THE SPECIFIC HEAT OF ANHYDROUS CHLORIDES OF THE IRON GROUP

AT LOW TEMPERATURES

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The specific heat of $CoCl_2$ is measured at temperatures between 1.8 and $4°K$. These measurements and previous ones for $FeCl_2$ and $NiCl_2$ are discussed from the point of view of the properties of the magnetic spectrum of layered antiferromagnets.

INVESTIGATING the properties of layered halides, we have carried out measurements of the specific heat of $CoCl_2$ at temperatures between 1.8 and $4°K$, augmenting previous specific heat measurements of $FeCl_2$[1] in the same range of temperatures and also those of $NiCl_2$ from 1.8 to $16°K$.[2] All these substances belong to the class of layered antiferromagnets first considered by Landau.[3] They have a layered crystal structure of the type D_{3d}^5. The principal axis of symmetry C_3 is perpendicular to the plane of the layer. Neutron-diffraction investigations[4] have shown that in $FeCl_2$ the spins are oriented along the principal C_3 axis, whereas in $CoCl_2$ they lie in the basal plane in which the anisotropy is small. $NiCl_2$ is in general completely isotropic[5] and its spins are apparently also oriented in the basal plane.

As indicated by calculations[6-8] and experimental data[9, 10] the spin vibrations of the usual uniaxial antiferromagnets and weakly ferromagnetic structures with an anisotropy of the "easy-plane" type contain two branches: a high-frequency and a low-frequency branch without a gap. In the case when the spins are directed along the principal axis, both branches have a gap. The characteristics of spectra of layered antiferromagnets have so far not been finally explained. The theoretical papers[11-13] are devoted to the spectrum of layered antiferromagnets.

Measurements of the specific heat of anhydrous halides of the iron group between 130 and $14°K$ were first carried out in the work of Trapeznikova, Shubnikov, and Milyutin, and subsequently by other authors. The antiferromagnetic transition temperatures determined from calorimetric data are: for $CoCl_2$ $T_c = 24.9-24.7°K$,[14, 15] for $FeCl_2$ $T_c = 23.5°K$,[16] and for $NiCl_2$ $T_c = 52.3°K$.[17]

A previously worked out method[18, 19] was used to measure the specific heat. The high vacuum in the calorimeter jacket was produced by sorption of the gaseous heat-exchange helium or hydrogen by carbon placed within the jacket. (In working with a hydrogen bath heat-exchange hydrogen was used, whereas heat-exchange helium was used in the range of helium and intermediate temperatures.) The samples of anhydrous chlorides were obtained from the hydrates of the salts. Dehydration was carried out in a stream of dry HCl with heating and subsequent sublimation in a stream of HCl.

The specific heat of $CoCl_2$ and the specific heats of $FeCl_2$[1] and $NiCl_2$[2] measured by us in the temperature range of $1.8-4°K$ are shown in Fig. 1. The small hump on the specific-heat curve of $CoCl_2$ near $T = 2.8°K$ is explained by the presence of traces of water in the sample of the highly hygroscopic cobalt chloride. Aqueous cobalt chloride $CoCl_2 \cdot 6H_2O$ has a transition to the antiferromagnetic state at $T_c = 2.3°K$ with the specific heat at the maximum reaching 3 cal/mole-deg.[20] In our sample of anhydrous $CoCl_2$ the anomalous specific heat at the maximum at $T = 2.8°K$ is smaller by three orders of magnitude and is about 15% of the total specific heat. One can therefore assume that the admixture of hydrate is very small and its effect is negligible above $3°K$.

In Fig. 2 the specific heats of $FeCl_2$ and $CoCl_2$ are plotted in CT^2 and T^5 coordinates. The dashed line shows the specific heat of the isomorphous and non-
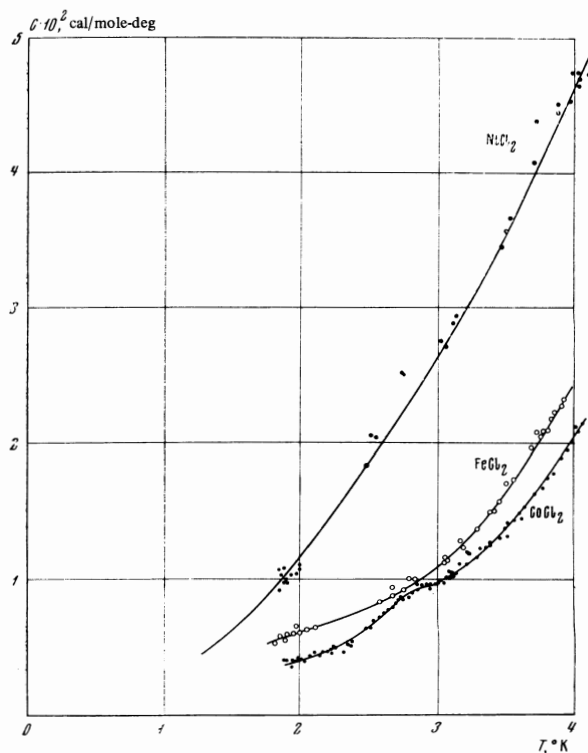

