

# LOW TEMPERATURE HEAT CAPACITIES OF SINGLE CRYSTALS

Thesis for the Degree of M. S. MICHIGAN STATE UNIVERSITY George Ormsbee Taylor, Jr. 1960



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By

George Ormsbee Taylor, Jr.

AN ABSTRACT

Submitted to the School for Advanced Graduate Studies of Michigan State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Physics

Approved Hand Forta

### ABSTRACT

The heat capacity of several single crystals has been examined in the helium temperature range. The purpose of this study has been to locate anomalies which are characterized by a very rapid increase in the heat capacity just below the transition temperature with a sudden drop above this point. Such an anomaly is one of the distinguishing features of a paramagnetic-antiferromagnetic transition.

The anomaly is caused by a drastic change in the degree of ordering in the spins of the magnetic atoms. In the paramagnetic state the spins have a random alignment while in the antiferromagnetic state there exists an ordered antiparallel arrangement of the spins. This anomaly which is part of the magnetic heat capacity is superimposed upon the normal lattice heat capacity, but in the helium temperature region the lattice heat capacity is very small so that the anomaly may be observed.

Paramagnetic-antiferromagnetic transitions were found in five of the crystals examined. The magnetic entropy associated with these transitions was estimated and found to be in good agreement in each case with the theoretical value. The theory of antiferromagnetism by Van Vleck predicts that all the ordering should be of a long-range nature, but in the crystals examined short-range forces accounted for from 3 to 55 percent of the entropy gained during the transformation.

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#### INTRODUCTION

This paper presents work that has been done in measuring the heat capacities of single crystals at low temperatures. These studies were conducted to determine whether there existed an anomaly in the heat capacity of a crystal, particularly, a large peak of the shape which is associated with a paramagnetic-antiferromagnetic transition.

The presentation is divided into three parts. First, the theory is presented. In this chapter the importance of heat capacity is discussed, and a simple picture of an antiferromagnetic system is given including the thermodynamical significance of such a system. Next, follows consideration of the apparatus and of the experimental procedures. The third chapter gives the results of these experiments and the conclusions which can be drawn from them.

#### THEORY

Heat Capacity. The heat capacity of a substance is defined as the  $\lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T}$  where  $\Delta Q$  is the heat added to the sample and  $\Delta T$  is the corresponding temperature change. Actually in a thermodynamic system there are two heat capacities: one at constant pressure, denoted by  $C_p$ , and the other at constant volume, denoted by  $C_v$ . Starting from the first law of thermodynamics:

$$d\mathbf{Q} = d\mathbf{U} + \mathbf{P}d\mathbf{V} \tag{1}$$

where U is the internal energy of the system

P is the pressure

V is the volume

 $C_{p} = \left(\frac{dQ}{dT}\right)_{p} = \left(\frac{dU}{dT}\right)_{p} + \left(\frac{PdV}{dT}\right)_{p}$ while (2)

 $C_v = \left(\frac{dQ}{dT}\right)_v = \left(\frac{dU}{dT}\right)_v$ .

It can now be seen why the heat capacity at constant volume is the one of principal interest in solids. It is directly coupled with the internal energy of the system while  $C_p$  has a much more complicated connection with this energy. Unfortunately, however, it is much more difficult to measure  $C_v$ , but on the other hand  $C_p$  can be determined more easily.

An expression for the difference of these heat capacities can be reduced to the form [1],

$$C_{p} - C_{v} = \frac{TVB^{2}}{K}.$$
 (3)

Here B is the volume expansivity, and K is the isothermal compressibility.

In the helium temperature range this difference becomes negligible; hence, at these very low temperatures it is possible, in effect, to measure  $C_v$ . The measurement of heat capacity in these experiments therefore resolved itself into the determination of the dependence of the internal energy of the system on the temperature. (Let  $C_v$  now be denoted simply by C.)

Many effects may contribute to the internal energy of a system, but only three of these need be considered.

In the first instance, the internal energy of a solid is due in part to the lattice vibrations and at higher temperatures these vibrations completely dominate other effects which contribute to the heat capacity of the solid. Dulong and Petit derived the classical expression for the heat capacity which would be correct were the theorem of equipartition of energy applicable. Their law is now known to be the high temperature limit for a solid's heat capacity. Einstein took a major step forward in 1907 when he applied Planck's quantum theory to the problem by replacing the mean energy per oscillator, kT, by

$$u = \frac{h\nu}{\exp(h\nu/kT) - 1}$$
(4)

k is the Boltzman constant, v is the frequency of vibration of an oscillator, and h is Planck's constant. Einstein's theory fell short, however, because of a simplifying assumption which he made, viz., that the energy of an oscillator could be written as the energy of three harmonic oscillators each having the same frequency.

In 1912 Debye attacked the problem by considering the solid as an elastic continuum [2]. Much work has been done since then, but Debye's theory is still used as a basis for comparison. Therefore, owing to its importance, the essential elements of this theory will be presented. In a solid both longitudinal and transverse modes of vibration are possible, and each transverse mode must be considered as two independent modes at right angles to each other. The number of longitudinal modes per unit volume in an elastic continuum is given by

$$dn_1 = \frac{4\pi d\lambda}{\lambda^4}$$

where  $\lambda$  is the wave length.

Since there are two independent transverse modes,

$$dn_t = \frac{8\pi d\lambda}{\lambda^4}$$

The total number of modes per unit volume is  $dn = dn_1 + dn_t$ , and using the fact  $v = \mathbf{V}/\lambda$ ,

$$dn = 4\pi \left(\frac{1}{v_1^3} + \frac{2}{v_t^3}\right) v^2 dv$$
 (5)

where v is the velocity of the lattice waves.

Debye postulated that there exists a cut-off frequency. To calculate this frequency,  $\nu_{\rm m}$ , the total number of modes of vibrations was set equal to the number of degrees of freedom of all the atoms.

$$\int_{0}^{\nu_{m}} V dn = 3N_{0}$$

$$(4/3)\pi V \left[\frac{1}{v_{1}^{3}} + \frac{2}{v_{t}^{3}}\right] \nu_{m}^{3} = 3N_{0}$$
(6)

N<sub>0</sub> is Avogadro's number.

The energy associated with each oscillator was assumed given by equation (4), so the total energy was

$$U = \int_{\eta(0)}^{\eta(\nu_{m})} \frac{Vh\nu}{\exp(h\nu/kT) - 1} dn$$

$$U = 4\pi V \left[\frac{1}{v_{1}^{3}} + \frac{2}{v_{t}^{3}}\right] \int_{0}^{\nu_{m}} \frac{h\nu}{\exp(h\nu/kT) - 1} \nu^{2} d\nu.$$
(7)

Upon differentiating this expression with respect to T,

$$C = \frac{dU}{dT} = 9R \left(\frac{kT}{h\nu_{m}}\right)^{3} \int_{0}^{\frac{h\nu_{m}}{kT}} \frac{e^{x}x^{4}dx}{(e^{x}-1)^{2}}$$

$$C = 9R \left(T/\bigoplus_{D}\right)^{3} f\left(\bigoplus_{D}/T\right) \qquad (8)$$
Where  $x = h\nu/kT$ ,  $\bigoplus_{D} = h\nu_{m}/k$ , and
$$f\left(\bigoplus_{D}/T\right)$$
 is the Debye function.

