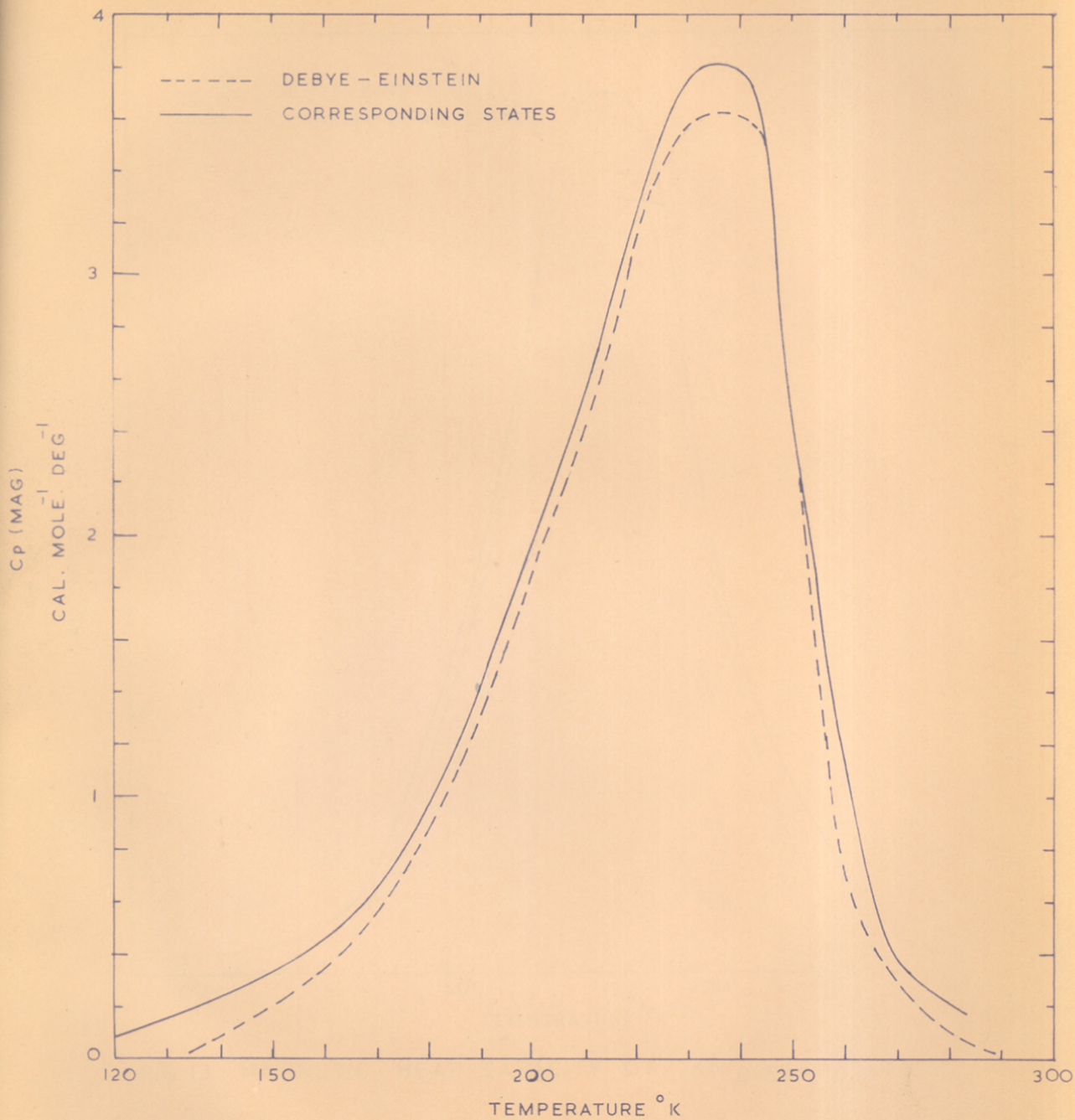


FIG. 12. MAGNETIC HEAT CAPACITY OF $\text{KNi}_{0.85}\text{Zn}_{0.15}\text{F}_3$

