SOVIET PHYSICS JETP VOLUME 34, NUMBER 2 FEBRUARY, 1972

SPECIFIC HEAT OF ANHYDROUS $CrCl_3$ *AT LOW TEMPERATURES*

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Submitted March 5, 1971

Zh. Eksp. Teor. Fiz. **61**, 732–736 (August, 1971)

The specific heat of anhydrous $CrCl_3$ is measured between 2 and 20° K. The linear temperature dependence of the magnetic specific heat characteristic of two-dimensional ferromagnetic systems is observed at temperatures between 2 and 8°K. The magnitude of exchange ferromagnetic interaction in a layer is $J_f/k = 5.61$°K.

ANHYDROUS $CrCl_3$ belongs to the class of layered antiferromagnets first considered by Landau[1]. It has a layered crystal structure of the type $CdCl_2$ $(R\bar{3})$. The layers of the metallic ions in $CrCl_3$ are separated by two layers of Cl ions, the principal symmetry axis C_3 is perpendicular to the plane of the layer, and unlike in $CdCl_2$ one-third of the sites of the metal ions in $CrCl_3$ are not occupied.

Neutron-diffraction investigations[2] have shown that in the antiferromagnetic state (below $T_c = 16.8$°K) the spins inside each layer are ferromagnetically ordered, and in the neighboring layers the spins are antiparallel. $CrCl_3$ possesses in this case an anisotropy of the "easy plane" type, i.e., the spins are oriented in the basal plane.

The energy spectrum of layered antiferromagnets was recently considered theoretically by a number of workers[3-6]. It has been shown that the spectrum of layered antiferromagnets with anisotropy of the "easy plane" type contains two branches: a low-frequency branch without a gap, and a branch with a gap $\Delta = 2s\sqrt{BD}$, where $B = I_{af}z$ determines the exchange interaction between the nearest neighbors (z is the number of neighbors) in adjacent layers and D is the anisotropy constant[3]. In addition, if the ferromagnetic exchange interaction inside a layer greatly exceeds the antiferromagnetic exchange interaction between layers, then the spectrum of the spin waves is strongly anisotropic and the spin waves with wave vector directed along C_3 reach the limits of the band at lower energies. In this connection, if the magnetic anisotropy energy is small, a transition from a three-dimensional antiferromagnet to a two-dimensional ferromagnetic system is observed already at low temperatures for spin waves with frequencies $\hbar\omega \gg \Delta$. The magnetic specific heat of such a two-dimensional system should vary linearly with temperature.

The data of Bizette and Terrier[7] on the magnetic susceptibility of $CrCl_3$ have shown that the antiferromagnetic coupling between layers is very weak and therefore the antiferromagnetic ordering becomes disturbed in weak fields ~4.5 kOe. It was also shown that the magnetic anisotropy in $CrCl_3$ is small, since the difference between the fields at which magnetic saturation takes place at $H \perp C_3$ and $H \parallel C_3$ does not exceed 2 kOe. Later, Narath and Davis determined the susceptibility $\chi_\perp$ more accurately and estimated the value of the exchange interaction between layers $J_{af}z/k = -0.037$°K ($z = 2$) and the value of the gap $\Delta \sim 0.4$°K.

Narath and Davis[5,6] investigated the temperature dependence of the magnetization of the $CrCl_3$ sublattices between 0.4 and 8°K, using the method of nuclear magnetic resonance. The observed temperature dependence of the sublattice magnetization is attributed by them to the peculiarities of the energy spectrum of the two-dimensional ferromagnetic system with low anisotropy, with allowance also for the spin-wave interaction.

Measurements of the specific heat of anhydrous $CrCl_3$ in the interval from 12 to 130°K were first carried out by Trapeznikova, Shubnikov and Milyutin[8], and later, between 12 and 300°K, by Hansen and Griffel[9]. They all determined the temperature of the transition from the paramagnetic to the antiferromagnetic state for $CrCl_3$ as $T_c = 16.8$°K.

As reported earlier[10], one of us measured the specific heat of $CrCl_3$ in the region between 2 and 4°K. The measurement results have shown that at helium temperatures the magnetic specific heat of $CrCl_3$ varies linearly with the temperature. In the present investigation, to determine more accurately the magnetic specific heat and also to ascertain the distinguishing features of its temperature dependence in a wide temperature interval, the measurements of the specific heat of $CrCl_3$ were performed between 4 and 20°K.