At low temperatures the heat capacity reduces to the form

$$C = \frac{12 R \pi^4}{5} \left(\frac{T}{\Theta}\right)^3 = \text{const. } T^3$$
 (9)

The proportionality to  $T^3$  is a consequence of the fact that the number of vibrations per frequency interval is proportional to  $v^2 dv$ . At low temperatures only slow vibrations are of importance. This means that waves with very long wavelengths will be excited, and hence the propagation of such waves whose wavelengths are long compared to interatomic distances should not be affected by atomic arrangements; the Debye theory should therefore apply to these waves. At the same time the proportionality to  $v^2 dv$  deduced from elastic equations is known to be applicable at low frequencies. Consequently, the proportionality to  $T^3$ follows for bodies at low temperatures. This law is valid to approximately  $\bigoplus D/12$  [3]. In the helium temperature region the constant in Debye's expression is small, so other terms contributing to the total heat capacity cannot be neglected. If the solid shows no anomalous effects, a second contribution to heat capacity will be that due to the free electrons. This electronic term varies as T.

$$C_e = const. T.$$

So, the total heat capacity at low temperatures has the form

$$C = aT^3 + bT.$$
(10)

As will be seen later, the electronic contribution will be negligible, since the single crystals to be examined are insulators.

The crystals in part A of Table 1 show paramagnetic-antiferromagnetic transitions. Such transitions are accompanied by large peaks in the heat capacity at the Néel (transition) temperature. Figures 14-18 show the heat capacity curves exhibiting such transitions. The heat capacity in the antiferromagnetic region, i.e., below the Néel temperature,  $T_N$ , has not been expressed in a simple analytical form as some function of T. Above the Néel point, however, the heat capacity may be expressed as a function of T. This is due to Van Vleck who considered a system having magnetic dipole-dipole and simultaneously feeble exchange coupling [4]. The crystals in part A, Table I, are thought to represent such a system, and the experimental data obeys Van Vleck's equation.

Van Vleck derives this expression by considering the partition function, Z, from which the heat capacity is derived

$$\mathbf{C} = -\frac{\partial}{\partial \mathbf{T}} \quad (\mathbf{k}\mathbf{T}^2 - \frac{\partial \ln \mathbf{Z}}{\partial \mathbf{T}}) . \tag{11}$$

To write the partition function, Van Vleck uses the following form for the Hamiltonian,

$$H = \sum_{j \neq i} \frac{[\frac{\mu_{i} \cdot \mu_{j}}{r_{ij}^{3}} - \frac{3(\mu_{i} \cdot r_{ij})(\mu_{j} \cdot r_{ij})}{r_{ij}^{5}}] + V_{ij}$$
(12)

 $\mu_i$  is the magnetic moment of atom i.

 $\mathbf{r}_{ij}$  is the distance between atoms i and j.

The first term in expression (12) represents the dipole-dipole coupling between atoms i and j, and  $V_{ij}$  is the exchange energy,

$$V_{ij} = \text{const.} \left(\frac{\mu_{i} \cdot \mu_{j}}{r_{ij}^{3}}\right)$$
(13)

The constant in (13) contains  $r_{ij}^3$  so that  $V_{ij}$  depends only on the relative orientation of  $\mu_i$  and  $\mu_j$ , and hence is isotropic. (This effect will be discussed in greater detail on page 10.) The two types of interactions in (13) are physically quite different, but mathematically rather similar since both couple together the angular momentum vectors of different atoms.

The partition function is then,

$$Z = \sum_{\lambda} \exp\left(-\frac{W_{\lambda}}{kT}\right)$$
(14)

where W, the characteristic value of H, is summed over all energy states of the system.

Van Vleck develops this partition function, then using equation (11) obtains an expression for the heat capacity which at low temperatures is best represented by

$$C = \frac{\text{const.}}{T^2} . \tag{15}$$

Therefore, the heat capacity of crystals which have paramagneticantiferromagnetic transitions can be represented in the paramagnetic state by

$$C = aT^3 + b/T^2$$
. (16)

where the term  $b/T^2$  is the paramagnetic contribution.

Antiferromagnetism. The anomalies in Figures 14-18 have been described as representing a paramagnetic-antiferromagnetic transition. The essential features implied by these terms will now be discussed.

If the ions in a medium are far enough apart for their mutual interaction to be negligible, then the medium is considered to be a simple paramagnetic substance with an induced magnetic moment M per unit volume in the presence of a field H given by [5]

$$M = Njg \beta B_j \left(\frac{g \beta jH}{kT}\right)$$
(17)

where  $\beta$  is the Bohr magneton, N is the total number of magnetic ions per unit volume, j is the total quantum number, g is the Landé factor, and **B**<sub>j</sub> is the Brillouin function,

$$B_{j}(y) = \frac{2j+1}{2j} \operatorname{coth} \left[\frac{(2j+1)y}{2j}\right] - \frac{1}{2j} \operatorname{coth} \frac{y}{2j}.$$
 (18)

For y < < 1 equation (17) can be simplified and gives for the susceptibility

$$X = \frac{M}{H} = \frac{Ng^2 \beta^2 j(j+1)}{3kT} .$$
 (19)

This is the Curie law for paramagnetic substance. However, when there exists exchange effects between atoms, this equation for susceptibility is no longer valid.

The susceptibility is one of the distinguishing features of an antiferromagnetic medium. This property shows a well defined kink at the transition temperature when it is graphed against temperature. Figure 1 compares the susceptibility between paramagnetic, ferromagnetic, and antiferromagnetic systems. For an antiferromagnetic system above its transition temperature the susceptibility obeys the relation

$$X = \frac{C}{T + \theta}$$
(20)



Figure 1. Susceptibility Curves

where  $C = N \beta^2 g^2 j$  (j + 1) is the Curie constant. The quantity  $\theta$  indicates the net effect of the internal fields in aiding or hindering an applied magnetic field to produce alignment [6]. The difference  $X_{11} - X_{1}$  is essentially due to the anisotropy energy, i.e., the excess energy needed to magnetize the crystal to saturation in a hard direction.

An antiferromagnetic medium can be defined as a system in which there exists very strong exchange coupling favoring antiparallel alignment of the electron spins. A ferromagnetic substance is just the opposite to this in that it is a medium in which strong exchange coupling favors parallel alignment of the electronic spins.

This exchange coupling is strictly a quantum mechanical phenomenon with no classical analogue. It concerns the degeneracy associated with the possibility of electrons trading places.

