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Specific Heats of $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$ between 1.4° and 20°K*

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The specific heats of $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$ have been measured from 1.4° to 20°K. Lambda-type anomalies were observed at 5.34°K and 2.29°K for $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$, respectively, associated presumably with antiferromagnetic-paramagnetic transitions. It has been possible in each case to separate out the magnetic contribution to the specific heat and thus to compute the total magnetic entropy gained in the transition from the fully ordered to completely disordered condition. This quantity was found to be given accurately by $R\ln(2S+1)$ with $S=\frac{1}{2}$ for Co^{++} and $S=1$ for Ni^{++}. Short range order is particularly pronounced in these substances, the fraction of the total magnetic entropy gained above the Néel point being 0.52 for $CoCl_2 \cdot 6H_2O$ and for 0.40 for $NiCl_2 \cdot 6H_2O$. Other features of the anomalies are discussed.

INTRODUCTION

The work to be described is an experimental investigation of the specific heats of two hydrated paramagnetic salts which exhibit antiferromagnetism in the liquid helium range. In some respects the thermal properties of these materials are simpler than those of anhydrous salts or oxides in which the interaction among magnetic ions may be much stronger. Of particular importance for our purposes will be the fact that at helium temperatures the contribution of lattice vibrations to the specific heat of the solid is both relatively small and easily identified with reasonable accuracy. It becomes feasible then to separate out the contribution to the specific heat associated with the magnetic ordering process from the measured total. This "magnetic specific heat" proves useful first of all as a source of information of primarily magnetic interest. For example, it indicates rather unambiguously the temperature at which the magnetic transformation occurs and thus gives a measure of the strength of the interactions among magnetic ions. At the same time, it yields a value of the effective spin of these ions in their ground state. An examination of the details of the specific heat anomaly accompanying the transition provides, furthermore, information relevant to the more general problem of order-disorder which is difficult to extract from observations on other types of ordering systems.

The choice of $CoCl_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ for investigation represents a natural extension of earlier work on the hydrated cupric[1] and manganous[2] chlorides. The need for such extension has been emphasized by the recently reported powder susceptibility measurements on $CoCl_2 \cdot 6H_2O$ by Haseda and Kanda[3] and $NiCl_2 \cdot 6H_2O$ by Haseda and Date.[4] In the first of these studies the existence of antiferromagnetism is strongly indicated, while in the case of $NiCl_2 \cdot 6H_2O$ temperature-independent paramagnetism is found below 4°K of a type which could presumably be interpreted without the assumption of antiferromagnetism. In both cases, however, our results will be seen to be consistent with the occurrence of antiferromagnetism.

EXPERIMENTAL

The salts used in the present measurements were so-called "Certified Reagents" supplied by Fisher Scientific Supply Company. These materials are of analytical quality. Analyses of the impurity content of the specimens provided by the supplier are reproduced in Table I. Particular care was taken during the handling of the specimens to prevent changes in their water content.

In each series of determinations approximately 80 grams (~0.3 mole) of the specimen material in the form of small crystals (of average dimension 0.5mm) were contained in a thin-walled cylindrical copper capsule. This was suspended by nylon threads inside a metal

Table I. Impurity content of specimens.

	$CoCl_2 \cdot 6H_2O$	$NiCl_2 \cdot 6H_2O$
Insoluble matter	0.004%	0.009%
Nitrogen compounds (N)	...	0.006%
Sulfate	0.004%	0.0004%
Alkalies and earths	...	0.08%
Ammonium	0.002%	...
Copper	0.000%	0.001%
Cobalt		0.009%
Nickel	0.05%	
Iron	0.002%	0.0007%
Zinc	0.02%	0.01%
Lead	...	0.005%
Substances not precipitated by $(NH_4)_2S$ (as SO_4)	0.06%	...

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[1] S. A. Friedberg, Physica 18, 714 (1952); also Leiden Comm. No. 289d.

[2] S. A. Friedberg and J. D. Wasscher, Physica 19, 1072 (1953); also Leiden Comm. No. 293c.

[3] T. Haseda and E. Kanda, J. Phys. Soc. Japan 12, 1051 (1957).

[4] T. Haseda and M. Date, J. Phys. Soc. Japan 13, 175 (1958).

TABLE II. Specific heat of $NiCl_2 \cdot 6H_2O$ in calories per mole degree.