To measure the specific heat we used a sample of powdered $CrCl_3$ of "KhCh" (chemically pure) grade, pressed in the form of a pellet weighing ~35 g. The sample was placed in a calorimeter, which was filled with a small amount of heat-exchange helium. The good heat exchange in the calorimeter did not indicate the presence of the sorption effect. The procedure for measuring the specific heat was similar to that described earlier[11,12]. High vacuum was produced in the jacket of the calorimeter by a carbon pump. To measure the temperature in the helium region, we used a phosphor-bronze thermometer, and above 4°K we used an Allen-Bradley carbon thermometer.

The results of our measurements of the specific heat of anhydrous $CrCl_3$ in the temperature region from 4 to 20°K, and also the previously obtained data between 2 and 4°K[10] are listed in the table and are shown in Fig. 1 in coordinates C and T. The circles of Fig. 1 show also the data of Hansen and Griffel[9], who measured the specific heat of $CrCl_3$ above 12°K. Our data are in good agreement with the latter, differing from them only in the peak region by approximately 5%. The value $T_c = 16.8$°K, which corresponds to the transition from the antiferromagnetic state into the paramagnetic one

Specific heat of $CrCl_3$ (cal/mole-deg)

T, °K	C	T, °K	C	T, °K	C	T, °K	C
1.955	0,103	3.952	0,249	7.93	0.682	13.34	1.67
1.955	0.114	3.975	0,250	8,32	0.706	13.77	1,78
1.991	0,108	4,000	0,253	8.59	0.768	14,12	1,90
2.097	0,111	4,199	0.255	8,70	0.760	14.22	1.97
2.430	0,140	4.281	0,267	8,91	0.815	14.68	2,08
2.491	0.137	4.461	0.284	9.05	0.815	14,89	2.15
2.496	0.155	4,630	0.304	9.27	0.863	15.35	2.25
2.607	0,145	4,941	0,330	9,81	0,943	15.42	2,36
2.707	0.155	5.189	0,344	9,83	0.931	15.76	2.43
2.730	0.166	5.349	0.357	10.18	1,02	16,06	2,56
2.805	0.165	5,421	0.377	10,35	1.00	16.30	2,60
3.003	0.175	5,649	0.399	10,68	1,08	16.70	2.71
3.101	0.179	5.776	0,408	10,91	1,12	17.04	2.74
3.323	0.203	6.021	0,426	11,05	1,13	17.11	2.75
3,417	0.205	6.341	0.472	11.56	1.23	17.74	2.60
3.453	0.205	6.628	0.504	11,93	1.28	17,83	2.57
3.563	0.218	6,882	0.535	12.24	1,38	19.25	2.33
3.732	0.228	7,15	0.558	12.41	1,41	19,61	2.32
3.790	0.238	7.25	0.578	12.96	1,56		
3.815	0.229	7.75	0.653	13.04	1.59		

and was obtained from calorimetric measurements by others[8,9], agrees with our data. As seen from Fig. 1, the specific heat of $CrCl_3$ decreases smoothly with temperature below T_C, without any abrupt changes.

To separate the magnetic part of the specific heat, we plotted our results between 2 and 10°K in coordinates C/T and T^2 (Fig. 2), assuming that in the low-temperature region the lattice specific heat is proportional to T^3, and that the magnetic specific heat depends linearly on the temperature. We see that up to ~8°K the experimental points fit a straight line with a scatter ~3–4% (wider scatter of the experimental data is observed only at the lowest temperatures, below 2.8°K).

Thus, in the temperature region from 2 to 8°K, the specific heat of $CrCl_3$ can be described by the relation

$$C\,[\text{cal/mole-deg}] = 0.0535T + 5.11 \cdot 10^{-4}T^3, \tag{1}$$

and above 8°K there is a deviation from this relation.

Earlier, using the measurement results obtained only in the helium-temperature region from 2 to 4°K, the specific heat of $CrCl_3$ was described by the relation $C = aT + bT^3$, with $a = 5.1 \times 10^{-2}$ and $b = 7.1 \times 10^{-4}$ (the dashed straight line in Fig. 2). The new value of the coefficient, $a = 5.35 \times 10^{-2}$, differs little from the earlier one (by approximately 5%), while the coefficient $b = 5.11 \times 10^{-4}$ differs from the earlier one by approximately 30%.