In antiferromagnetic interactions it proves useful to divide the lattice of magnetic atoms into sublattices, to account for the various types of magnetic ordering [6]. The method of subdivision depends upon the symmetry of the specific lattice, but there should be at least division into enough sublattices so that a given atom has neither first or second nearest neighbors on its own sublattices and only one kind of neighbor on any other lattice. Consider, as did Van Vleck in his original treatment of the problem [7], a crystal divided into only two interpenetrating sublattices A and B such that all nearest neighbors of an atom on sublattice A lie on sublattice B. This condition is satisfied for s.c. and b.c.c. lattices but not by f.c.c. lattices.

The exchange interactions are equivalent to an interatomic potential

$$V_{ij} = -1/2 J(1 + 4 \sigma_i \cdot \sigma_j)$$
 (21)

where  $\sigma_i$  and  $\sigma_j$  are the spin vectors of atoms i and j measured in units of Th and J is the exchange integral. J is negative for an antiferromagnetic system. Actually equation (21) is an operator equation, and  $\sigma_i$  and  $\subset_j$  should be considered as operators. It is a good first approximation, however, to consider these spins simply as vectors. The atoms are in effectively an S state with a common exchange integral J. Since the quantum number j now represents only the spin quantum number, let it be denoted as s.

The effective potential acting on an atom i is to a good approximation

$$V_{i} = -2|J| \sigma_{i} \Sigma_{j} \sigma_{j} = -2z|J| \sigma_{i} \overline{\sigma_{j}}.$$
 (22)

The summation which extends over the z nearest neighbors of atom i may be replaced by z multiplied by the mean value of the spin of any neighbor of atom i. These neighbors have the same alignment on the average and there is a common exchange integral J.

At thermal equilibrium the mean average of the spins of atoms on sublattices A and B will have the same value. Also, in the absence of an applied field it may be supposed that this mean average has an opposite direction for the two sublattices. If a field is applied, it will give a displacement  $\delta \sigma_i$  and  $\delta \sigma_j$  to the spins of atoms i and j. It is possible to take  $\delta \sigma_i = \delta \sigma_j = \delta \sigma$  since for small fields the susceptibility is the same even when the external field is rotated 180° with respect to the internal field. Hence,

$$\overline{\tau}_{i} = \tau_{0} + \delta \sigma; \quad \overline{\tau}_{j} = -\tau_{0} + \delta \tau. \quad (23)$$

An atom i will experience, besides the exchange potential, an energy  $-g\beta H \cdot \sigma_i$  due to the applied field H. The effective field acting on atom i then becomes

$$H_{eff} = H + \frac{2|J| z (- \sigma_0 + \delta \sigma)}{g\beta}$$

$$H_{eff} = H - \frac{2|J| z \sigma_0}{g\beta} + \frac{2|J| zM}{Ng^2\beta^2}$$
(24)

where

$$M = 1/2 Ng β (σi + σj) = Ng β c σ.$$
 (25)

M is the magnetic moment per unit volume.

Applying equations (17) and (24) to the two sublattices separately, the variation of  $\sigma_0$  with temperature may be obtained.

$$| \subset_0 + \mathcal{O} | = sB_s \left(\frac{sg \beta H_{eff}}{kT}\right)$$
 (26)

If the applied field is set equal to zero, then

$$|\tau_0| \simeq sB_s \left(\frac{2zs|J|\sigma_0}{kT}\right)$$

The value of  $\frac{|\mathcal{T}_0|}{s}$  approaches s as  $T \longrightarrow 0$ , but this value falls to zero at  $T = T_N$ . The conclusion from this is that above the transition temperature there is no exchange interaction, while below this temperature the exchange potential increases in strength until at T = 0 the spins of the individual atom are completely aligned in parallel or antiparallel directions. A graph of this is shown in Figure 2.

For small values of the argument, y,

$$sB_s(y_0) = 1/3(s + 1) y_0$$

where

$$y_0 = \frac{2zs|J|\sigma_0}{kT}.$$

So,

$$T_{N} = \frac{2|J|zs(s+1)}{3k} .$$
 (27)



Figure 2. Variation of |  $\sigma_0$  |/S With T/ $\dot{T}_N$ 



Figure 3. Magnetic Heat Capacity

The transition temperature thus depends upon the magnetic structure below this temperature and it can be considered as essentially a measure of the energy necessary to bring the system from a state of perfect order to one where the long-range order is destroyed.

The magnetic internal energy may now be expressed as

$$\mathbf{U} = -\mathbf{N}\mathbf{z}|\mathbf{J}| \quad \mathbf{\sigma_0}^2 \tag{28}$$

and the magnetic heat capacity as

$$C = \frac{dU}{dT} = -2Nz|J| \sigma_0 \frac{d|\sigma_0|}{dT}.$$
 (29)

A graph of this heat capacity is shown in Figure 3.

<u>Comparison of Antiferromagnetic Model with Experiment</u>. Compare Figure 3 with the graphs drawn from experimental data in Figures 14-18. This comparison may be made directly, for the lattice heat capacity contributes only a very small percent to the total heat capacity in this low temperature region. It can be seen that they have a strong resemblance, but the experimental plots exhibit a tail above  $T_N$  while the heat capacity falls directly to zero in Figure 3. This difference is due to short-range ordering, an effect which was ignored in the theory of Van Vleck which was presented. This short-range ordering is the tendency for the spins of the nearest neighbor's of an atom to remain aligned in antiparallel positions even above the transition temperature. Van Vleck considers only long-range ordering; i.e., the tendency for atoms on the same sublattice to have their spins aligned on the average in the same direction. This ordering vanishes at  $T_N$ . (See Figure 2.)

At absolute zero there will be perfect long-range order and perfect short-range order. Suppose that the spins of the atoms on sublattice A point in a north direction, and the spins of the atoms on sublattice B point south. At a finite temperature below  $T_N$  there will be a certain number of atoms on sublattice A whose spins do not point north. This makes it energetically easier for atoms on sublattice B which are nearest neighbors to these "bad" atoms on sublattice A not to have their spins aligned and pointed in a southerly direction. As the temperature increases, the thermal energy of the atoms will increase, and it will become less difficult for long-range disorder to increase. This effect will avalanche and lead finally to complete and abrupt disappearance of long-range order at the critical temperature. This increasing disorder requires energy, thus producing a steep rise in the heat capacity curve just below  $T_N$ . This manner of increasing disorder is an example of what is known as a cooperative phenomenon.

Increasing energy requires a rise in the heat capacity curve because the area under this curve represents the magnetic internal energy of the system. This is the energy required to take the system from a state of complete magnetic order,  $T < T_N$ , to a state of complete magnetic disorder,  $T > T_N$ .

A quantity of considerable interest is the entropy. This gives a measure of the disorder of the system, increasing entropy corresponding to increasing randomness of the internal motion of a system. Mathematically, entropy enters thermodynamics by the second law, dQ = TdS. A useful relation will new be obtained.

$$\frac{TdS}{dT} = \frac{dQ}{dT} = C$$

$$dS = \frac{C}{T} dT$$

$$S = \int \frac{C}{T} dT$$
(30)

So, it is possible to calculate the entropy having measured the heat capacity. The manner of evaluating this integral is discussed on page 44.