Temperature (°K)	ΔT (°K)	C_p	Temperature (°K)	ΔT (°K)	C_p
1.6104	0.1666	0.0842	4.7918	0.1096	2.859
1.7412	0.1370	0.1184	4.9148	0.1399	3.220
1.9740	0.0959	0.1767	5.0452	0.1244	3.626
2.2363	0.1750	0.2820	5.1764	0.1374	4.365
2.4239	0.2380	0.3499	5.2652	0.0403	7.845
2.6182	0.2064	0.4466	5.3122	0.0592	5.952
2.8012	0.1686	0.5493	5.4142	0.1448	2.293
2.9495	0.1454	0.6378	5.5826	0.1951	1.777
3.1500	0.2676	0.7126	5.8208	0.2871	1.545
3.3805	0.2054	0.9327	6.1765	0.4338	1.349
3.5624	0.1747	1.098	6.6360	0.4797	1.206
3.7186	0.1548	1.241	7.1344	0.5359	1.063
3.8587	0.1402	1.372	7.6764	0.5761	0.971
4.0222	0.2032	1.543	9.4747	0.6192	0.852
4.1842	0.1811	1.732	10.109	0.613	0.842
4.3488	0.1564	2.008	10.688	0.583	0.872
4.4688	0.0880	2.192	11.259	0.558	0.903
4.5520	0.0820	2.352	11.805	0.534	0.930
4.6108	0.0383	2.453	12.358	0.573	1.01
4.7348	0.0205	2.705	12.958	0.628	1.09
4.7550	0.0198	2.803	13.564	0.584	1.17
4.7740	0.0197	2.815	14.126	0.540	1.25
4.7998	0.0318	2.958	14.644	0.497	1.36
4.8472	0.0631	3.028	15.172	0.557	1.45
4.9088	0.0600	3.219	15.712	0.524	1.52
4.9848	0.0921	3.415	16.269	0.590	1.66
5.0743	0.0826	3.811	16.842	0.555	1.75
5.1828	0.1351	4.453	17.372	0.505	1.95
5.3095	0.1176	5.119	17.864	0.481	2.03
5.5198	0.3074	1.936	18.333	0.456	2.14
5.8648	0.3877	1.524	18.774	0.425	2.31
6.2788	0.4471	1.308	19.184	0.397	2.49
6.6208	0.2599	1.168	19.588	0.410	2.37
4.6444	0.0515	2.524	19.976	0.366	2.71
4.7041	0.0718	2.676			

jacket which could be either highly evacuated or filled with helium gas for heat transfer purposes. The vacuum jacket was immersed in either liquid helium or hydrogen and the heat capacity of the composite specimen determined by the conventional discontinuous heating procedure. Rapid attainment of thermal equilibrium throughout the sample was assured by an egg-box type copper grid silver-soldered to the inner wall of the capsule and the inclusion of helium transfer gas. Attached to the capsule were a heater winding of No. 38 manganin wire and a resistance thermometer consisting of a 51 ohm, $\frac{1}{2}$ watt Allen Bradley resistor.

The thermometer was calibrated at numerous temperatures against the vapor pressure of either the helium or the hydrogen bath. The temperatures were taken from the liquid helium vapor pressure-temperature relation compiled by Clement[5] in 1955 (T_{55E} scale), and the vapor pressure-temperature relation for equilibrium liquid hydrogen established at the National Bureau of Standards.[6] The vapor pressure over the bath was measured with mercury or oil manometers, and, where necessary, a correction applied for the hydrostatic pressure head above the calorimeter. The calibration data were fitted approximately with an expression of the form suggested by Clement,[7] $(\log R/T)^{\frac{1}{2}}=a+b \log R$. Having chosen a reasonable value for the constant b, precise values of a were computed for each calibration point and plotted against $\log R$. A smooth curve was drawn through these points providing not only a continuous calibration in the helium and hydrogen ranges but also in the region from 4.2 to 14°K. For a given resistance value R, the appropriate a could then be read from this curve and substituted in the above formula to give the corresponding temperature T.

The correction for the heat capacity of the empty capsule (plus He transfer gas) was determined in a series of independent measurements over the entire range 1.4 to 20°K.

The molar specific heat of $NiCl_2 \cdot 6H_2O$ as a function of temperature is shown in Table II and in Fig. 1. The results for $CoCl_2 \cdot 6H_2O$ appear in Table III and Fig. 2.

DISCUSSION OF RESULTS

As is seen in Figs. 1 and 2, the specific heat of each specimen exhibits a lambda-shaped anomalous peak. Such an anomaly is generally associated with the occurrence of some sort of cooperative transformation with rising temperature from a highly ordered to a disordered state. In the present cases this ordering process is evidently one of magnetic orgin. The ordered state in each case is probably antiferromagnetic so that we shall refer to the transition temperature as indicated by the position of the anomalous maximum as a Néel

TABLE III. Specific heat of $CoCl_2 \cdot 6H_2O$ in calories per mole degree.