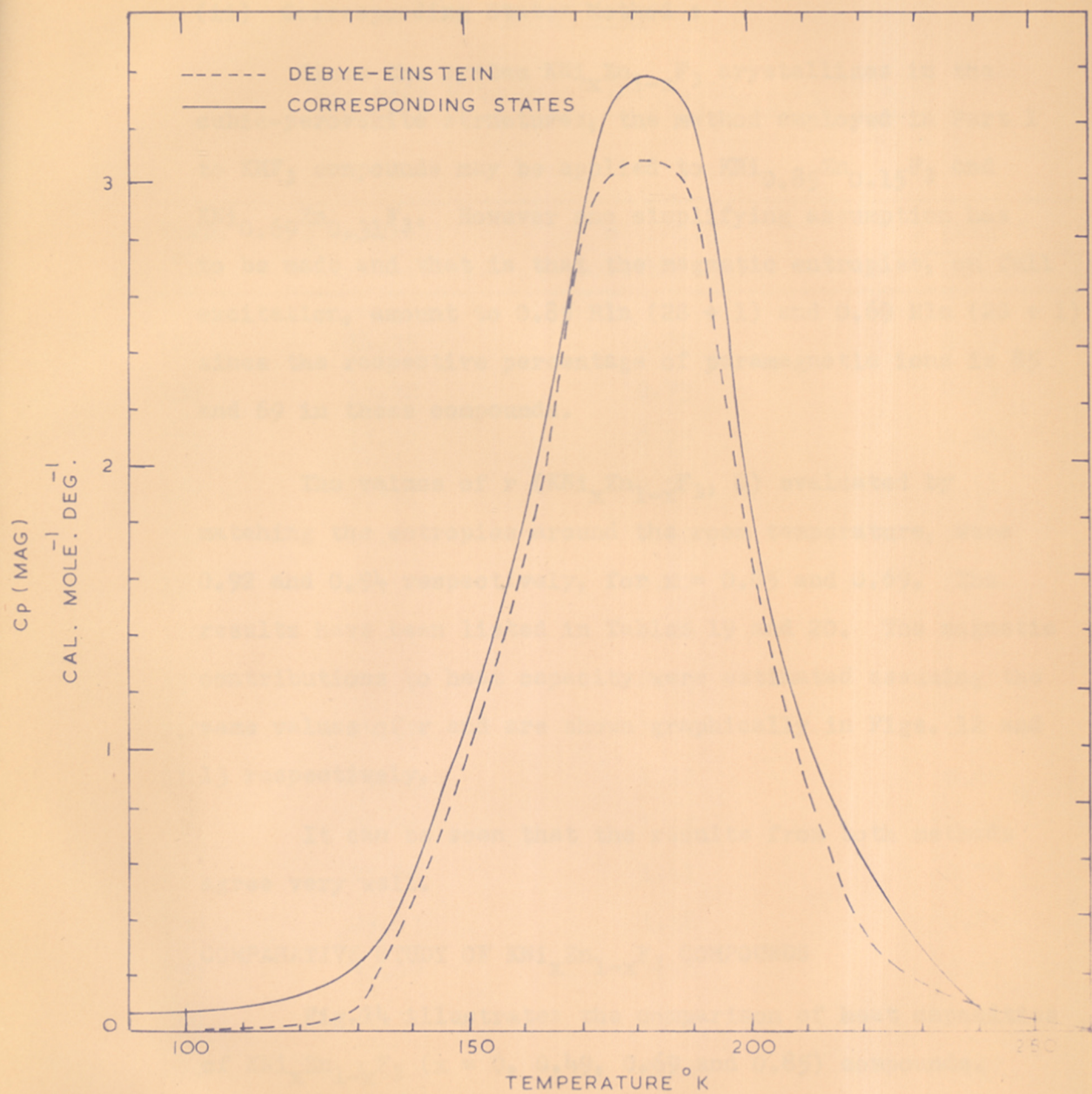


FIG.13. MAGNETIC HEAT CAPACITY OF $\text{KNi}_{0.69}\text{Zn}_{0.31}\text{F}_3$

(ii) Corresponding States Method :

