Letters to the Editor

Paramagnetic Relaxation in Monocrystals of Some Salts of the Iron Group Elements

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Studies of paramagnetic absorption in parallel fields at room temperature have so far been conducted only in powders of paramagnetic salts. Meanwhile, it follows from the theory of paramagnetic relaxation [1] that anisotropy of the constant of magnetic heat capacity b/c and the spin-lattice relaxation time ρ should be observed in monocrystals of paramagnetic salts.

Presented herein are the results of measurements of the coefficient of absorption χ in the monocrystalline salts $Cu(SO_4) \cdot 5H_2O$, $Mn(SO_4) \cdot 4H_2O$ and $Fe(NH_4) \cdot (SO_4)_2 \cdot 12H_2O$ as a function of the direction of the static magnetic field with respect to the crystallographic axes. The measurements were carried out using Zavoiskii's method.[2,3] Monocrystals fresh from the mother solution were used in the investigation; this has essential significance for the results.

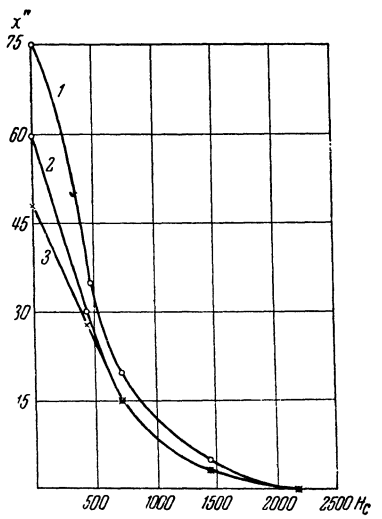

FIG. 1

A generator of the Esau type at a frequency of 6×10^8 cps was assembled for the measurement of the constant of magnetic heat capacity b/c. The monocrystal under study was formed into a sphere of 8 mm diameter. The direction of the magnetic axis was determined[4]. (In the monocrystal $Cu(SO_4) \cdot 5H_2O$, the magnetic axis coincides with the bisector between the tetragonal axes of symmetry). The sample was placed in the coil of the generator.

Measurement of the coefficient χ'' was carried out for three mutually perpendicular orientations of the crystal along the magnetic axis and in two directions perpendicular to the magnetic axis. The results of measurement of χ'' in the monocrystal $Cu(SO_4) \cdot 5H_2O$ as a function of H_c and the direction of the axis is shown in Fig. 1. It is clear from the figure that along the magnetic axis the null absorption (curve 1) is greater than in the direction perpendicular to it (curve 3). The dependence of χ'' on H_c in powdered $Cu(SO_4) \cdot 5H_2O$ is shown on the same Figure (curve 2). The constant of magnetic heat capacity is determined by the formula

$$b/c = \delta^2/0.41, \qquad (1)$$

where δ is the halfwidth of the experimental curve in oersteds[5]. Formula (1) results from Shaposhnikov's theory[6]. The results of measurements of b/c for a monocrystal along and perpendicular to the magnetic axis are:

$$(b/c)_{\parallel} = 0.4 \cdot 10^6\ (\mathrm{Oe})^2, \quad (b/c)_{\perp} = 0.6 \cdot 10^6\ (\mathrm{Oe})^2.$$

The magnetic heat capacity along the magnetic axis in the monocrystal $Cu(SO_4) \cdot 5H_2O$ is less than in the perpendicular direction by about 33%, i.e., to the same extent that the static susceptibility is greater. These results agree with the data of Krishnan and Mookherji[4] who found $\chi_{\parallel} = 1922 \times 10^{-6}$, $\chi_{\perp} = 1371 \times 10^{-6}$, and in powder $\chi_0 = 1555 \times 10^{-6}$.

For powdered $Cu(SO_4) \cdot 5H_2O$ our measurements yield $b/c = 0.47 \times 10^6\ (\mathrm{Oe})^2$ which agrees with data obtained earlier by Sitnikov[7].

Studies of paramagnetic relaxation in the monocrystals $Mn(SO_4) \cdot 4H_2O$ and $Fe(NH_4) \cdot (SO_4)_2 \cdot 12H_2O$ yield $b/c = 6.3 \times 10^6\ \mathrm{Oe})^2$ and $0.28 \times 10^6\ (\mathrm{Oe})^2$, respectively for the value of the constants of magnetic heat capacity, which agree with Gorter's data[8]. Here, no dependence of absorption on the orientation of the crystal in the magnetic field was observed.