Temperature (°K)	ΔT (°K)	C_p	Temperature (°K)	ΔT (°K)	C_p
1.5269	0.1288	0.4630	8.1258	0.5729	0.3285
1.8316	0.0637	1.003	8.6108	0.5737	0.3559
1.9084	0.0913	1.190	9.0914	0.5657	0.3961
2.0014	0.1025	1.468	9.5798	0.5139	0.4335
2.0870	0.0845	1.792	10.028	0.4642	0.480
2.1700	0.0996	2.254	10.436	0.4277	0.521
2.2494	0.0759	2.960	10.160	0.503	0.491
2.3448	0.1296	1.726	10.663	0.502	0.549
2.3681	0.1060	1.422	11.165	0.503	0.616
2.5112	0.1947	1.142	11.678	0.523	0.664
2.6952	0.2232	0.9926	12.199	0.532	0.747
2.8913	0.2594	0.8506	12.738	0.546	0.838
3.0891	0.2794	0.7880	13.293	0.564	0.945
3.3666	0.3300	0.6630	13.872	0.595	1.05
3.6250	0.3563	0.6111	14.438	0.537	1.17
3.8760	0.3853	0.5616	14.996	0.579	1.28
4.4122	0.4612	0.4620	15.547	0.522	1.42
4.7498	0.4169	0.4296	16.091	0.566	1.58
5.0361	0.4580	0.3851	16.693	0.639	1.72
5.3512	0.4833	0.3595	17.309	0.593	1.84
5.6220	0.6103	0.3303	17.875	0.538	2.06
6.0752	0.5729	0.3143	18.409	0.522	2.09
6.4688	0.5767	0.3025	18.908	0.477	2.32
6.8450	0.5553	0.3071	19.366	0.439	2.55
7.2534	0.5430	0.3047	19.795	0.419	2.67
7.6630	0.5544	0.3185			

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[5] J. R. Clement, U. S. Naval Research Laboratory Report (1955); Clement, Logan, and Gaffney, Phys. Rev. **150**, 743 (1955).

[6] Wooley, Scott, and Brickwedde, J. Research Natl. Bur. Standards **41**, 379 (1948).

[7] J. R. Clement, *Temperature* (Reinhold Publishing Corporation, New York, 1955), Vol. II, p. 382.

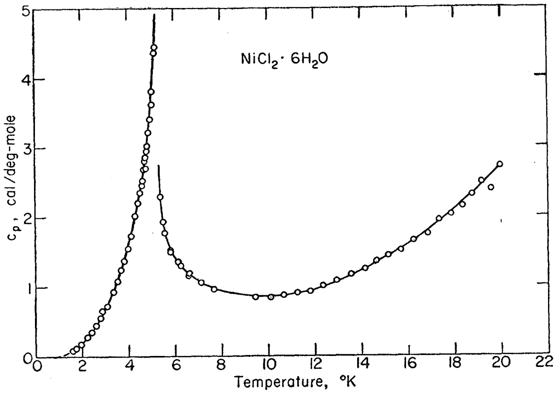

FIG. 1. Molar specific heat of $NiCl_2 \cdot 6H_2O$ as a function of temperature.

temperature, T_N. The values of T_N quoted below correspond to points of discontinuous slope on temperature-time curves obtained in continuous heating measurements through the transition regions.

The powder susceptibility measurements on $CoCl_2 \cdot 6H_2O$ by Haseda and Kanda[3] revealed a broad maximum near 3°K, which they attributed to an antiferromagnetic transition. Our measurements locate the Néel point at 2.29_1°K, a temperature somewhat lower than that of the susceptibility maximum. This is analogous to the situation in $CuCl_2 \cdot 2H_2O$[8] which was shown by Marshall[9] to be due to the presence of rather persistent short range order at temperatures above the Néel point.

Haseda and Date's measurements[4] of the powder susceptibility of $NiCl_2 \cdot 6H_2O$ show temperature-independence below 4°K. They attribute this behavior to a crystalline Stark splitting of the lowest spin triplet of the Ni^{++} ion. In attempting to fit the data with a theoretical expression of the type which proves adequate for other Ni^{++} salts they note that the required zero field splittings for $NiCl_2 \cdot 6H_2O$ must be unusually large, about twenty times those found for $Ni(NH_4)_2(SO_4)_2 \cdot 6H_2O$. No cooperative effects are anticipated on this scheme, the specific heat being expected to show only a Schottky-type anomaly similar to that found by Stout and Hadley[10] for α-$NiSO_4 \cdot 6H_2O$.

The cooperative anomaly revealed by our measurements indicates, however, that $NiCl_2 \cdot 6H_2O$ transforms into an ordered state below 5.34_1°K. That the ordered condition is antiferromagnetic is strongly suggested by the sign of the Weiss constant needed to fit the observations of Haseda and Date at hydrogen temperatures and above. The fact that the susceptibility is approximately temperature-independent in the helium range is not inconsistent with this conclusion. It is unfortunate that the Néel point comes at a rather inaccessible temperature. It is quite possible that the susceptibility would be found to exhibit a maximum slightly above $T_N = 5.3$°K.