Statistical mechanics shows that the entropy of a paramagnetic system at low temperatures and in the absence of any magnetic fields is given by

$$S = R \ln(2s + 1)$$
 [8]. (31)

Therefore, it is possible to compare a measured entropy with this theoretical value. By determining the entropy gained above and below the Néel point it is also possible to determine the amount of order remaining in a crystal above the Néel point.

Phase Transition. A paramagnetic-antiferromagnetic transition may be a second-order phase transformation; i.e., a transition occurring between two crystal modifications [9]. If this transition is indeed second-order, then one would expect an infinity in the specific heat at the Néel temperature, as is the case in the Helium I-Helium II transition. The symmetry of the body undergoes a sudden change at the transition point, and at any moment it can be said to which of the two phases the crystal belongs. At a first-order transition point the two phases of the body are in equilibrium while at a second-order transition point the two phases are identical. A change of symmetry by means of a second-order phase transformation has the property that the symmetry of one of the phases is higher than that of the other. The functions of the thermodynamic state of the body (entropy, energy, etc.) remain continuous as the transition point is passed, but derivatives of the thermodynamic quantities are discontinuous. Also there is no latent heat associated with a second-order transformation.

The heat capacity of single crystals at low temperatures is seen to be the study of the dependence of internal energy upon temperature. In the antiferromagnetic state the dominating force is the exchange interaction. Above the transition temperature this exchange interaction still persists in what is known as short-range ordering. The total effect of this short-range ordering can be determined by measuring the entropy gain above and below the critical temperature. The magnetic internal energy of this antiferromagnetic ordering process is represented by the area under the heat capacity curve.

#### APPARATUS AND EXPERIMENTAL PROCEDURES

<u>Apparatus.</u> The crystals which have been examined for paramagnetic-antiferromagnetic transitions are listed in Table I. All of these were grown at room temperature from aqueous solutions except for the minerals, azurite and dioptase. All of the single crystals were examined in the helium temperature range. The heat capacity studies indicated paramagnetic-antiferromagnetic transitions in five of these crystals.

The experiments were conducted in a double Dewar system. This is a Pyrex glass system and is shown in Figure 4. The inner Dewar which contains the liquid helium is a double wall construction with the intervening space evacuated. This space must be periodically re-evacuated, because helium gas will diffuse through Pyrex and thus introduce a path of heat flow into the helium bath. The outer jacket is filled with liquid air. The outside of this jacket is silver coated except for two narrow slits on each side which extend the entire length of the Dewar. This slit is used to observe the helium level and to align the apparatus.

To measure the heat capacity of a sample, two things are necessary: first, there must be a means for measuring the exact temperature of the crystal; and second, there must be a mechanism whereby known amounts of power can be added to the sample. The thermometers used in these experiments were Allen-Bradley 1/10-watt carbon resistors [14]. They have a room temperature resistance of approximately 56 ohms. This resistance increases to approximately 80 ohms at liquid air temperature (roughly  $80^{\circ}$ K), is approximately 500 ohms at the boiling point of helium (4.2°K) and increases to 10,000

TABLE I

	Crystals	Crystalline Form	т <sub>N</sub> ( <sup>о</sup> к)	Color
А.	Cu <sub>3</sub> (CO <sub>3</sub> ) <sub>2</sub> . (OH) <sub>2</sub> [10] (Azurite)	Monoclinic	1.84	Blue
	$NiBr_2 \cdot 6H_2O[11]$	Monoclinic	6.50	Green
	CoBr <sub>2</sub> .6H <sub>2</sub> O [12]	Monoclinic	3.07	<b>R</b> ed-violet
	MnCl <sub>2</sub> • 4H <sub>2</sub> O [13]	Monoclinic	1.60	Rose
	MnBr <sub>2</sub> ·4H <sub>2</sub> O	Monoclinic	2.12	Rose-red
в.	MnSO4 · 4H2O	Monoclinic		Pink
	$Ni(NO_3)_2 \cdot 6H_2O$	Monoclinic		Green
c.	H2O•CuO•SiO2 (Dioptase)	Trigonal		Green
	Co <b>SO</b> 4.7H2O	Monoclinic		Red



Figure 4. Double Dewar System

to 15,000 ohms as the temperature is lowered toward 1<sup>°</sup>K. For each experiment these thermometers were calibrated over the entire temperature range covered.

A thermometer was mounted in a sample by placing the resistor in a small hole drilled in the crystal and gluing it in place with a small amount of Glyptal (GE 1202 varnish).

A heater of manganin wire (approximately 400 ohms) was used for each sample. This was wound onto the surface of the crystal and also glued in place with Glyptal. The heater wire (as well as the thermometer) was soldered to Teflon insulated leads which were used to make the electrical connections to the measuring circuits external to the calorimeter system.

The thermometer and heater leads on the sample were brought out of the calorimeter through tungsten-glass seals. The Teflon insulated wires were soldered to the tungsten-glass seal on the outside of the can (see Figure 5) and were then connected to the external circuit outside the Dewar. The electrical leads were handled in this manner so that they would pass through the helium bath, thus greatly reducing any heat leaks which might occur along the wires. Both ends of the tungsten were tipped with silver solder. This served a two-fold purpose: first, to prevent any flow of superfluid along the wire, and second, to make possible quick attachment and removal of samples.

Some crystals reacted upon exposure to the atmospheric conditions in the laboratory. To prevent such action the surfaces of the samples were coated lightly with Glyptal, thus insuring that the crystals would not change their water content during preparatory stages of the experiment.

The calorimeter is diagramed in Figure 5 [10]. Actually two different calorimeters have been used in these measurements which have extended over a period of one and a half years. The second calorimeter is almost a duplicate of the first with the exception of a few small



Figure 5. Calorimeter

refinements. These refinements were: increasing the thickness of the top plate, enlarging the screws which held the can to the rest of the assembly, and inclusion of a second radiation shield. Pictures of the assembly are shown in Figures 6 and 7.

Two radiation shields are shown in the picture, Figure 6. One of these was rigidly attached to the bottom of the pumping line. The other shield fitted around the sample and was held in place by two small screws. It was not possible to use this shield if the crystal was larger than approximately one-half inch in diameter.

The calorimeter can was attached to the rest of the apparatus with eight No. 8 x 32 screws. The vacuum was sealed with a lead "0"-ring [15] which seated in a small groove in the upper plate. This arrangement worked very well, and there have been no helium leaks when this "0"-ring was properly seated.

The pumping system used to evacuate the calorimeter is shown in Figure 8. An N. R. C. ionization gauge fastened in the pumping line at the top of the Dewar (see Picture, Figure 7), has been used to measure the vacuum. Vacuums of the order of  $10^{-5}$  mm of Hg have been recorded, but it has been suggested that the actual vacuum in the calorimeter might be several orders of magnitude greater than this, due possibly to helium being driven off the sample and subsequent adsorption by the calorimeter walls [16].