Since the system $\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$ crystallizes in the cubic-perovskite structures, the method employed in Part I to KMnF_3 compounds may be applied to $\text{KNi}_{0.85}\text{Zn}_{0.15}\text{F}_3$ and $\text{KNi}_{0.69}\text{Zn}_{0.31}\text{F}_3$. However one simplifying assumption has to be made and that is that the magnetic entropies, on full excitation, amount to $0.85 R \ln (2S + 1)$ and $0.69 R \ln (2S + 1)$ since the respective percentage of paramagnetic ions is 85 and 69 in these compounds.

The values of r ($\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$, S) evaluated by matching the entropies around the room temperature, were 0.92 and 0.94 respectively, for $x = 0.85$ and 0.69. The results have been listed in Tables 19 and 20. The magnetic contributions to heat capacity were estimated assuming the same values of r and are shown graphically in Figs. 12 and 13 respectively.

It can be seen that the results from both methods agree very well.

COMPARATIVE STUDY OF $\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$ COMPOUNDS

Fig. 14 illustrates the comparison of heat capacities of $\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$ ($x = 0, 0.49, 0.69$ and 0.85) compounds. It is interesting to note that the variation of the Néel

TABLE - 19

Magnetic Entropy of $\text{KNi}_{0.85}\text{Zn}_{0.15}\text{F}_3$ ($S = 1$)

Temp. °K	S(lattice) cal./mole.deg.	S (mag.) cal./mole.deg.	S (mag.) $0.85 \text{ Rln}(2S + 1)$
120	14.35	0.72	0.39
130	15.72	0.73	0.39
140	17.07	0.75	0.40
150	18.39	0.77	0.41
160	19.68	0.80	0.43
170	20.95	0.82	0.44
180	22.19	0.86	0.46
190	23.39	0.93	0.50
200	24.57	1.02	0.55
210	25.73	1.12	0.60
220	26.86	1.25	0.67
230	27.96	1.41	0.76
240	29.03	1.58	0.85
250	30.09	1.70	0.91
260	31.11	1.79	0.96
270	32.11	1.81	0.97
280	33.08	1.83	0.98

TABLE - 20Magnetic Entropy of $\text{KNi}_{0.69}\text{Zn}_{0.31}\text{F}_3$ ($S = 1$)

Temp. °K	S (lattice) cal./mole.deg.	S (mag.) cal./mole.deg.	S (mag.) $0.69 \text{ Rln}(2S+1)$
100	11.83	0.52	0.34
110	13.28	0.54	0.36
120	14.71	0.54	0.36
130	16.11	0.55	0.36
140	17.47	0.59	0.39
150	18.81	0.65	0.43
160	20.13	0.73	0.48
170	21.41	0.87	0.58
180	22.66	1.05	0.70
190	23.89	1.22	0.81
200	25.08	1.36	0.90
210	26.26	1.41	0.93
220	27.39	1.46	0.97
230	28.50	1.48	0.98
240	29.58	1.49	0.99
250	30.65	1.49	0.99