It is interesting to note that Kim and Sugawara[11] have reported the disappearance of proton resonance in $NiCl_2 \cdot 6H_2O$ below a temperature of $\sim$8°K. This fact is completely consistent with our conclusion that this salt becomes antiferromagnetic somewhat below that temperature. That the proton resonance disappears at a temperature above the Néel point is probably another manifestation of the persistence of short-range order after long-range order has been destroyed at T_N. The importance of short-range order in both the nickel and the cobalt salt is clearly evident in the large specific heat "tail" seen above T_N in each case. Additional implications of this effect are discussed below.

The observed specific heat includes contributions from both the magnetic spin system and the lattice vibrations. The lattice contribution, C_L, must be subtracted from the total to determine what we may call the magnetic specific heat, C_{Mag}. C_L may be expected to vary approximately as T^3 at temperatures well below the Debye temperature of the lattice (about 200°K for these salts). Since C_{Mag} should become proportional to T^{-2} at some temperature above the Néel point, i.e., vary in the way expected of a paramagnetic material with isotropic exchange coupling among the magnetic ions,[12] it is reasonable to attempt to describe the observed specific heat above T_N with an equation of the form $C_p = aT^3 + bT^{-2}$. A plot of CT^2 *vs* T^5 should be linear and enable one to determine a and b. Such plots are shown in Figs. 3 and 4 for $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$, respectively. They are linear to about 15°K where the T^3 dependence of C_L fails. The equation of the indicated straight line is shown in each figure. It will be noted that the lattice contribution, i.e., the

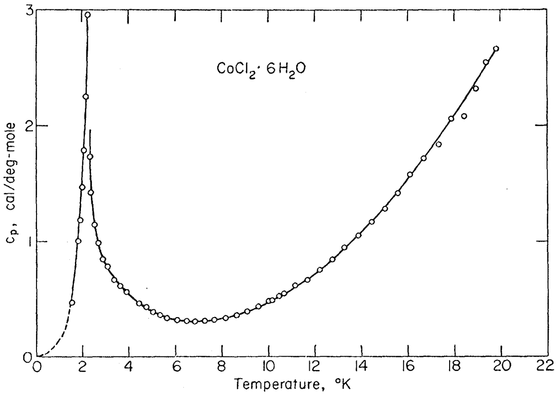

FIG. 2. Molar specific heat of $CoCl_2 \cdot 6H_2O$ as a function of temperature.

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[8] Van der Marel, van den Broek, Wasscher, and Gorter, Physica **21**, 685 (1955), also Leiden Comm. No. 300d.

[9] W. Marshall, J. Phys. Chem. Solids **7**, 159 (1958).

[10] J. W. Stout and W. B. Hadley, *Conference de Physique des Basses Températures, Paris, 1955* (Centre National de la Recherche Scientifique and UNESCO, Paris, 1956), p. 162.

[11] P. H. Kim, and T. Sugawara, J. Phys. Soc. Japan **13**, 968 (1958).

[12] J. H. Van Vleck, J. Chem. Phys. **5**, 320 (1937).

term aT^3, is nearly the same for each salt. This fact is consistent with the known isomorphism of these materials and the nearly identical ionic masses. It also strengthens the belief that we have by this means, in fact, separated C_L and C_{Mag} in the region above T_N. While some variation in the coefficient a of the lattice terms is expected as $T \rightarrow 0°\mathrm{K}$, negligible error will probably be incurred in the present instance by assuming a to be constant between 0 and 15°K. Near T_N in each case C_L evaluated in this way is less than one percent of the total specific heat. Separation of C_{Mag} has been carried out between 1.4°K and $\sim$15°K by subtracting $C_L = aT^3$ as indicated in Figs. 3 and 4 from the observed total.