During the course of an experimental run, three D. C. circuits were used. One of these gave the temperature of the sample (Figure 9). This was actually done by measuring the potential drop across the carbon thermometer with a Leeds and Northrup type K-2 potentiometer. Since the resistance of the thermometer changes continuously as the temperature changes, the unbalance in the potentiometer was amplified by a Leeds and Northrup microvolt amplifier and recorded on a Leeds and Northrup Speedomax recorder.



Second Radiation Shield Added to Top Plate



Top Plate of Calorimeter



Figure 7

Calorimeter Can Fitted to Top Plate






Figure 9. Thermometer Circuit

Since there is considerable change in the resistance of the thermometer during an experiment, the recorder was calibrated against this range of resistance to determine its sensitivity. This is shown graphically in Figure 10 where the resistance is plotted against the voltage change per large division of recorder paper. (A typical recorder chart is shown in Figure 11.) When the thermometer's resistance is approximately 16,000 ohms, (corresponding to roughly  $1.3^{\circ}$ K) potential changes of 2.1 x  $10^{-5}$  volts could be detected. This changes linearly until at about 500 ohms (roughly  $4.0^{\circ}$ K) a potential drop of  $0.3 \times 10^{-5}$  volts could be observed. These numbers might lead to the conclusion that it was possible to determine the temperature more accurately as the thermometer's temperature increased. This would be incorrect, for the resistance of the thermometer does not vary linearly with temperature, but this resistance changes extremely rapidly at the very low temperatures.

The current in the thermometer circuit was determined by reading a Weston microammeter. During an experiment the current might vary from 8.5 to 11.0 microamperes, as the thermometer resistance changed.

Another very important circuit was that for the heater. This is shown diagrammatically in Figure 12, and it can be seen to be very similar in principle to the thermometer circuit. Both the current through and the voltage drop across the heater were measured with a Leeds and Northrup type K-1 potentiometer, the current being measured by measuring the voltage drop across a 100 ohm standard resistance. The current was measured to  $\pm 0.5$  microamperes, while the voltage was increased to  $\pm 0.1$  mv. Energy supplied to the samples varied depending on the characteristics of the individual crystals, but it was generally in the millijoule region. The time interval was measured manually with a stop watch, the  $\Delta$ t varying from a few seconds to more than a minute.





Figure 11. Chart of Experimental Points

30



Figure 12. Heater Circuit

An automatic stop clock had been connected in the circuit, but it was found that this electric timer set up a signal which was detected on the Speedomax recorder. Therefore, this device could not be used; at the same time, sufficient accuracy could be obtained by the use of the manual stop watch. This measurement was made to  $\pm 0.1$  sec.

The third circuit used was for controlling the temperature of the helium bath below the  $\lambda$ -point during the calibration [17]. This consisted of a Wheatstone bridge arrangement, one arm of which was a carbon resistor in the bath. A constant bath temperature could easily be maintained by adding heat, via a heater circuit in the bath, or by adjusting the pumping speed on the helium bath and by observing the deflection of the bridge galvanometer. By this technique temperatures could be maintained constant to  $0.001^{\circ}$ K.

This was the equipment used in these studies. Another description of the entire apparatus can be found in reference 10.

Experimental Procedures. The measurement of the heat capacity of a sample at low temperatures usually averages about 10 or 12 hours to complete. The steps taken in each experiment were very distinct and have been listed in Table II. Some of these steps are self-explanatory.

Roughly 1 mm of Hg of exchange gas (helium) was added to the calorimeter. This gas was introduced so that good thermal contact would exist between the sample and the helium bath. Equilibrium conditions could be achieved within a few minutes after the temperature of the bath was under control.

Calibrating the sample required recording the thermometer's resistance and the bath's temperature at a number of different points covering the entire temperature range that was to be studied. At each point the thermometer and helium bath had to be in an equilibrium state. This calibration actually consisted of two phases: one was the

## TABLE II

## STEPS IN AN EXPERIMENTAL RUN

- 1. Connect sample in calorimeter.
- 2. Place calorimeter in Dewar.
- 3. Add helium exchange gas to calorimeter.
- 4. Precool apparatus with liquid air.
- 5. Transfer liquid helium.
- 6. Calibrate thermometer in sample.
- 7. Evacuate calorimeter.
- 8. Add heat to sample and observe temperature change.

temperature region from the boiling point of helium (4.21°K at 76.0 cm of Hg) to the  $\lambda$ -point (2.17°K at 3.79 cm of Hg), the other was the region below the  $\lambda$ -point to the lower temperature limit of the apparatus. The bath temperature was controlled above the  $\lambda$ -point by adjusting the pumping speed on the bath; the vapor pressure of the bath was determined with a Hg manometer. Below the  $\lambda$ -point the temperature was controlled by a slightly different method [17]. In this region the vapor pressure was determined with an oil manometer, the density of this oil being 1/13.84 that of Hg. A T<sub>55E</sub> helium vapor pressure scale [18] converted this data to temperatures.

A graph of log R vs (1/T) was made for each experiment. (See Figure 13.) This is a linear relation except for a break at approximately the  $\lambda$ -point. This plot was subsequently used to determine the crystal's temperature.

When the calibration was completed, the calorimeter was evacuated to approximate adiabatic conditions. Some heat leaks into the sample still occurred. The parameters of the system were adjusted until this leak was small and of constant magnitude. Then the heater circuit was actuated for a short period and the input power recorded.

To compensate for the heat leak during a heating cycle, the before and after drifts were extrapolated to the mid-point of the heating curve. The fore drift was always begun on the reference line so that with the aid of the recorder calibration (Figure 10), the potential, and thus resistance, of these two points could be determined. With this information two temperatures were found; then the  $\Delta$  T and the average temperature at which the heat capacity was measured were obtained. On the average of 50 to 60 points per experiment were taken in exactly this manner.

By using the equation,

$$C = \frac{VIt}{T_{f} - T_{i}}$$
(32)



Figure 13. Log Resistance versus Temperature<sup>-1</sup>

where

V is the potential drop across the heater,

I is the current through the heater,

t is the time of heating,

- T<sub>i</sub> is the initial temperature (before the heater circuit is turned on), and
- $T_{f}$  is the final temperature (after heater circuit is turned off).

The heat capacity is obtained at the average temperature

$$\frac{T_{f} + T_{i}}{2}$$

Corrections to the heat capacity (thermometer, heater, and Glyptal) were small and usually amounted to less than 0.5% of the total measured heat capacity.

It is now seen how the requirements (page 18) necessary to measure heat capacity were met. The Speedomax recorder gave a continuous account of the sample's temperature while from the heater circuit one could determine the power input to the system.

