

# SOVIET PHYSICS

# JETP

*A translation of the Zhurnal Éksperimental'noi i Teoreticheskoi Fiziki.*

Vol. 12, No. 3 pp. 365-625

(Russ. orig. Vol. 39, No. 3, pp. 521-901, Sept., 1960)

March, 1961

## INVESTIGATION OF PARAMAGNETIC RELAXATION IN MAGNETICALLY DILUTE SYSTEMS

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Submitted to JETP editor July 4, 1959; revised May 16, 1960

J. Exptl. Theoret. Phys. (U.S.S.R.) 39, 521-526 (September, 1960)

The internal magnetic field  $H_i$  and the splitting  $\delta$  are evaluated for some paramagnetic substances on the basis of measured values of the specific heat  $b$  of the spin-system and of its electric component  $b_e$ . It is experimentally demonstrated that by means of magnetic dilution it is possible to distinguish between the effects on the specific heat of the interaction between the magnetic ions and the electric and magnetic crystalline fields. It is also shown that the spin-lattice relaxation time depends on the concentration of the magnetic ions in the paramagnetic substance.

### 1. CALCULATION OF THE SPECIFIC HEAT

FOR ions of elements of the iron group situated in a crystalline lattice the interaction with the surroundings may be considered weak and may be treated as a perturbation: the interaction energy  $\epsilon_i \ll kT$  (cf., for example, references 1 and 2). Crystalline hydrates and their solutions are suitable materials in which such conditions are realized.

In crystals of salts of elements of the iron group the lowest orbital energy level of the ion  $E_1$  lies lower than the next level  $E_2$  by an amount  $E_2 - E_1 \gg kT$ . Moreover, the orbit of the ground level should be considered as fixed by the electric field of the crystal, and the orbital angular momentum should be taken as  $L = 0$ . Consequently, there remains the orbital singlet which is  $(2S + 1)$ -fold degenerate with respect to spin. This level is subject to the influence of the internal electric and magnetic fields, as a result of which the degeneracy is removed completely. The difference in energy between the highest and the lowest sublevels of the multiplet is  $\epsilon - \epsilon_0 \ll kT$ .

By setting up on the basis of the concepts of a free ion and of multiplet structure the spin partition function

$$Z^{\text{sp}} = \sum e^{-\epsilon_i/kT} \Omega(\epsilon_i)$$

[where  $\Omega(\epsilon_i)$  is the multiplicity of the sublevel  $\epsilon_i$ ] we can with the aid of the usual statistical formulas calculate the free energy, the entropy, and the specific heat. Let us discuss several concrete cases.

Spin  $S = 1/2$ . In this case the electric field does not affect the spin, and the remaining Kramers degeneracy is removed by the magnetic field of the crystal. Consequently, the specific heat will have its origin in the interaction of the magnetic ion with the magnetic field of the crystal. Then we have

$$Z^{\text{sp}} = 1 + e^{-\epsilon_1/T},$$

where  $\epsilon_1 - \epsilon_0 = k\Theta_1$  is the splitting of the sublevels of the multiplet in the magnetic field of the crystal. On taking into account the fact that  $\Theta_1 \ll T$  we obtain the following approximate expression for the molar specific heat of the spin system:

$$c = b_m T^{-2}, \quad b_m = 0.25 R \Theta^2. \quad (1)$$

Spin S = 1. Let the electric field have rhombic symmetry. Then the degeneracy will be already completely removed by the electric field. In this case the specific heat of the spin system has its origin in the interaction of the magnetic ions with the electric field of the crystal. In accordance with the symmetry of the field and with the value of the spin we have

$$Z^{\text{SP}} = 1 + e^{-\delta_1/T} + e^{-\delta_2/T},$$

where  $\delta_i$  is the splitting of the sublevels of the multiplet by the crystalline electric field. For the specific heat we obtain

$$c = b_e T^{-2}, \quad b_e = 0.222 R (\delta_1^2 + \delta_2^2 - \delta_1 \delta_2). \quad (2)$$