We wish to obtain the magnetic entropy increase, $\Delta S = \int_0^\infty (C_{\mathrm{Mag}}/T)dT$, associated with the transition from a perfectly ordered to a fully disordered state. On the basis of the statistical interpretation of entropy and the third law of thermodyanmics we expect ΔS to be just $R \ln\omega_0$ regardless of the mechanism by which the change occurs so long as only the ground state of the paramagnetic ions, having a degeneracy ω_0, is occupied during the process. We shall be concerned only with cases in which $\omega_0 = 2S+1$, where S is the effective electronic spin of the paramagnetic ion in its ground state. The extrapolation of C_{Mag} to infinite temperature required for the evaluation of ΔS was carried out analytically using the relation $C_{\mathrm{Mag}} = b/T^2$ with the b values given in Figs. 3 and 4. For $NiCl_2 \cdot 6H_2O$ below the Néel point, the rapid fall of C_p dies out by 4.3°K and a T^3 law is then followed to the lowest temperature obtained, possibly the behavior expected on the basis of spin wave theory.[13] For the cobalt salt, in the limited range in which data were taken below T_N, the fall is more rapid than as T^3. It does not seem likely, however, that this rapid fall will continue at lower temperatures so C_{Mag} was extrapolated to 0°K according to a T^3 relation as for the nickel salt. This assumption could probably introduce at most a three percent error in the calculation of ΔS for the cobalt salt. In the case of the nickel salt, less than one percent of the total ΔS is found below 1.4°K so that the extrapolation of C_{Mag} to 0°K introduces negligible error. In the vicinity of T_N, $\int (C_{\mathrm{Mag}}/T)dT$ has been evaluated both graphically and analytically, the two methods yielding essentially identical results. The analytical procedure utilizes expressions for C_{Mag} *vs* T, the fitting of which is discussed below.

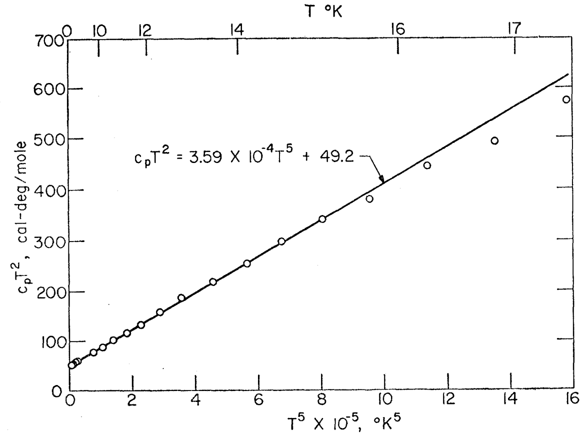

FIG. 3. Plot of CT^2 *vs* T^5 for $NiCl_2 \cdot 6H_2O$.

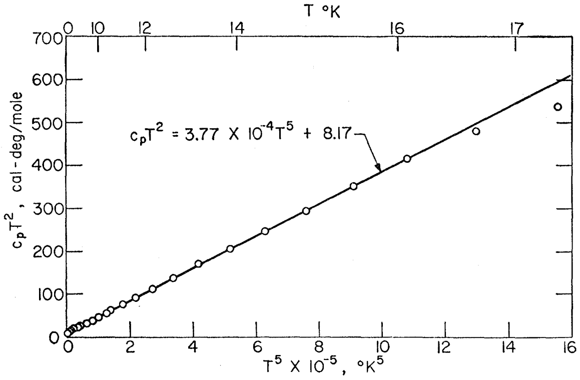

FIG. 4. Plot of CT^2 *vs* T^5 for $CoCl_2 \cdot 6H_2O$.

The total magnetic entropy increase ΔS deduced in this way, ignoring possible nuclear contributions below 1°K, is 9.13 joules/mole-degree for the nickel salt and 5.80 joules/mole-degree for the cobaltous chloride. These values are given accurately (to better than 1%) by the expression $R \ln(2S+1)$ as expected theoretically provided one uses $S = \frac{1}{2}$ for the cobaltous ion and $S = 1$ for the nickelous ion. These effective spin values are the ones expected on the basis of the theory of the influence of the crystalline electric field on the electronic levels of the transition metal ions.[14] In both instances the effective spin deduced in this way is consistent with the notion that each magnetic ion is surrounded by six ligands arranged in a distorted octahedron so that the crystalline field has less than cubic symmetry. The effect of the crystalline field is particularly striking in the case of Co^{++} where the effective spin is $S = \frac{1}{2}$ rather than $\frac{3}{2}$ as for the free ion.

Having concluded from the calculation of the magnetic entropy increase that the effective spin of the cobaltous ion in the ground state is $\frac{1}{2}$ one can turn to the Curie constant of $CoCl_2 \cdot 6H_2O$ observed by Haseda and Kanda and determine an average g factor for the magnetic ion. Well above the Néel point they found

$$\chi_M = 2.65/(T+20) = C/(T+\theta).$$

Since $C = g^2\beta^2NS(S+1)/3k$, where β is the Bohr magneton, we find $g = 5.3$. This average powder value is consistent with the results of paramagnetic resonance

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[13] R. Kubo, Phys. Rev. 87, 568 (1952).