FIG. 1

magnetic $CdCl_2$[21] which follows in the region of helium temperatures the cubic law

$$C = 2.75 \cdot 10^{-4} \, T^3 \text{ cal/mole-deg}$$

Deviations from a cubic dependence, characteristic of layered lattices, occur in $CdCl_2$ at higher temperatures.

The specific heat of $FeCl_2$ between 1.8 and 4°K is well described by the relation

$$C[\text{cal/mole-deg}] = 3.7 \cdot 10^{-4} \, T^3 + 12 \cdot 10^{-3} \, T^{-2}.$$

With the exclusion of the region where the small hump occurs, one can also describe the specific heat of $CoCl_2$ by this type of dependence. For $CoCl_2$ between 1.8 and 4°K we have

$$C[\text{cal/mole-deg}] = 3.1 \cdot 10^{-4} \, T^3 + 6 \cdot 10^{-3} \, T^{-2}.$$

It is seen that between 3 and 4°K the law governing the temperature variation of the specific heat of $CoCl_2$ and $FeCl_2$ is close to cubic (the second term aT^{-2} is small in this temperature range).

The presence of a term proportional to T^{-2} in the expressions for the specific heat indicates the presence of a low-temperature anomaly. In $CoCl_2$ this anomaly can be attributed to the nuclear specific heat which appears as a result of the ordering of the nuclear magnetic moments of the cobalt. Making use of the Schottky formula, one can represent the nuclear specific heat of $CoCl_2$ in the form

$$C_{nuc} T^2 / R = {}^{21}/_4 \Theta^2,$$

where Θ characterizes the spacing between neighboring sublevels of the cobalt nucleus. Taking $C_{nuc}T^2/R = 3 \times 10^{-3}$, we obtain $\Theta = 0.024°K$. However, this value of Θ is by a factor of 2.7 larger than the splitting in antiferromagnetic CoF_2.[22] The admixture of hydrate in the $CoCl_2$ sample results possibly in an additional contribution to the aT^{-2} term. The magnetic moment of the iron nuclei is small, and the reason for the anomaly in $FeCl_2$ is not clear.
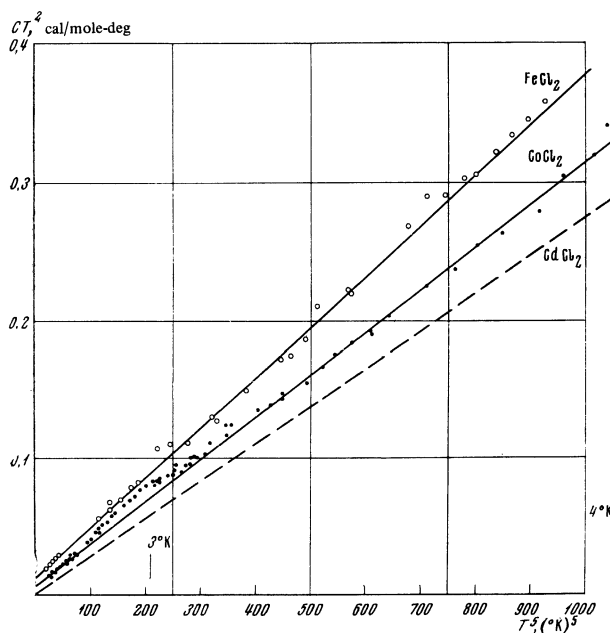
It is interesting to compare the specific heat of $FeCl_2$ and the nonmagnetic $CdCl_2$, since at high temperatures their specific heats are close, and the laws governing their temperature variation are similar.[1] At low temperatures between 3 and 4°K the specific heat of $CdCl_2$ is approximately 25% lower than that of $FeCl_2$ (Fig. 2). This difference can be ascribed to the magnetic contribution of the spin waves to the specific heat of $FeCl_2$, if it is assumed that the specific heat of the $FeCl_2$ lattice is the same as the specific heat of $CdCl_2$. Although such an estimate is approximate, it is seen that the magnetic contribution to the specific heat of $FeCl_2$ is at any rate small compared with the contribution from the lattice, and the temperature dependence of the specific heat between 3 and 4°K is close to cubic.