Spin S = 3/2. In this case the magnetic interactions are superimposed on the electric ones. On taking into account the value of the spin and the fact that the degeneracy is completely removed by the electric and the magnetic fields of the crystal, we can write

$$Z^{\text{SP}} = 1 + e^{-\Theta_1/T} + e^{-\delta_1/T} + e^{-(\delta_1 + \Theta_2)/T},$$

where  $\Theta_i$  and  $\delta_i$  are the splittings of the sublevels respectively due to the magnetic and the electric fields of the crystal. From this we obtain the following expression for the specific heat

$$c = b T^{-2},$$

$$b = \frac{3}{16} R \left\{ \Theta_1^3 + \Theta_2^3 - \frac{2}{3} \Theta_1 \Theta_2 - \frac{4}{3} \delta_1 (\Theta_1 - \Theta_2) + \frac{4}{3} \delta_1^3 \right\}. \quad (3)$$

If in the case  $S = 3/2$  we take into account the interaction of the ion with only the electric crystalline field (for example, of trigonal symmetry), then the partition function assumes the form

$$Z^{\text{SP}} = 2(1 + e^{-\delta_1/T}).$$

From this we obtain for the specific heat

$$c_e = b_e T^{-2}, \quad b_e = 0.25 R \delta_1^2. \quad (4)$$

Spin S = 5/2. We consider first the case when the degeneracy is removed completely by the electric and the magnetic fields of the crystal. On taking into account the value of the spin and the effect of the fields the partition function must be written in the form

$$Z^{\text{SP}} = 1 + e^{-\Theta_1/T} + e^{-\delta_1/T} (1 + e^{-\Theta_2/T}) + e^{-\delta_2/T} (1 + e^{-\Theta_3/T}),$$

where  $\Theta_i$  and  $\delta_i$  are, as before, the splittings of the sublevels due to the magnetic and the electric fields respectively. From this we obtain the following formula for the total specific heat of the spin-system

$$c = b T^{-2},$$

$$b = \frac{5}{36} R \left\{ \Theta_1^3 + \Theta_2^3 + \Theta_3^3 - \frac{2}{3} (\Theta_1 \Theta_2 + \Theta_1 \Theta_3 + \Theta_2 \Theta_3) - \frac{4}{3} (\delta_1 + \delta_2) (\Theta_1 + \Theta_2 + \Theta_3) + \frac{12}{5} (\delta_1 \Theta_2 + \delta_2 \Theta_3) + \frac{8}{5} (\delta_1^2 + \delta_2^2 - \delta_1 \delta_2) \right\}. \quad (5)$$

We can obtain an approximate formula for the electric component of the specific heat of the spin system for the same ion by setting in (5)  $\Theta_1 = \Theta_2 = \Theta_3 = 0$ :

$$c_e = b_e T^{-2}, \quad b_e = 0.222 R (\delta_1^2 + \delta_2^2 - \delta_1 \delta_2). \quad (6)$$

## 2. DEPENDENCE OF THE SPECIFIC HEAT OF THE SPIN SYSTEM ON THE CONCENTRATION OF MAGNETIC IONS

We have investigated the paramagnetic absorption in parallel fields at room temperature. The object of the investigation was to find the dependence of the specific heat  $b$  and the spin-lattice relaxation time  $\rho$  on the concentration of magnetic ions in paramagnetic substances.

The thermodynamic theory of paramagnetic relaxation in parallel fields due to Shaposhnikov<sup>3</sup> leads to the following formula for the imaginary part  $\chi''$  of the complex susceptibility:

$$\chi''/\chi_0 m = F/\rho\nu + (1 - F)^2 \rho_s \nu, \quad F = H_c^2/(b/C + H_c^2), \quad (7)$$

where  $\chi_0$  is the equilibrium susceptibility,  $m$  is the mass of the substance being investigated,  $\rho$  is the spin-lattice relaxation time,  $\rho_s$  is the spin-spin relaxation time,  $\nu$  is the frequency of the alternating field,  $H_c$  is the constant external field, and  $C$  is the Curie constant. Formula (7) refers to the case when  $\rho_s \ll \rho$ ,  $\rho_s \nu \ll 1$  and  $\rho \nu \gg 1$ . When  $\rho_s$  and  $\rho$  differ sufficiently from one another it is possible to choose the frequency  $\nu$  so large that the first term of formula (7) is much smaller than the second one. Then absorption will take place in accordance with the following formula

$$\chi''/\chi_0 m = (1 - F)^2 \rho_s \nu \quad (8)$$

and will be due only to internal relaxation. This is exactly what occurs at the 600 Mc/sec which we used.

