SPECIFIC HEAT OF ANHYDROUS FERROUS CHLORIDE AT LOW TEMPERATURES

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The specific heat of anhydrous ferrous chloride was measured between 1.8 and 4° K and the magnetic contribution to the specific heat determined. The results obtained are compared with the conclusions of the spin wave theory.

THE specific heat of anhydrous ferrous chloride was measured between 4 and 1.8° K.

Antiferromagnetism in anhydrous iron-group halides was first predicted by Landau[1] and confirmed by neutron-diffraction studies.[2] In particular, in $FeCl_2$, which has a rhombohedral lattice and a layered structure, the spins of the metal ions are directed along a threefold axis c_3 and are located in layers perpendicular to this axis, being oriented parallel to one another in one layer, and opposite to one another in two neighboring layers.

The specific heat of $FeCl_2$ was measured earlier by Trapeznikova and Shubnikov[3] above 16° K and the results of these measurements, together with the data obtained by Itskevich and Strelkov[4] for the specific heat of isomorphous nonmagnetic $CdCl_2$, are given in Fig. 1. From these results, it is clear that at temperatures above the antiferromagnetic transition point of ferrous chloride (T_c = 23.6° K), the specific heat of this compound is close to the specific heat of $CdCl_2$. However, at $T < T_c$, right down to the lowest temperatures of the order of 16° K, the specific heat of $FeCl_2$ is greater than the specific heat of $CdCl_2$ because of the magnetic contribution.

To find the characteristic features of the temperature dependence of the magnetic specific heat of layered antiferromagnets, the present author carried out measurements of the specific heat of $FeCl_2$ below 4° K.

A sample of anhydrous ferrous chloride was prepared from the hydrated salt $FeCl_2 \cdot 4H_2O$ by drying in vacuum at temperatures up to 200° C, followed by sublimation at $\approx$ 670° C. The powdered sublimate of $FeCl_2$ was placed in a thin-walled quartz ampoule and fused. Since anhydrous ferrous chloride is very hygroscopic, the salt was not taken out from the ampoule but the ampoule was filled with a small amount of helium for heat exchange purposes and then sealed. A 40 g sample of anhydrous $FeCl_2$, enclosed in a thin-walled quartz ampoule, was placed in a calorimeter whose construction was described earlier.[5]

The results of the measurements of the specific heat of $FeCl_2$ between 4 and 1.8° K are given in Fig. 2 in the coordinates CT^2 and T^5. From these data, it follows that the specific heat of $FeCl_2$ below 4° K is described by the relationship

$$C\,[\,\text{cal.mole}^{-1}.\ \text{deg}^{-1}] = 3.7 \cdot 10^{-4}T^3 + 12 \cdot 10^{-3}T^{-2}, \quad (1)$$

where the cubic term is related to the lattice specific heat and the magnetic-spin specific heat.

The dashed line in Fig. 2 represents the specific heat of $CdCl_2$,[4] which was used to estimate the lattice contribution to the specific heat of ferrous chloride. The specific heat of $CdCl_2$ below $\sim 4.5°$ K obeys the cubic law

$$C = 2.75 \cdot 10^{-4}T^3 \ \text{cal. mole}^{-1}. \ \text{deg}^{-1}$$

and above 4.5° K it departs from the Debye curve, like other layered structures; the general relationships for the temperature dependence of the specific heat of several cadmium halides with layered structures were established by Itskevich and Strelkov.[4]

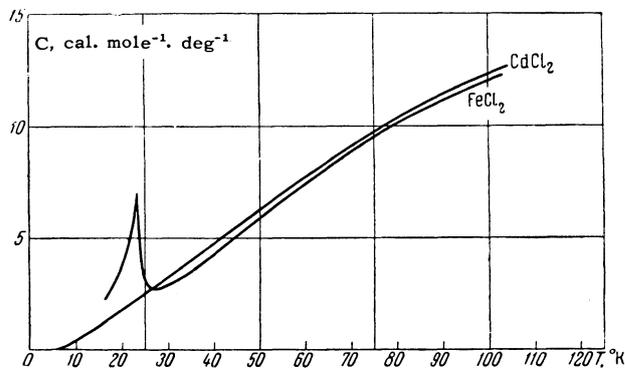The experimental points for $FeCl_2$ at rela-

FIG. 1

tively high temperatures (above 26°K) lie slightly above (up to 10%) the specific heat curve of $CdCl_2$ (Fig. 1) but the temperature dependence laws are very similar for the two compounds. Moreover, our measurements show that the cubic dependence of the lattice specific heat of $FeCl_2$ applies also below 4°K. Assuming that the laws of the temperature dependence of the lattice specific heats of $FeCl_2$ and $CdCl_2$ are similar right down to helium temperatures, we may conclude that the lattice specific heat of $FeCl_2$ is not greater than the specific heat of $CdCl_2$ even at low temperatures.