From a comparison with the specific heat of $FeCl_2$ one can conclude that the magnetic contribution to the specific heat of $CoCl_2$ at helium temperatures is apparently also small, since the magnitudes of the specific heats of these chlorides are close (the curve for $CoCl_2$ is about 20% lower than for $FeCl_2$). Both in the range of high temperatures and at helium temperatures the specific heat of $CoCl_2$ does not exceed the specific heat of $FeCl_2$ and one can therefore surmise that the lattice specific heat of $CoCl_2$ is less than that of $FeCl_2$.

Figure 3 shows for comparison the specific heats of $CoCl_2$,[15] $FeCl_2$,[16] and $NiCl_2$[17] in the 15–120°K temperature range. The dashed line shows the lattice specific heat of $CoCl_2$ at high temperatures estimated in [15]. In the total specific heat of $CoCl_2$ above T_C one notes the contribution of the Schottky-type anomaly due to higher-lying electron levels located relatively close to the ground level.

Thus, below 4°K calorimetric measurements exhibit in $FeCl_2$ and $CoCl_2$ a small magnetic contribution to their specific heat and similar laws governing the temperature variation of the specific heat. The calorimetric data give no obvious indications as to the presence of a sharp difference in the spectra of these chlorides which differ in their type of anisotropy.

Investigations of cobalt and iron chlorides by electron resonance methods revealed only high-frequency absorption at T = 4°K and H = 0 at frequencies ν = 19.2 cm^{-1} in $CoCl_2$ and ν = 16.3 cm^{-1} in $FeCl_2$ respectively.[23] These branches in the spectra of $CoCl_2$ and $FeCl_2$ with the large energy gap $\Delta E/k \sim 20°K$ could
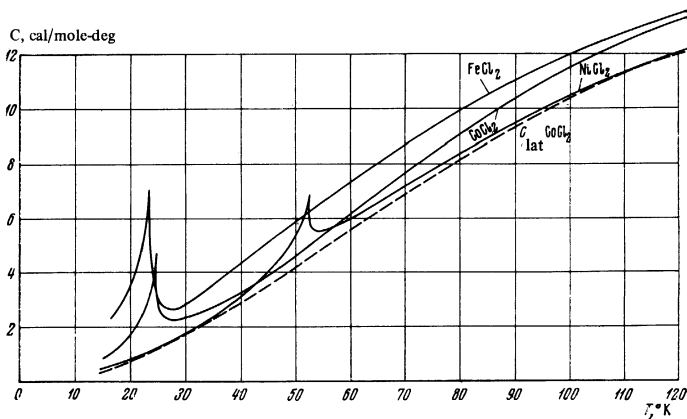

FIG. 2

FIG. 3

possibly yield a small magnetic specific heat at helium temperatures.

We have measured the specific heat of $NiCl_2$ in the temperature range between 1.8 and 16°K.[2] The results of these measurements are presented in Figs. 1–4 and in the Table. The specific heat of $NiCl_2$ exceeds the specific heat of $CoCl_2$ and $FeCl_2$ by more than a factor of two in the region of helium temperatures (Fig. 2), whereas at high temperatures the lattice specific heats of $CoCl_2$ and $NiCl_2$ are close (Fig. 3). In view of the fact that there are no reasons for expecting anomalies in the behavior of the lattice specific heat of $NiCl_2$ at low temperatures, these data allow one to assume that the magnetic contribution to the specific heat of $NiCl_2$ at helium temperatures is considerably larger than in the cobalt and iron chlorides.

The specific heat of $NiCl_2$ below 5°K follows well the quadratic dependence

$$C = 2.93 \cdot 10^{-3} T^2 \text{ cal/mole-deg}$$

This is seen from the $NiCl_2$ data presented in Fig. 4 in the range of 1.8–8°K in C and T^2 coordinates.

A large magnetic contribution to the specific heat of $NiCl_2$ was to be expected in connection with the presence in its spectrum of a low-frequency branch.[24] As has already been mentioned,[2] the observed quadratic temperature dependence of the specific heat of $NiCl_2$ apparently reflects the peculiarities of the dispersion law of spin waves in a layered antiferromagnet. This problem is considered theoretically by Yoshimori.[11] It has been shown that with increasing temperature, when one can neglect the interaction between the layers the three-dimensional layered antiferromagnet $NiCl_2$ corresponds to the case of a two-dimensional ferromagnetic system. In this connection, according to estimates of Yoshimori, the T^3 law for the magnetic specific heat of $NiCl_2$ should be valid for $T \ll 4°K$; at higher temperatures ($T \gg 10°K$) it goes over to a linear law. Our measurements are in the intermediate range of temperatures.