Formula (8) has been checked in a number of investigations,<sup>4,5</sup> and has been found to agree well with experiment if we assume that  $\rho_s$  does not depend on the constant field  $H_c$ . Formula (8) enables us to evaluate the constant  $b/C$  from the absorption curve.

The absorption curve whose ordinates are proportional to  $\chi''$  was obtained by utilizing the

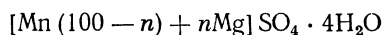
grid current method proposed by Zavoiskii.<sup>6</sup> A detailed description of the oscillator used by us has been given by Salikhov.<sup>7</sup>

On assuming that the electric field of the crystal retains its symmetry on dilution (isomorphism) and that, consequently, the contribution to the specific heat due to the interaction of the magnetic ions with the electric field of the crystal does not depend on the concentration of the magnetic ions, we can measure this specific heat by eliminating the magnetic component by means of magnetic dilution of the paramagnetic substance.<sup>8</sup>

For this purpose we prepared solid solutions of potassium chrome alum in which chromium ions are replaced by aluminum ions:



and also of the hydrate of manganese sulphate, in which manganese ions are replaced by magnesium ions:



( $n$  is the concentration of the diamagnetic  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  ions in these solutions). A single crystal grown in a solution of appropriate concentration was pulverized prior to the experiment and an ampoule containing this powder was placed inside the coil that produced the high-frequency field. This coil was placed in the gap of a magnet parallel to the constant field. The chromium and manganese concentrations in the solutions were determined chemically.

The absorption curves obtained as functions of the constant field  $H_C$  in solutions of chrome alum with different concentrations of the magnetic ions are shown in Fig. 1. It turns out that these curves are in good agreement with formula (8), and this allows us to evaluate the constant  $b/C$ .

The values of the constant  $b/C$  obtained for different concentrations of the magnetic ions are shown in Fig. 2. It may be seen from the figure that the constant  $b/C$  falls off rapidly with the magnetic dilution approaching the value

$$(b/C)_e = 0.22 \cdot 10^6 \text{ oe}^2. \quad (9)$$

Thus, in the case of chrome alum the following quantities are obtained from the measurements: the values of the total constant  $b/C$  (cf. reference 5) and of its electric component  $(b/C)_e$ . Then, on taking into account the additive properties of specific heat, we can also obtain the magnetic component of this quantity:

$$b/C = (b/C)_m + (b/C)_e. \quad (10)$$

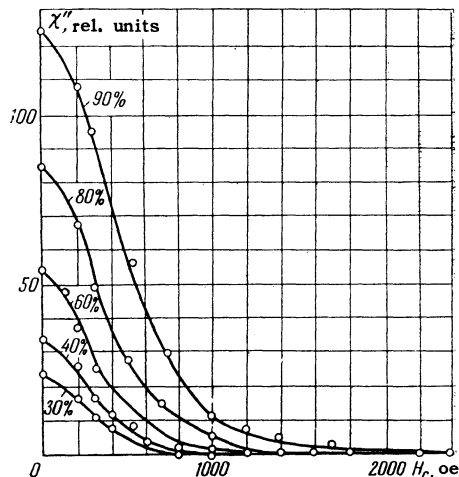


FIG. 1. Absorption curves in solid solutions of potassium chrome alum. Numbers beside the curves indicate the concentration of magnetic ions in solution;  $\nu = 600 \text{ Mc/sec}$ .

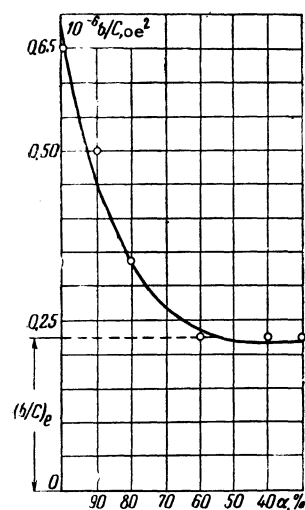


FIG. 2. Dependence of the constant  $b/C$  for the spin system on the concentration  $\alpha$  of magnetic ions in solutions of potassium chrome alum. Circles indicate measured values of  $b/C$ .