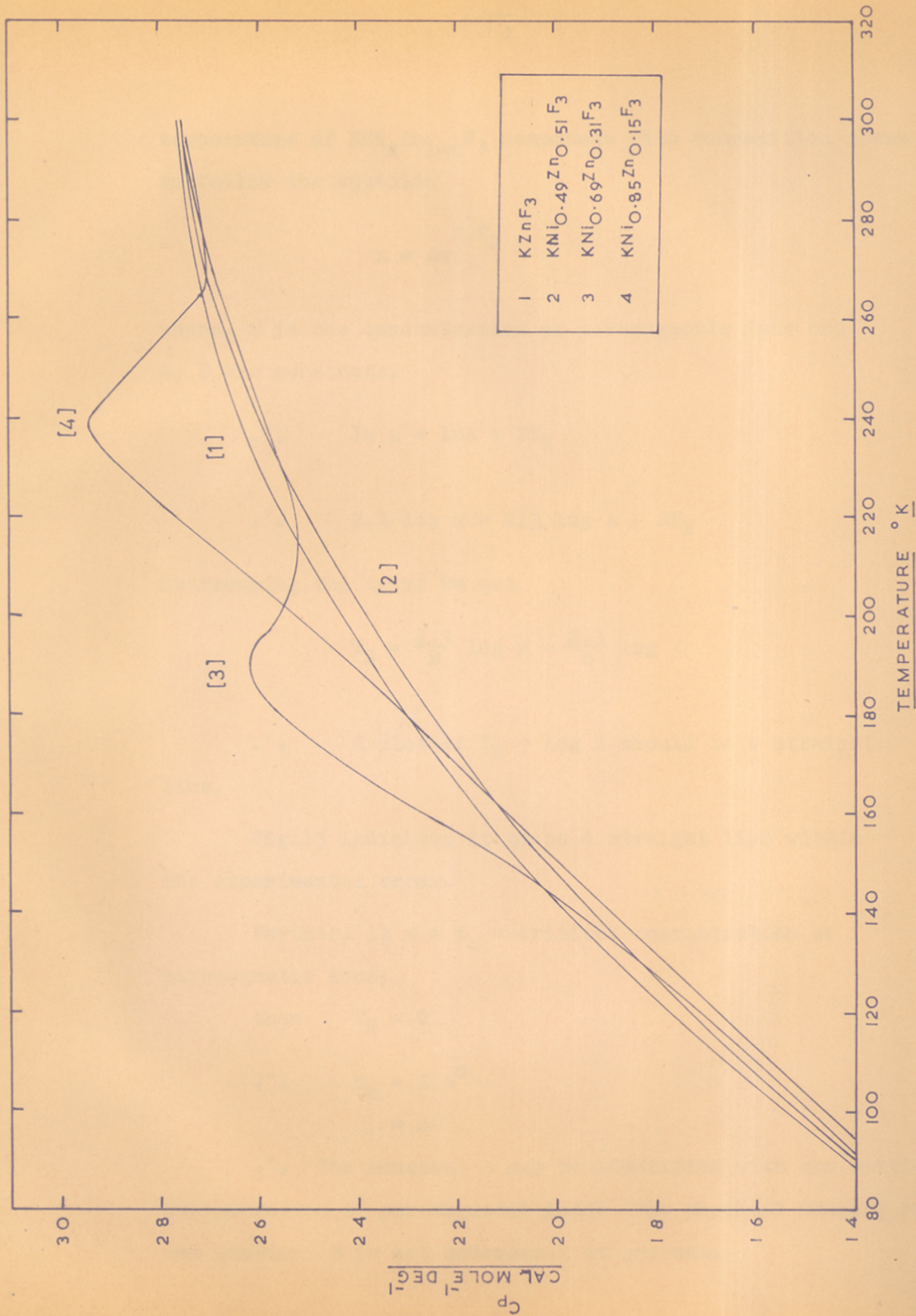


Fig. 14 HEAT CAPACITIES OF $\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$ COMPOUNDS

temperature of $\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$ compounds with composition seems to follow the equation

$$x = Ae^{\frac{B \cdot T_N}{T}}$$

where, x is the concentration of paramagnetic ions and A, B are constants.

$$\therefore \ln x = \ln A + \frac{B T_N}{T}$$

$$\therefore 2.3 \log x = 2.3 \log A + \frac{B T_N}{T}$$

Rearranging the terms we get

$$T_N = \frac{2.3}{B} \log x - \frac{2.3}{B} \log A$$

\therefore A plot of $T_N \rightarrow \log X$ should be a straight line.

Fig.15 indicates it to be a straight line within the experimental error.