## **RESULTS AND CONCLUSIONS**

The heat capacities of the crystals that have been examined were calculated with equation (32). This experimental data is listed in the Appendix; the temperature which is listed with each value of heat capacity is the average temperature at which that value was calculated. Heat capacity versus temperature graphs are shown in Figures 14-19. The accuracy of the points was approximately 2.5%. By observing these graphs the crystals were divided into three groups: (A) those crystals which exhibited a paramagnetic-antiferromagnetic transition, (B) crystals which did not exhibit such a transition, and (C) crystals for which there is not sufficient reliable data to determine whether there exists a transition. The statements concerning the existence or non-existence of a transformation are made relative only to the temperature region studied.

Crystals Having Paramagnetic-Antiferromagnetic Transitions. The heat capacity of these crystals was drawn such that it has a finite value at the Néel temperature. However, if this point represents a second-order transition as was speculated on page 16, the heat capacity might become infinite but should show a discontinuity. To establish definitely whether or not this peak represents a second-order transformation, it would be necessary to examine the heat capacity in the region of the Néel point much more closely to determine if there exists a logarithmic singularity at this transition temperature.

Two of the crystals which exhibited paramagnetic-antiferromagnetic transitions,  $MnCl_2 \cdot 4H_2O$  and  $MnBr_2 \cdot 4H_2O$ , had been previously studied [19, 20]. This earlier work had been done upon samples consisting of a great number of small crystals, or what was effectively a powder measurement. This work on single crystals agreed, within the experimental error, with the experiments on powders.



Heat Capacity (cal. /mole. deg.)





Heat Capacity (cal. /mole·deg.)



4.5

41









Heat Capacity (cal./mole·deg.)

Table III lists the Néel temperatures of a number of samples which exhibit paramagnetic-antiferromagnetic transitions. This table is not intended to be complete, but it is sufficient to illustrate some rather general characteristics of these transformations. Observe the hydrated salts of nickel, cobalt, and manganese. It appears that the transition temperature for the nickel salts is higher than that for the cobalt salts which in turn is higher than that for the manganese salts.

Another characteristic which can be observed from Table III is that the Néel temperature decreases as the number of waters of hydration in a sample is increased (note for the case of manganese and nickel). An increase in the waters of hydration in a sample increases the magnetic dilution of the crystal and hence tends to lower the temperature at which antiparallel spin alignment can occur.

The magnetic entropy gained in paramegnetic-antiferromagnetic transition is of great interest. This has been measured experimentally and is compared with its theoretical value,  $R \ln(2s + 1)$ . Also, the entropy has been separated into that gained below and above the Néel temperature, and from this the net effect of the short-range ordering is estimated.

The experimental value of the entropy is computed by using equation (30). This expression presents the task of integrating the heat capacity, divided by the temperature, over the entire temperature range.

Above the Néel point it is possible to represent the heat capacity by an expression of the form

$$C = aT^3 + \frac{b}{T^2} \qquad (16)$$

It should be remembered that in applying this formula two assumptions are made: one, that the heat capacity due to lattice vibrations follows a  $T^3$  law; and two, the magnetic heat capacity can be represented by a term of the form  $b/T^2$ . To calculate the constants a and b in equation

TABLE III

Sample	т <sub>N</sub> ( <sup>о</sup> к)
MnBr <sub>2</sub> .4H <sub>2</sub> O	2.12
MnCl <sub>2</sub> ·4H <sub>2</sub> O	1.60
MnCl <sub>2</sub> [21]	1.81 and 1.96
CoBr <sub>2</sub> .6H <sub>2</sub> O	3.07
CoCl <sub>2</sub> .6H <sub>2</sub> O [22]	2.29
NiBr <sub>2</sub> .6H <sub>2</sub> O	6.50
NiCl <sub>2</sub> .6H <sub>2</sub> O [22]	5.34
NiCl <sub>2</sub> [23]	53.0
CuCl <sub>2</sub> · 2H <sub>2</sub> O [24]	4.31
Cu <sub>3</sub> (CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>	1.84

(16), CT<sup>2</sup> versus T<sup>5</sup> must be plotted. If this equation is valid, the experimental points will fall on a straight line, and a and b may be determined from this graph. Such a graph is shown for azurite in Figure 20. Notice that as the Néel temperature is approached, the curve deviates from linearity. This furnishes another very important fact;
i. e., the exact temperature at which equation (16) is no longer applicable. Therefore, the magnetic entropy gained in the paramagnetic state can be calculated by evaluating the integral

$$\int_{T_1}^{\infty} \frac{b}{T^3} dT.$$

 $T_1$  represents the temperature at which the experimental points deviate from a straight line. Only a very small error is introduced by extending the upper limit to  $\infty$ , since the integrand decreases as  $1/T^3$ . The constant b and the temperature  $T_1$  are presented for the crystals with paramagnetic-antiferromagnetic transitions in Table IV.

Below  $T_1$  the heat capacity cannot be represented as a simple function of T. To calculate the entropy in this region, C/T versus T is graphed and the curve is extrapolated to  $0^{\circ}$ K. This graph for azurite is shown in Figure 21. The area under the curve is measured graphically; it represents the entropy gained in this temperature region. The lattice heat capacity here is negligible, within the limit of experimental error; hence, the entropy gain in this region due to the thermal motion of the lattice may be ignored. Thus, the entropy measured graphically may be considered as entirely due to the increasing magnetic disorder.

The total magnetic entropy increase during a paramagnetic-antiferromagnetic transition is obtained by adding the entropy measured above and below  $T_1$ . The experimental values for the entropy are listed along with the theoretical values in Table IV. It can be seen that these values compare very well.









Crystal	S <sub>exp</sub> . (Cal/Mole·Deg)	Ca (Ca	theory 1/Mole•Deg)	Ø	above Néel Point
Azurite	1.17		1.38	1/2	35
ViBr <sub>2</sub> ·6H <sub>2</sub> O	2.30		2.19	I	55
CoBr2. 6H2O	1.42		1.38	1/2	38
AnCl <sub>2</sub> ·4H <sub>2</sub> O	3.50		3.55	5/2	9
AnBr <sub>2</sub> • 4H <sub>2</sub> O	3.69		3.55	5/2	3.3
Crystal	b (Cal·Mole <sup>-1</sup> ·Deg)	Tı	S <sub>below</sub> Néel	Sabove Néel	S <sub>exp</sub> .
Azurite	3.70	2.08	0.74	0.43	1.17
ViBr2·6H2O	139	7.36	1.02	1.28	2.30
CoBr2. 6H2O	11.0	3.20	0.88	0.54	1.42
AnCl <sub>2</sub> · 4H <sub>2</sub> O	1.92	2.17	3.30	0.20	3.50
AnBr <sub>2</sub> • 4H <sub>2</sub> O	2.50	3.30	3.57	0.12	3.69

49

Also in Table IV are listed the approximate percent of entropy due to the short-range ordering. This percentage is the fraction of entropy gained above  $T_1$  to the total value. The entropy due to this ordering is much smaller for the Mn salts than for the other crystals examined. This indicates that the antiferromagnetic ordering in Mn salts is due primarily to the long-range ordering forces. Notice the strong similarity between the heat capacity curves for  $MnBr_2 \cdot 4H_2O$  and  $MnCl_2 \cdot 4H_2O$ , Figures 17 and 18, with the heat capacity curve predicted by Van Vleck's model, Figure 3.