[14] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

experiments on various cobalt salts which yield values of 3.0 to 6.5 for g.[15]

Haseda and Date's susceptibility measurements on $NiCl_2 \cdot 6H_2O$ well above the Néel point may be summarized by the relation $\chi_M = 1.18/(T+7)$ giving a Curie constant of 1.18. Using an effective spin of one we find $g = 2.17$ in reasonable agreement with the value 2.25 observed for other nickel salts.[15]

It is interesting to note that $\theta/T_N \approx 8.7$ for $CoCl_2 \cdot 6H_2O$ while for $NiCl_2 \cdot 6H_2O$, $\theta/T_N \approx 1.3$ where the Weiss constants, θ, have been quoted in the preceding paragraphs. At first sight one might expect these ratios to be roughly the same if magnetic ordering of the same same kind were to occur in these structurally similar salts.[16] That they differ is not immediately attributable, however, to different kinds of ordering in the two antiferromagnetic systems. It is probable that θ for the cobalt salt is unusually large for the same reason that the splitting factor g is large, namely, the proximity of excited states to the ground state.[17] This effect contributes to the observed θ in addition to the exchange interaction and could well be dominant.

While the total entropy gain in the transition from magnetically ordered to disordered states has a simple interpretation quite independent of any model of the ordered condition, the interpretation of the total ordering energy, $W = \int_0^\infty C_{\mathrm{Mag}} dT$, is somewhat less direct. If the system is assumed to contain one mole of magnetic ions, each of spin S, coupled by exchange to z identical neighbors then in the approximation in which the antiferromagnetic ground state corresponds to a perfect alternating arrangement of oppositely directed spins,[18] $W = N_0 z |J| S^2$ where $|J|$ is the magnitude of the exchange integral, and N_0 is the Avogadro number. Thus $|J| z/k$ is given by W/RS^2 where $R = N_0 k$, the universal gas constant. W has been computed for the two salts, extrapolating C_{Mag} as was done above in the entropy calculations. Using these values one finds $|J| z/k = 9.8$ for $CoCl_2 \cdot 6H_2O$ and 7.4 for $NiCl_2 \cdot 6H_2O$. We may compare these values with the ones given by Van Vleck's molecular field theory of antiferromagnetism which yields the relation[19] $|J| z/k = 3T_N/S(S+1)$. The theoretical values on this basis become 9.2 for $CoCl_2 \cdot 6H_2O$ and 8.0 for $NiCl_2 \cdot 6H_2O$. The agreement is rather satisfactory in view of the obvious limitations of the molecular field model and suggests that the relationship between T_N and W is not particularly sensitive to the model used.

Kubo[13] has shown that, under certain simplifying assumptions, the spin wave theory of antiferromagnetism predicts a T^3 dependence of C_{Mag} in a temperature range for which $(2z|J|S\beta H_A)^{\frac{1}{2}} \ll kT \ll z|J|S$ where H_A is the anisotropy field and β is the Bohr magneton. Below this region, C_{Mag} is expected to fall exponentially with T. As was mentioned earlier, C_{Mag} for $NiCl_2 \cdot 6H_2O$ actually follows a T^3 law quite closely below 4.3°K. Kubo has given explicit expressions for the coefficient of the T^3 term for NaCl- and CsCl-type structures. Either of these reproduces the measured coefficient to within a factor of two upon insertion of the quantity $z|J|/k$ obtained by either of the methods of the preceding paragraph. It appears rather likely that the observed T^3 behavior in $NiCl_2 \cdot 6H_2O$ is a spin wave effect in spite of the fact that it occurs quite near the Néel point.

Let us consider more closely some of the features of the anomalous peaks themselves. The very rapid variation of C_{Mag} with T near T_N suggests that the data for this region be analyzed by plotting C_{Mag} *vs* $\log|T-T_N|$. Such a plot of the $NiCl_2 \cdot 6H_2O$ data (omitting three points for which ΔT includes T_N) is shown in Fig. 5. The points fall on two straight lines corresponding to $T > T_N$ and $T < T_N$. Similar lines are obtained for $CoCl_2 \cdot 6H_2O$. At least to the limits of their resolution the present measurements are thus consistent with the existence of a logarithmic singularity in the specific heat at the Néel point. Such a singularity is, of course, integrable, giving both finite enthalpy and entropy. The equations describing C_{Mag} as a function of T in the vicinity of T_N used in the analytical evaluation of the entropy mentioned earlier were obtained from linear plots of the kind shown in Fig. 5.

The simple molecular field models and the more elaborate Bethe-Peierls models of cooperative behavior predict finite specific heats (with finite discontinuities) at the transition temperature. However, the exact solution of the two dimensional Ising problem does reveal a logarithmic singularity at this point.[20] Unfortunately, the three-dimensional Ising problem has not been solved exactly and it is not yet possible to predict accurately the behavior of a three-dimensional Ising model at the transition temperature. It is not

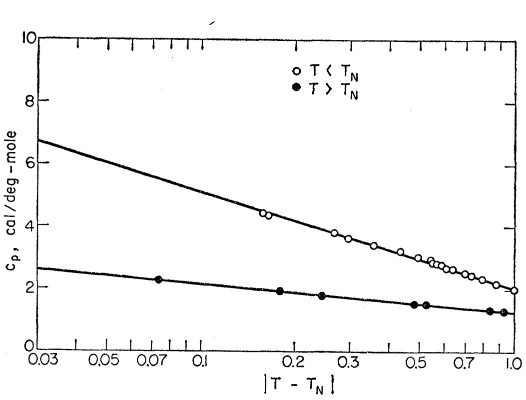

FIG. 5. Plot of C_{Mag} *vs* $\log|T-T_N|$ for $NiCl_2 \cdot 6H_2O$.