The values of these quantities are shown in Fig. 2.

The paramagnetic absorption curves in solutions of the hydrate of manganese sulphate with a concentration of magnetic ions equal to 90, 80, 60, 50, 20, and 10% are similar to the curves of Fig. 1; we do not reproduce them here.

The dependence of  $b/C$  on the concentration of magnetic ions is shown in Fig. 3. From this figure it can be seen that in this case  $b/C$  falls off rapidly with magnetic dilution, approaching the constant value

$$(b/C)_e = 0.40 \cdot 10^6 \text{ oe}^2. \quad (11)$$

Thus experiments have shown that it is possible to distinguish between the effects on the specific heat of a spin-system due to the interaction of the magnetic ions with the electric and the magnetic fields of the crystal.

**3. DEPENDENCE OF THE SPIN-LATTICE RELAXATION TIME ON THE CONCENTRATION OF THE MAGNETIC IONS**

At sufficiently low frequencies paramagnetic absorption in parallel fields is determined only by spin-lattice relaxation (cf. Sec. 2) and takes place in accordance with the first term in formula (7), the exact expression for which (cf. reference 9) is of the following form

$$\chi'' / \chi_0 m = \rho \nu F / (1 + \rho^2 \nu^2). \quad (12)$$

We have utilized formula (12) for the measurement of  $\rho$  in solid magnetic solutions of  $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  and  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$  (cf. reference 10). The absorption in these salts was studied at 7 and 13 Mc/sec respectively. The absorption curves in potassium chrome alum are shown in Fig. 4. The absorption curves in manganese sulphate are just as representative of spin-lattice relaxation as

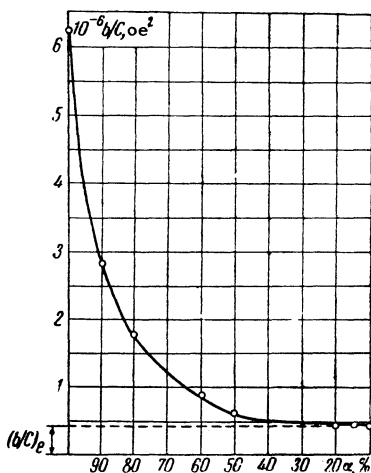


FIG. 3. Dependence of the constant  $b/C$  for the spin system on the concentration  $\alpha$  of magnetic ions in manganese sulphate.

those shown in Fig. 4, and are therefore not reproduced here.

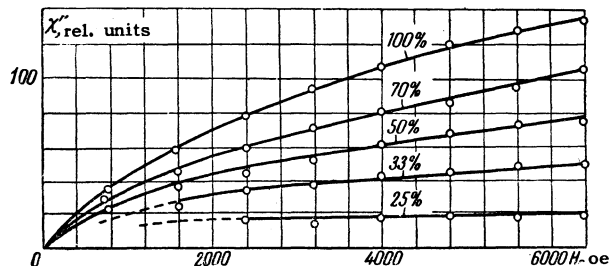


FIG. 4. Absorption curves in solid solutions of potassium chrome alum. Numbers beside the curves indicate the concentration of magnetic ions in solution;  $\nu = 7$  Mc/sec.

The calculated values of  $\rho$  for different concentrations of magnetic ions in the solutions, and for different values of the constant field  $H_c$  are given in Tables I and II for potassium chrome alum and for manganese sulphate respectively. It can be seen from the tables that the spin-lattice relaxation time increases as the concentration of magnetic ions in solution is decreased. The observed increase in the spin-lattice relaxation time ceases in chrome alum at a magnetic dilution by a factor of approximately two, and in manganese sulphate by a factor of approximately four, which is evidently related to the concentration of magnetic ions in the initial material. It should be noted that the observed effect is more pronounced in weak fields.