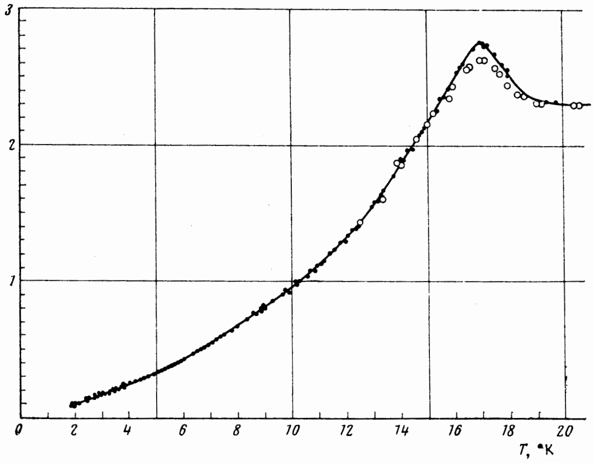

FIG. 1

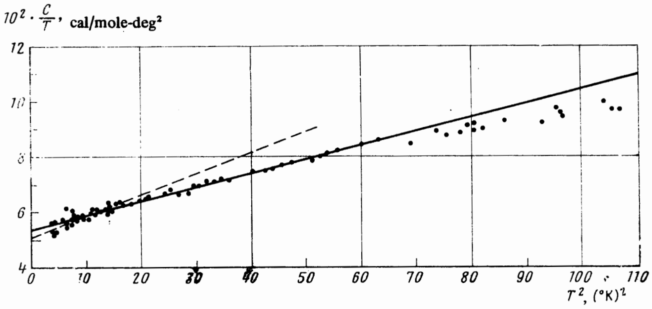

FIG. 2

Using the approximation of the two-dimensional ferromagnetic model with small anisotropy for the case of three nearest neighbors in a hexagonal plane lattice[3], we get for the magnetic specific heat

$$\frac{C_M}{R} = \frac{0.0535T}{R} = \frac{\pi k\sqrt{3}}{24J_f s}T. \tag{2}$$

From this we estimated the exchange ferromagnetic interaction in the layer ($s = 3/2$ for Cr ions):

$$J_f / k = 5.61° \text{ K}$$

Values of J_f/k close to ours were obtained by Narath and Davis from the results of the measurement of the magnetization of the $CrCl_3$ sublattices[5,6]. In the approximation of the two-dimensional model, in accordance with the data of Narath and Davis, $J_f/k = 4.5$°K, and using the three-dimensional model with allowance for the spin-wave interaction we get $J_f/k = 5.25$°K.

According to our measurements, a linear dependence of the magnetic specific heat on the temperature holds true up to 8°K, i.e., approximately up to $0.5T_C$. At higher temperatures, the deviation from the obtained relation (1) can be due either to the violation of the T^3 law for the lattice specific heat, or to the linear temperature dependence of the magnetic specific heat.

From measurements of the specific heats of a number of layered halides[13] it is known that below 4–5°K their lattice specific heat varies in accord with the T^3 law. For nonmagnetic cadmium halides[13], the measurements have shown that above 4–5°K and up to 10°K the exponent of T increases somewhat, apparently as a result of the contribution of the soft optical branches of the interlayer interaction, and at 7–8°K the deviation of the lattice specific heat from the T^3 law amounts to 10–15%. At higher temperatures (above 10°K), the anomalies inherent in layered lattices[15] are observed in the specific heat of cadmium halides.

As shown by the present measurements, the specific heat of the $CrCl_3$ lattice amounts to approximately 4% of its total specific heat at 2°K, and to 30% at 8°K, i.e., the magnetic specific heat is appreciably larger than the contribution of the lattice in this temperature region. Consequently, a small deviation from the cubic dependence of the specific heat of the $CrCl_3$ lattice (similar to that observed for cadmium halides above 4–5°K) cannot strongly influence the character of the linear temperature dependence obtained by us for the magnetic specific heat from 2 to 8°K, since this effect is comparable with the accuracy of our measurements at 7–8°K and decreases with decreasing temperature.

Thus it can apparently be assumed that our data on the specific heat of $CrCl_3$ reveal no noticeable deviations from the conclusions of the two-dimensional ferromagnetic model in the temperature region from 2 to 8°K.

In conclusion, we are deeply grateful to N. B. Brandt for interest in the work. We are most indebted to A. S. Borovik-Romanov for useful discussions.

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Translated by J. G. Adashko
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