The difference between the cubic terms in the specific heats of $FeCl_2$ and $CdCl_2$ is

$$\Delta C = 3.7 \cdot 10^{-4}T^3 - 2.75 \cdot 10^{-4}T^3$$

$$\approx 1 \cdot 10^{-4}T^3 \text{ cal. mole}^{-1}.\text{deg}^{-1}$$

i.e., the cubic component of the specific heat of $FeCl_2$ is 36% greater than the specific heat of $CdCl_2$ at helium temperatures. The value $\Delta C = 1 \times 10^{-4} T^3$, extrapolated to the hydrogen temperature region, amounts to ~ 0.4 cal. $\text{mole}^{-1}.\text{deg}^{-1}$ at 16°K and the experimental data (Fig. 1) show that the specific heat of $FeCl_2$ is greater than the specific heat of $CdCl_2$ by ~ 0.9 cal. $\text{mole}^{-1}.\text{deg}^{-1}$ at 16°K. Obviously, the cubic temperature dependence of the spin specific heat, observed by the present author, does not apply at liquid hydrogen temperatures which are close to T_C.

The results obtained allow us to conclude that the magnetic specific heat of $FeCl_2$ at helium temperatures obeys a cubic law and contributes $C_m \sim 1 \times 10^{-4} T^3$ cal.$\text{mole}^{-1}.\text{deg}^{-1}$.

It should be noted that when the value $C_m = 1 \times 10^{-4} T^3$ is substituted into the spin wave formula[6] obtained for antiferromagnets magnetized along the principal axis

$$C_m = (8\pi^2 R/15)(T/\Theta_c)^3,$$

it is found that $\Theta_C = 48°K$, i.e., its order of magnitude is close to T_C. However, if we use the relationship

$$C_m/T\chi_\| = 4\pi^2 k^2/5g^2\beta^2$$

and the data of Bizette, Terrier and Tsäi,[7] taking the molar susceptibility at 4°K to be $\chi_\| \sim 0.05$ (which is quoted by Bizette et al. for the weakest fields), the calculated value of C_m at 4°K is found to be of the order of 2 cal.$\text{mole}^{-1}.\text{deg}^{-1}$, which is two orders of magnitude greater than the experimental value. This difference may be related to the fact that the susceptibility $\chi_\|$ of $FeCl_2$ depends on the field intensity even in weak
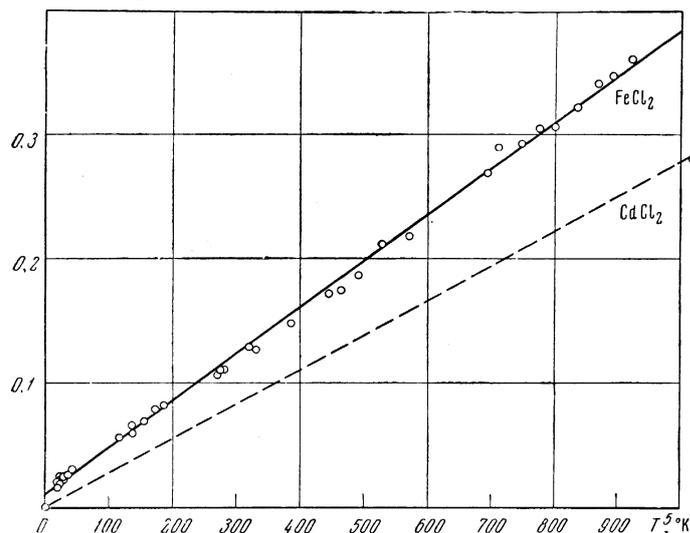
CT², cal. deg. mole⁻¹

FIG. 2

fields. It should be noted also that a consistent theoretical analysis of the energy spectra of layered antiferromagnets has not yet been carried out.

The presence in Eq. (1) for the specific heat of $FeCl_2$ of a term proportional to T^{-2} indicates the existence of a low-temperature anomaly, which is not related to the nuclear contribution of Fe^{2+} ions to the specific heat because the magnetic moments of ions are small. It is possible that this anomaly is due to the presence of traces of water in the sample (also the hydrated ferrous chloride may have a low antiferromagnetic transition temperature).

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