**4. EXAMPLES OF THE EVALUATION OF THE CONSTANTS  $\delta$  AND  $H_i$**

$\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ . Let us evaluate the splitting of the sublevels by the electric field of the crystal

TABLE I. Spin-lattice relaxation time  $\rho$  in potassium chrome alum for different concentrations  $\alpha$  of  $\text{Cr}^{3+}$  ions

$H_c$	$\rho, 10^{-4}$ sec					$H_c$	$\rho, 10^{-4}$ sec				
	$\alpha = 100\%$	70%	50%	33%	25%		$\alpha = 100\%$	70%	50%	33%	25%
800	0.3	0.5	0.6			4000	1.2	1.4	1.6	1.5	1.7
1600	0.5	0.8	0.9	1.0	1.0	4800	1.3	1.5	1.6	1.8	1.8
2400	0.8	1.0	1.2	1.3	1.3	5600	1.4	1.6	1.9	2.0	2.1
3200	1.0	1.2	1.4	1.5	1.6	6400	1.4	1.9	2.3	2.4	2.3

TABLE II. Spin-lattice relaxation time in manganese sulphate for different concentrations of  $\text{Mn}^{2+}$  ions

$H_c$	$\rho, 10^{-7}$ sec					$H_c$	$\rho, 10^{-7}$ sec				
	$\alpha = 100\%$	60%	33%	25%	10%		$\alpha = 100\%$	60%	33%	25%	10%
800	3.4	11.0	13.9	14.1		4000	7.5	14.1	19.8	20.5	21.0
1600	4.1	12.5	17.0	18.0		4800	8.6	15.6	20.5	21.0	22.0
2400	5.2	13.0	18.4	18.3	18.2	5600	9.6	16.0	21.0	22.0	22.0
3200	6.4	13.4	18.7	20.0	20.0	6400	10.0	16.6	21.0	22.0	22.0

in this salt. On comparing (4) and (9), and on utilizing the value  $C = 1.87$  for the Curie constant, we obtain  $\delta_1 = 0.14^\circ$ , which agrees with the value  $\delta_1 = 0.17^\circ$ , obtained by other investigators.<sup>11,12</sup>

On substituting into formula (3) the numerical values  $b/C = 0.66 \times 10^6$ ,  $C = 1.87$ ,  $\delta_1 = 0.14^\circ$ , and on setting in accordance with Hund's rules  $\Theta_1 = \sqrt{15}\beta H_i/k$  and  $\Theta_2 = \sqrt{3}\beta H_i/k$  ( $\beta$  is the Bohr magneton), we obtain  $H_i = 1170$  oe.

MnSO<sub>4</sub> · 4H<sub>2</sub>O. In accordance with formula (6) we obtain for the value of the splitting  $\delta_{\text{eff}} = 0.30^\circ$  (the Curie constant is  $C = 4.37$ ). In formula (6) we have set  $\delta_1 = \delta_2$ . This is possible because  $\delta_1, \delta_2 \ll T$  and the sublevels may be regarded as coincident. The value of  $\delta_{\text{eff}}$  for MnSO<sub>4</sub> · 4H<sub>2</sub>O is apparently measured here for the first time.

For the evaluation of the internal field  $H_i$  in the same salt we again set  $\delta_1 = \delta_2$  in formula (5). Further, on substituting the numerical values  $b/C = 6.20 \times 10^6$ ,  $C = 4.37$ ,  $\delta_{\text{eff}} = 0.30^\circ$  and on setting in accordance with Hund's rules  $\Theta_1 = \sqrt{35}\beta H_i/k$ ,  $\Theta_2 = \sqrt{15}\beta H_i/k$  and  $\Theta_3 = \sqrt{3}\beta H_i/k$ , we obtain  $H_i = 3913$  oe.

CuSO<sub>4</sub> · 5H<sub>2</sub>O. On substituting into formula (1) the numerical value  $b/C = 0.47 \times 10^6$ , and the Curie constant  $C = 0.37$  we obtain  $H_i = 790$  oe.

In accordance with Gorter's estimate<sup>9</sup> made on the basis of the concept of dipole-dipole interaction, the internal field  $H_i$  in CrK(SO<sub>4</sub>)<sub>2</sub> · 12H<sub>2</sub>O,

MnSO<sub>4</sub> · 4H<sub>2</sub>O, and CuSO<sub>4</sub> · 5H<sub>2</sub>O is respectively equal to 310, 1200, and 370 oe.

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Translated by G. Volkoff