The other crystals in this group gain a considerable percentage of their entropy above the Néel temperature. This indicates a rather slow diminishing of the short-range ordering forces, an effect which was not considered in the theory of Van Vleck. Corroborating evidence for the existence of the antiferromagnetic state in these crystals has been supplied by the proton resonance work of R. D. Spence [11, 12, 25, 26], and in the case of  $CoBr_2 \cdot 6H_2O$  and azurite further evidence has been supplied by the magnetic susceptibility work of M. Garber [27, 28].

<u>Crystals Without Transitions</u>. These are examples of crystals which do not show a paramagnetic-antiferromagnetic transiton in the helium temperature range. The heat capacity curves are shown in Figure 19.

The heat capacity of these crystals can probably be represented by

$$C = aT + bT^3.$$

The first term represents the electronic contribution to the heat capacity while the second term is for the lattice vibrations. However, the general shape of the curve for  $MnSO_4 \cdot 4H_2O$  appears to be very similar to the part of the graphs, in the paramagnetic state, for those crystals of group A. There is consequently, some slight evidence that this crystal may show some magnetic ordering below  $1.3^{\circ}K$ . <u>Crystals in Group C</u>. Due to experimental difficulties it has not been possible to measure the heat capacity for these crystals. The difficulties center in the fact that it has been impossible to achieve a temperature change in the sample by adding heat. Upon accentuating the heater circuit, heat is observed to flow into the crystal, but this will immediately flow out of the crystal when the circuit is turned off. This phenomenon occurs even though there appears to be a good insulating vacuum in the calorimeter. The procedures followed in this work were exactly the same as those outlined in Table II. Whether this is due to a very large heat capacity, a thermal conductivity phenomenon, or some other factor is yet to be determined. Further work needs to be done on these crystals.

The studies which have been done on the heat capacity of a number of single crystals has now been presented. This property shows anomolous peaks in five of the crystals, and these peaks have been explained as representing paramagnetic-antiferromagnetic transitions. The entropy gained through the transformation was found to compare very favorably with the theoretical value of the entropy for each crystal. Also, it was found that the short-range ordering contributed to the entropy, the amount of this contribution varying from 3 to 55 percent. Van Vleck's model does not take into account any short-range ordering.

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APPENDIX

		March 10, 1959	
T		T	C
(~K)	(Cal/Mole Deg.)	(°K)	(Cal/Mole Deg.)
1.717	1.11	1.950	1.85
1.763	1.18	1.997	1.49
1.782	1.21	2.081	1.08
1.799	1.42	2.137	0.92
1.802	1.39	2.198	0.94
1.814	1.57	2.357	0.87
1.818	1.50	2.413	0.80
1.831	1.74	2.541	0.84
1.844	3.93	2.611	0.83
1.852	3.33	2.775	0.75
1.876	2.49	3.018	0.84
1.914	2.18	3.625	0.61
	Ni	iBr <sub>2</sub> ·6H <sub>2</sub> O	
		Mar	ch 28, 1959
4.150	0.45	6.234	3.60
4.905	1.16	6.366	2.94
5.260	1.00	6.530	5.88
5.531	1.17	7.357	2.13

8.619

9.595

13.295

1.94

1.55

0.95

1.65

2.58

2.06

5.735

5.944

6.092

AZURITE

 $CoBr_2 \cdot 6H_2O$ 

June 4, 1959

T	С	T	С
(°K)	(Cal/Mole·Deg)	( <sup>0</sup> K)	(Cal/Mole·Deg)
1.649	0.29	2.700	1.08
1.660	0.27	2.745	1.15
1.677	0.39	2.786	1.93
1.682	0.27	2.831	1.97
1.694	0.27	2.878	2.74
1.713	0.27	2.947	2.47
1.722	0.41	3.012	2.79
1.795	0.45	3.071	3.35
1.892	0.45	3.138	1.87
1.931	0.43	3.204	1.39
1.948	0.47	3.275	1.14
2.010	0.58	3.356	1.24
2.090	0.59	3.436	1.14
2.242	0.68	3.526	0.99
2.267	0.73	3.613	1.07
2.407	0.72	3.909	1.01
2.477	0.84	4.103	0.78
2.520	0.87	4.425	0.84
2.561	0.97	5.066	0.57
2.645	0.98		

		I	December 3, 1959
Ŧ	С	$\overline{\mathrm{T}}$	С
(°K)	(Cal/Mole•Deg)	( <sup>0</sup> K)	(Cal/Mole•Deg)
1.170	3.44	1.472	5.49
1.175	3.49	1.490	5.65
1.180	3.52	1.503	5.75
1.193	3.70	1.515	6.32
1,198	3.28	1.533	6.52
1.204	3.13	1.549	6.99
1.208	3.43	1.567	7.03
1.212	3.77	1.582	7.14
1.221	3.95	1.598	8.15
1.230	3.76	1.653	1.73
1.240	3.81	1.671	1.53
1.244	3.75	1.688	1.34
1.253	3.66	1.708	1.24
1.274	3.83	1.728	1.10
1.279	3.84	1.746	1.20
1.293	4.02	1.808	0.96
1.307	4.64	1.829	0.86
1.341	4.33	1.853	0.78
1.353	4.68	1.881	0.67
1.360	4.70	1.904	0.75
1.383	4.76	1.932	0.67
1.403	4.44	1,959	0.63
1.439	5.52	1.991	0.60
1.453	5.36	2.052	0.60

MnCl<sub>2</sub>·4H<sub>2</sub>O

Ŧ	С	Ŧ	С
( <sup>0</sup> K)	(Cal/Mole · Deg)	(°K)	(Cal/Mole. Deg)
2.138	0.45	3.500	0.16
2.167	0.39	3.681	0.18
2.302	0.39	3.806	0.18
2.363	0.35	3.951	0.16
2.542	0.36	4.083	0.20
2.747	0.28	4.257	0.14
3.402	0.18	4.426	0.23
		MnBr <sub>2</sub> .4H <sub>2</sub> O	
		Mar	ch 18, 1960
1.455	3.05	1.584	3.60
1.466	3.16	1.595	3.38
1.474	3.37	1.606	4.27
1.480	3.41	1.618	4.05
1.490	3.02	1.633	3.81
1.498	2.90	1.644	3.93
1.504	3.16	1.676	4.13
1.513	3.18	1.695	4.19
1.524	3.65	1.728	4.16
1.532	3.50	1.749	4.16
1.538	3.50	1.772	4.13
1.548	3.29	1.800	4.93
1.560	3.58	1.850	4.56
1.572	3.72	1.869	4.35

(Cont'd)