Further, it $x = x_c$ = critical concentration of paramagnetic ions,

$$\text{then } T_N = 0$$

$$\begin{aligned} \therefore x_c &= A e^0 \\ &= A \end{aligned}$$

\therefore The constant A may be identified with the critical concentration of paramagnetic ions. The physical meaning of the constant B is not understood at present.

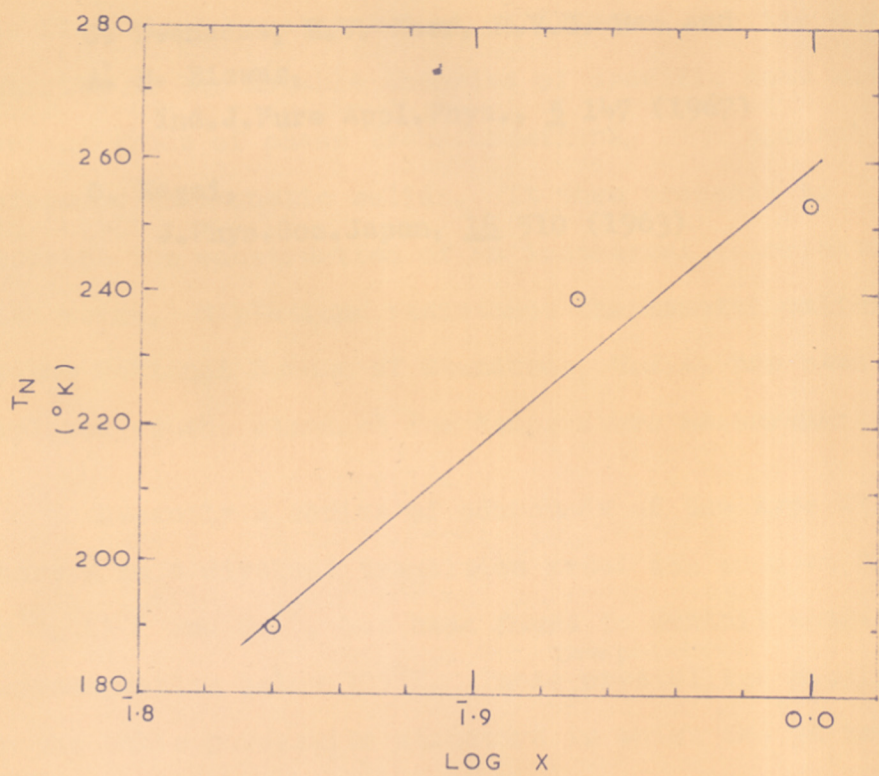


FIG. 15. VARIATION OF NÉEL TEMPERATURE WITH COMPOSITION

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SUMMARY

The thesis begins with an introductory survey of the historical development of calorimetry, merits and demerits of the notable theories of specific heat and various types of phase transformations, with special reference to magnetic solids. It then proceeds to describe the construction of an isothermal calorimeter with vanes. A platinum resistance thermometer calibrated by the National Bureau of Standards, U.S.A. has been employed as the standard for temperature measurements.

Recently a series of compounds of the type KMF_3 , where M is a divalent transition metal ion such as Mn^{+2} , Co^{+2} , Ni^{+2} and Cu^{+2} , has been found to exhibit anti-ferromagnetism below $300^\circ K$. These ^{compounds} crystallize mostly in the cubic perovskite structure in which the 3d ion is coupled antiferromagnetically to its six nearest neighbours below the Néel temperature. Lambda-type anomalies in heat capacity, associated with the destruction of the magnetic order of the transition metal ions, have already been reported by us. In order to estimate the heat capacity and entropy related with the antiferromagnetic \rightarrow paramagnetic transitions in these solids, thermal studies of the

corresponding isomorphous diamagnetic potassium zinc trifluoride, KZnF_3 , were undertaken and are reported in Part I of the thesis. As expected, the heat capacity exhibited a normal sigmoid behaviour over the entire temperature range of measurements ($80^\circ\text{--}300^\circ\text{K}$). Applying the corresponding states method suggested by Stout, magnetic heat capacities, entropies and exchange constants were evaluated and employed for testing some of the existing theories.