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[15] K. D. Bowers and J. Owen, *Reports on Progress in Physics* (The Physical Society, London, 1955), Vol. XVIII, p. 304.

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[17] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932), p. 305.

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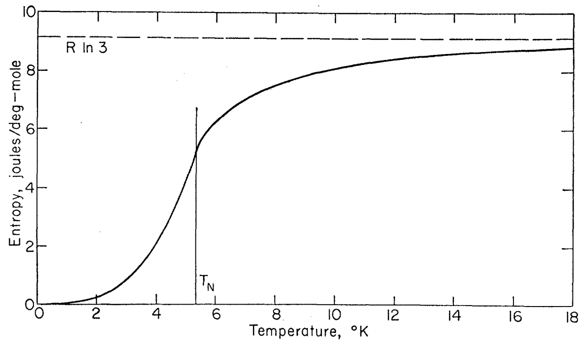

FIG. 6. Magnetic entropy as a function of temperature for $NiCl_2 \cdot 6H_2O$.

impossible, however, that here too a logarithmic singularity would be indicated. There is known at least one order-disorder transformation, namely the lambda transition in He^4, in which the existence of a logarithmic singularity in the specific heat has been established experimentally with extremely high resolution.[21] We hope that it may prove feasible to re-examine the anomalies in cobaltous and nickelous chlorides with comparable resolution.

The low Néel temperatures of $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$ suggest that the coupling among magnetic ions in these salts is sufficiently weak that an external magnetic field H of 10 or 15 kilogauss could produce an appreciable shift of T_N. It should be feasible, therefore, to study in these substances at least a portion of the phase boundary in the H, T plane separating paramagnetic and antiferromagnetic regions. Rather detailed prediction of the nature of such boundaries has been given for several microscopic models of antiferromagnets.[22] These may have limited applicability to a particular salt, however, so that a purely thermodynamic analysis of the observations will probably be extremely helpful. This would normally be attempted for a simple second order transition, for example, by means of the appropriate Ehrenfest relations.[23] From the form of the specific heat anomalies in zero external field described in the preceding paragraph, however, it is evident that we are dealing with higher order phase transitions for which Ehrenfest's analysis yields little useful information. Without entering into details we wish merely to note here that an alternative thermodynamic approach recently proposed by Pippard[24] may well be applicable in these cases. This treatment should make possible interesting deductions from the observed dependence of T_N on an external magnetic field when these data become available.

In the course of the calculation of the total magnetic entropy change discussed earlier, the magnetic entropy as a function of temperature, $S(T)=\int_0^T (C_{\mathrm{Mag}}/T)dT$, has also been evaluated. The plotted results are shown for $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$ in Figs. 6 and 7, respectively, the limiting value $R\ln(2S+1)$ being indicated in each case. It will be seen that as the temperature is raised to the Néel point, only 0.60 of the total magnetic entropy is gained by the nickel salt and 0.48 by the cobalt salt. Thus the amount of short range order persisting after destruction of the long range order at T_N is really quite large. A similar, but less pronounced effect, was observed in $CuCl_2 \cdot 2H_2O$.[1] In this connection the work of Domb[25] on Ising models is rather instructive. He points out that the fraction of the total magnetic entropy gained above T_N increases as the coordination number, z, decreases. This result is clearly reasonable since in the limit of infinite coordination all order must be long range in character, whereas in the limit of zero coordination only short range order is possible.

Domb shows, for example, that for a two dimensional square lattice with $z=4$ the fraction of the entropy gained above the transition temperature is 0.56, a value comparable with that observed for $CoCl_2 \cdot 6H_2O$. The comparison suggests that z is rather small in this salt. This result, however, is not unambiguous since, as in the case of $CuCl_2 \cdot 6H_2O$,[9] the interactions of a given ion with nearest and next nearest neighbors may prove to be of comparable magnitude and opposite sign.