A generator of the Esau type at a frequency of 10.5×10^6 cps was used for measurements of spin lattice relaxation times. The results of

measurements of χ'' as a function H_c and the direction of the crystallographic axes are shown in Fig. 2. It is clear from the Figure that the coefficient of absorption along the magnetic axis

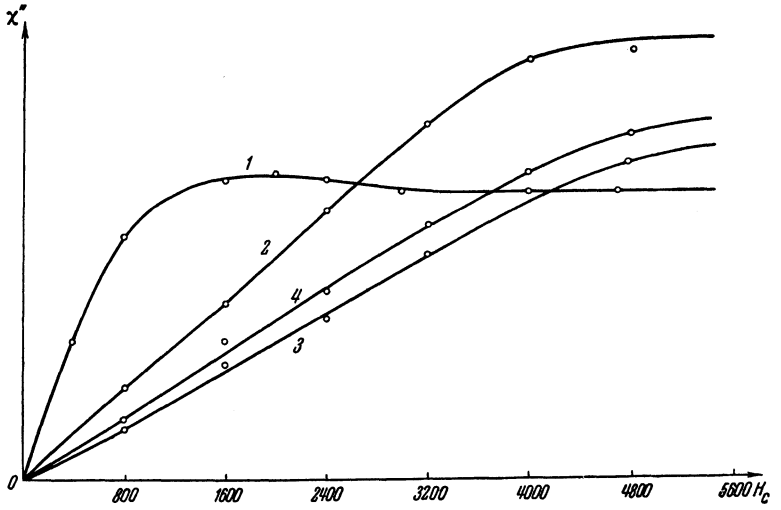

FIG. 2

$\chi''_{||}$ is smaller than in the perpendicular direction $\chi''_{\perp}$ by about 36%. Here, $\chi''_{\perp}$ differed by 10-12% for two mutually perpendicular orientations with respect to the magnetic axis. The mean of these values was used for $\chi''_{\perp}$ in Fig. 2. The measurements were carried out by comparison with a standard[7], for which the substance $Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O$. was used. In addition, a verification was carried out by means of a comparison of the effect on the substance $Mn(SO_4) \cdot 4H_2O$.

Curve 1, Fig. 2, refers to the substance $Mn(NH_4)_2(SO_4) \cdot 6H_2O$, curves 2 and 3 refers to a monocrystal of $Cu(SO_4) \cdot 5H_2O$, the magnetic axis of which was located respectively parallel to and perpendicular to the field H. Curve 4 was obtained for powdered $Cu(SO_4) \cdot 5H_2O$.

The spin-lattice relaxation time ρ was calculated according to the formula of Kazimir and du-Pre[8]

$$\chi'' = \chi_0 Fm \rho\nu / (1 + \rho^2\nu^2). \qquad (2)$$

Results of the measurement of spin-lattice relaxation time in the monocrystal $Cu(SO_4) \cdot 5H_2O$ are given in the Table. The relaxation times are denoted by ρ for the powder, and by $\rho_{||}$ and $\rho_{\perp}$ for the monocrystal. The magnitude ρ for powdered $Cu(SO_4) \cdot 5H_2O$ is approximately equal to the arithmetic mean of the relaxation times along the magnetic axis and perpendicular to it.

The measurement of ρ for the monocrystals $Mn(SO_4) \cdot 4H_2O$ and $Fe(NH_4)(SO_4)_2 \ 12H_2O$ also showed no dependence on the orientation of the crystals in the magnetic field.

TABLE

H_c (Oe)	$\rho \cdot 10^8$ sec	$\rho_{\perp} \cdot 10^8$ sec	$\rho_n \cdot 10^8$ sec
800	0.8	1.0	0.5
1600	1.1	1.4	0.9
2400	1.6	2.1	1.1
3200	2.1	2.9	1.3
4000	2.4	3.2	1.6
4800	2.8	3.3	1.8
5600	3.0	4.0	2.0

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Translated by D. Lieberman
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