Consideration of the magnetic contribution to the heat capacity and entropy of potassium manganese trifluoride, KMnF_3 , below 80°K enabled a better evaluation of the thermodynamic properties than that reported earlier. In the case of potassium cobalt trifluoride, KCoF_3 , two values of spin, namely $1/2$ and $3/2$, were assigned to the Co^{+2} ion. The evaluated exchange constant corresponded to the latter value. Since the Néel temperatures of potassium nickel trifluoride, KNiF_3 , and potassium copper trifluoride, KCuF_3 , lie at relatively high temperatures, the results obtained were less accurate. Besides, KCuF_3 exhibits a tetragonal distortion from the cubic symmetry, which tended to make the value of the exchange constant still more approximate. In general, the exchange constants evaluated from the heat capacity measurements showed good agreement with those calculated from other methods.

Since the mechanism of super-exchange is considered to be responsible for the magnetic behaviour of KMnF_3 compounds, a study of the effect of dilution of the magnetic ions with diamagnetic ones would be of importance, especially from the point of view of the lowering of the Néel temperature and its complete disappearance at a critical concentration of paramagnetic ions. Accordingly, thermal studies of the compounds, $\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$ ($x = 0.85, 0.69$ and 0.49) were undertaken and are presented in Part II. The first two compounds exhibited peaks at 239.2°K and 190.0°K , respectively, corresponding to their Néel points. No anomalous behaviour was detected in the last compound, indicating that the value of the critical concentration lies between 0.69 and 0.49 . This observation is in agreement with the magnetic susceptibility measurements by Nyholm and coworkers. However, the Néel temperatures observed by us for $\text{KNi}_{0.85}\text{Zn}_{0.15}\text{F}_3$ and $\text{KNi}_{0.69}\text{Zn}_{0.31}\text{F}_3$ are lower than those found by these authors. Explanations have been offered for this discrepancy. Magnetic heat capacities and entropies have been evaluated by a modified procedure of the corresponding states method employed in Part I. The results have been compared with those obtained from Bebye-Einstein functions for separation of lattice contributions.

Thermodynamic properties of KZnF_3 , $\text{KNi}_{0.49}\text{Zn}_{0.51}\text{F}_3$, $\text{KNi}_{0.69}\text{Zn}_{0.31}\text{F}_3$ and $\text{KNi}_{0.85}\text{Zn}_{0.15}\text{F}_3$ were evaluated at

regular temperature intervals in the range 80° - 300° K. The extrapolation of heat capacities below 80° K was made by the conventional combination of Debye-Einstein functions. The values of heat capacity C_p° , entropy ($S^{\circ} - S_0^{\circ}$), enthalpy ($H^{\circ} - H_0^{\circ}$) and free energy $-(F^{\circ} - H_0^{\circ})/T$ at 298.15° K for all these compounds along with the Néel temperatures (T_N), if any, have been listed in the following Table:

TABLE : Néel Temperatures and Thermodynamic Properties
of $KN_{1-x}Zn_xF_3$ Compounds at $298.15^\circ K$

Compound	T_N °K	C_P^0 cal./mole.deg.	$S^0 - S_0^0$ cal./mole.deg.	$H^0 - H_0^0$ cal./mole	$-(F^0 - F_0^0)/T$ cal./mole.deg.
$KZnF_3$	-	27.58	37.08	5362	19.09
$KN_{0.49}Zn_{0.51}F_3$	-	27.43	36.27	5263	18.62
$KN_{0.69}Zn_{0.31}F_3$	190.0	27.45	36.88	5382	18.83
$KN_{0.85}Zn_{0.15}F_3$	239.2	27.46	36.62	5398	18.52

A P P E N D I X

PUBLISHED WORK OF THE AUTHOR NOT INCLUDED IN THIS THESIS

S.No.	Title of the publication	Reference
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6.	Imperfect Vapour Phase, Compressibility and Force Constants of Liquids	Ind. J. Chem., <u>2</u> , 27-8 (1964)
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