As was noted by Haseda and Kanda,[3] the occurrence of a Néel point above 1°K for such a dilute salt as $CoCl_2 \cdot 6H_2O$ is rather unexpected in view of the behavior of $CuCl_2 \cdot 2H_2O$ ($T_N=4.3°K$) and $MnCl_2 \cdot 4H_2O$ ($T_N=1.6°K$). A similar observation must now be made for $NiCl_2 \cdot 6H_2O$ although the element of surprise has been somewhat reduced by the knowledge that these

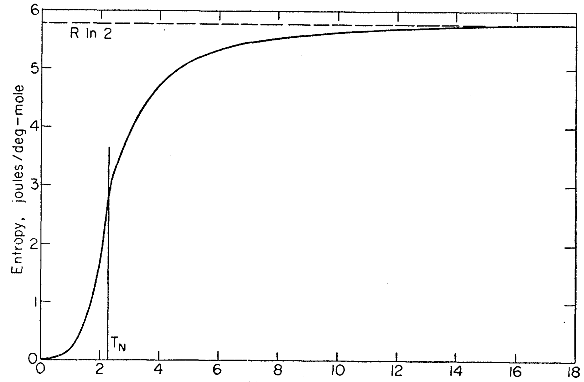

FIG. 7. Magnetic entropy as a function of temperature for $CoCl_2 \cdot 6H_2O$.

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[23] P. Ehrenfest, Proc. Koninkl. Akad. Wetenschap. Amsterdam **36**, 153 (1933); also Leiden Comm. Suppl. No. 75b.

[24] A. B. Pippard, *Classical Thermodynamics* (Cambridge University Press, New York, 1957), p. 143.

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two substances are isomorphous. There is perhaps reason to believe that the occurrence of comparatively strong cooperative interaction is a distinctive feature of hydrated chlorides (and possibly other halides) of nickel and cobalt not exhibited by other salts of these metals hydrated to a comparable degree. For example, in $\alpha NiSO_4 \cdot 6H_2O^{10}$, a Schottky-type specific heat anomaly has been found at liquid helium temperatures but no evidence of cooperative interaction. X-ray analysis has shown[26] that each Ni^{++} ion in this salt is surrounded by an octahedron of six water molecules which apparently help to isolate it rather effectively from its neighbors. While similar octahedra might be expected to surround the metallic ions in $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$, recent x-ray studies by Mizuno *et al.*[27] show this not to be the case. They find that each metallic ion is actually surrounded by an octahedron consisting of four water molecules and two chloride ions. The Cl^- ions are at opposite vertices of the octahedron while the H_2O molecules form a square in the plane bisecting the line joining the Cl^-'s and containing the metallic ion. On the basis of preliminary reports of this x-ray work, Haseda and Kanda[3] suggested that the Cl^- ions, replacing as they do water molecules in the usual octahedral coordination scheme, are responsible for the "high" Néel point in $CoCl_2 \cdot 6H_2O$. Presumably they provide paths for the indirect exchange coupling of Co^{++} moments. Our observation of a cooperative transition in $NiCl_2 \cdot 6H_2O$ is certainly consistent with this conjecture. Further speculation as to the mechanism of such coupling should perhaps await the development of a clearer picture of the arrangement of ionic moments in the antiferromagnetic state in both salts.

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Evaluation of Thermal Activation Energies from Glow Curves

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A new method for the evaluation of thermal activation energies from glow curves of excited crystals is described. Use is made of the symmetry of the glow peak, from which the activation energy is calculated by a simple formula: $E=(q/\delta)kT_g^2$, where T_g is the peak temperature, k—Boltzmann's constant, δ—the half-width towards the falloff of the glow peak, and q—a factor which can be computed from the shape of the glow peak. Values of $q \leqslant 1$ were found for monomolecular processes, while $1 \leqslant q \leqslant 2$ correspond to bimolecular ones. The method thus enables to determine the type of kinetics.

INTRODUCTION

THE method of thermoluminescence has been extensively used in the study of trapping states in crystals.[1] In this method energy stored up in the crystal by suitable excitation, is subsequently released with emission of light on warming up the crystal from the low temperature at which it has been excited.

Randall and Wilkins[2] were the first to investigate the thermoluminescence theoretically. They used a model in which electrons in metastable states are raised thermally to an excited state from which they return to the ground state with emission of luminescence. Assuming a uniform rate of heating they obtained an expression for the variation of the thermoluminescence with temperature, but they neglected the bimolecular nature of the process. Later the theory was extended by other investigators,[3–6] who assumed bimolecular kinetics and also allowed for the retrapping of the released electrons.

Computation of activation energies remained still quite complicated, not only for mathematical, but also for physical reasons. The difficulty lies in the fact that in addition to the activation energy, the equations

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[1] For references see: G. F. J. Garlick, *Luminescent Materials* (Oxford University Press, Oxford, 1949); G. F. J. Garlick, *Encyclopedia of Physics*, (Springer-Verlag, Berlin, 1958). Vol. XXVI, pp. 1–28; W. Hoogenstraaten, Philips Research Repts. **13**, 515 (1958).

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