Thus, measurements of the specific heat of the anhydrous cobalt, iron, and nickel chlorides at low temperatures carried out in this work and in[1, 2] have shown that the magnetic specific heat of $CoCl_2$ and $FeCl_2$ constitutes a small part of their total specific heat whose temperature dependence is close to cubic. The magnetic specific heat of $NiCl_2$ exceeds appreciably the lattice specific heat, and the total specific heat of $NiCl_2$ follows

Specific heat of $NiCl_2$

T, °K	$\dfrac{C, \text{cal}}{\text{mole-deg}}$	T, °K	$\dfrac{C, \text{cal}}{\text{mole-deg}}$	T, °K	$\dfrac{C, \text{cal}}{\text{mole-deg}}$	T, °K	$\dfrac{C, \text{cal}}{\text{mole-deg}}$
1.84	0.0092	4.006	0.0474	7.76	0.129	11.33	0.295
1.85	0.0106	4.012	0.0474	7.85	0.150	11.45	0.285
1.862	0.0104	4.029	0.0465	8.26	0.166	11.48	0.261
1.866	0.0107	4.041	0.0470	8.34	0.135	11.58	0.288
1.884	0.00981	4.106	0.0473	8.48	0.151	11.59	0.305
1.887	0.00987	4.147	0.0484	8.52	0.158	11.93	0.328
1.896	0.00969	4.655	0.0674	8.54	0.171	12.27	0.314
1.938	0.0103	4.73	0.0574	8.60	0.170	12.68	0.341
1.966	0.0104	5.03	0.0715	8.66	0.154	12.78	0.358
1.998	0.0108	5.07	0.0775	8.89	0.164	12.84	0.359
2.008	0.0109	5.51	0.0745	8.89	0.180	13.02	0.315
2.479	0.0183	5.54	0.0896	9.05	0.180	13.16	0.339
2.512	0.0206	5.82	0.103	9.07	0.179	13.36	0.354
2.541	0.0205	5.852	0.0996	9.23	0.207	13.37	0.382
2.742	0.0253	5.90	0.1004	9.35	0.205	13.78	0.424
2.75	0.0252	5.99	0.0876	9.49	0.201	13.97	0.397
3.032	0.0276	6.25	0.0911	9.62	0.215	14.31	0.400
3.063	0.0273	6.41	0.1001	9.65	0.223	14.36	0.446
3.094	0.0289	6.465	0.1096	9.70	0.206	14.46	0.402
3.13	0.0294	6.51	0.0999	9.76	0.179	14.62	0.406
3.458	0.0346	6.53	0.113	9.87	0.212	14.67	0.420
3.493	0.0357	6.67	0.105	9.95	0.222	14.83	0.421
3.52	0.0366	6.91	0.103	10.05	0.240	14.98	0.497
3.706	0.0406	7.23	0.123	10.14	0.221	15.0	0.441
3.717	0.0438	7.391	0.134	10.24	0.239	15.98	0.476
3.869	0.0450	7.45	0.128	10.31	0.260	16.17	0.493
3.883	0.0444	7.59	0.130	11.09	0.285	16.49	0.614
3.97	0.0455	7.71	0.137	11.13	0.290		

at helium temperatures the T^2 law, this being due to the specific nature of the magnetic spectrum of this chloride.

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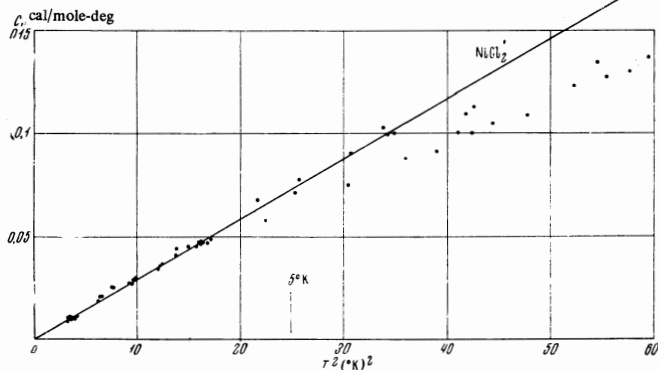
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FIG. 4

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