Ŧ  $\overline{\mathbf{T}}$ С С (Cal/Mole.Deg) (°K) (Cal/Mole.Deg) (°K) 4.86 1.892 2.371 1.34 1.919 4.65 2.417 1.17 6.42 1.997 2.488 1.07 2.031 6.17 2.539 0.89 2.052 6.95 0.91 2.588 2.072 7.33 2.707 0.85 2.095 8.89 2.796 0.70 2.113 12.71 3.023 0.74 2.129 3.12 3.588 0.34 2.156 2.21 3.673 0.35 2.191 1.69 3.808 0.37 2.290 1.67 3.903 0.35 2.328 1.56

 $Ni(NO_3)_2 \cdot 6H_2O$ 

		Jar	nuary 28, 1960
<del>Т</del> (°К)	C (Cal/Mole•Deg)	Т ( <sup>0</sup> К)	C (Cal/Mole•Deg)
1.376	1.30	1.743	1.16
1.392	1.12	1.759	1.16
1.400	1.17	1.773	1.37
1.464	1.33	1.789	1.26
1.485	1.25	1.809	1.16
1.502	1.27	1.832	1.24
1.513	1.16	1.861	1.04
1.521	1.25	1.889	1.13
1.534	1.18	1,917	1.09
1.546	1.22	1.944	1.42
1.557	1.16	1.978	1.41
1.568	1.18	2.001	1.39
1.577	1.09	2.028	1.36
1.584	1.13	2.063	1.23
1.600	1.38	2.116	1.32
1.614	1.36	2,160	1.20
1.627	1.31	2.203	1.23
1.638	1.31	2.243	1.35
1.653	1.24	2.306	1.26
1.668	1.23	2.373	1,18
1.690	1.29	2.418	1.17
1.725	1.20	2.465	1.10
2.519	1.09	2.989	1.12
2.579	1.19	3.435	1.08
2.719	1.30	3,586	1.08
2.823	1.21	3.770	1.24

 $Ni(NO_3)_2 \cdot 6H_2O$  (Cont'd)

February 11, 1960

Ŧ	С	Ŧ	С
(°K)	(Cal/Mole.Deg)	( <sup>0</sup> K)	(Cal/Mole. Deg)
1.361	1.39	1.481	1.38
1.367	1.29	1.488	1.38
1.372	1.26	1.496	1.22
1.377	1.34	1.503	1.37
1.382	1.30	1.510	1.37
1.390	1.27	1.519	1.36
1.396	1.28	1.534	1.28
1.402	1.34	1.544	1.30
1.410	1.31	1.553	1.34
1.421	1.22	1.564	1.45
1.427	1.27	1.574	1.39
1.433	1.42	1.590	1.35
1.443	1.36	1.608	1.44
1.449	1.38	1.621	1.39
1.454	1.31	1.636	1.34
1.463	1.23	1.649	1.31
1.474	1.33	1.660	1.38
1.677	1.30	2.318	1.17
1.693	1.33	2.357	1.17
1.719	1.41	2.530	1.30
1.733	1.37	2.582	1.34
1.751	1.44	2.641	1.23
1.775	1.35	2.710	1,33
1.792	1.31	2.789-	1.36
1.814	1.29	2.873	1.30

 $Ni(NO_3)_2 \cdot 6H_2O$  (Cont'd)

		Fe	bruary 11, 1960
Т (°К)	C (Cal/Mole•Deg)	т ( <sup>о</sup> К)	C (Cal/Mole•Deg)
1.833	1.30	2.972	1.26
1.852	1.49	3.087	1.15
1.877	1.27	3.160	1.26
1.908	1.40	3.241	1.22
1.926	1.22	3.523	1.02
1.950	1.30	3.638	0.96
1.983	1.23	3.763	0.89
2.084	1.23	3.942	0.91
2.131	1.25	4.101	0.87
2.178	1.25	4.440	0.76
2.228	1.23	4.806	0.62
2.275	1.21		

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MnSO_4 \cdot 4H_2O
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			April 19, 1960
1.378	0.24	1.554	0.14
1.384	0.21	1.574	0.14
1.390	0.20	1.585	0.15
1.396	0.20	1.595	0.13
1.403	0.19	1.611	0.13
1.410	0.20	1.622	0.13
1.416	0.18	1.635	0.14
1.421	0.19	1.651	0.13
1.425	0.19	1.679	0.11
1.430	0.18	1.706	0.15
1.436	0.18	1.726	0.11
		April 19, 1960	
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T	C (Cal/Mala Dar)	T (OK)	C
(°K)	(Cal/Mole Deg)	( <sup>0</sup> K)	Cal/Mole. Deg
1.443	0.18	1.749	0.11
1.449	0.22	1.775	0.14
1.457	0.17	1.801	0.09
1.463	0.29	1.846	0.10
1.469	0.14	1.867	0.09
1.479	0.17	1,905	0.09
1.487	0.16	1.953	0.11
1.494	0.17	2.002	0.07
1.506	0.14	2.054	0.06
1.516	0.15	2.084	0.07
1.521	0.18	2.100	0.08
1.539	0.16	2.126	0.07
1.547	0.16	2.147	0.06
2.182	0.08	2.798	0.07
2.211	0.07	2.932	0.11
2.246	0.06	3.063	0.10
2.301	0.07	3.224	0.23
2.345	0.07	3.577	0.19
2.393	0.05	3.663	0.28
2.446	0.09	3.807	0.26
2.517	0.05	3.921	0.28
2.572	0.06	3.986	0.31
2.672	0.09		

		May 5, 1960	
Т (°К)	C (Cal/Mole•Deg)	т (°К)	C (Cal/Mole•Deg)
1.289	0.22	1.357	0.21
1.298	0.19	1.366	0.16
1.304	0.21	1.371	0.19
1.313	0.19	1.380	0.18
1.321	0.20	1.391	0.19
1.325	0.19	1.397	0.19
1.330	0.19	1.404	0.18
1.333	0.19	1.414	0.17
1.337	0.19	1.421	0.19
1.343	0.25	1.429	0.15
1.351	0.20	1,439	0.16
1.458	0.15	1.801	0.16
1.472	0.15	1.823	0.20
1.488	0.14	1.843	0.12
1.503	0.16	1.868	0.09
1.513	0.15	1.910	0.09
1.522	0.13	1.944	0.09
1.542	0.15	1.997	0.09
1.549	0.15	2.072	0.09
1.569	0.16	2.114	0.13
1.581	0.14	2.160	0.16
1.594	0.14	2.217	0.11
1.613	0.14	2.332	0.09
1.626	0.12	2,364	0.07

<del>Т</del> ( <sup>о</sup> К <b>)</b>	C (Cal/Mole•Deg)	May 5, 1960	
		т ( <sup>о</sup> к)	C (Cal/Mole•Deg)
1.661	0.13	2.414	0.09
1.667	0.12	2.459	0.08
1.728	0.11	2.563	0.05
1.760	0.09	3.339	0.22
1.785	0.16		

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 $MnSO_4 \cdot 4H_2O$  (Cont'd)

