

*PARAMAGNETIC RELAXATION IN SINGLE CRYSTALS OF CERTAIN SALTS OF THE  
ELEMENTS OF THE IRON GROUP*

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Submitted to JETP editor April 27, 1957

J. Exptl. Theoret. Phys. (U.S.S.R.) **33**, 856-860 (October, 1957)

Measurements have been made of the constant  $b/c$  ( $b$  = constant of magnetic thermal capacity,  $c$  = Curie constant) and the spin-lattice relaxation time  $\rho$  in single crystals of certain paramagnetic salts. The dependence of  $b/c$  and  $\rho$  on the direction of the static magnetic field  $H$  relative to the crystallographic axes has been found in the copper sulfates  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . The anisotropy of  $b/c$  and  $\rho$  has not been detected, within experimental error, in single crystals of  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ,  $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .

### 1. INTRODUCTION

UP to the present time, investigations on paramagnetic absorption in parallel fields at room temperature have been carried out only on powders of paramagnetic salts. However, one can expect that a dependence ought to exist of the constant  $b/c$  and the spin-lattice relaxation time on the orientation of the external magnetic field  $H$  relative to the crystallographic axes.<sup>1</sup> The presence of such a dependence for the quantity  $b/c$  follows from the anisotropy of the static magnetic susceptibility,<sup>2</sup> and consequently of the transition probability  $A_{hk}$  between the energy levels of the spin system under the action of the vibrations of the lattice.<sup>3</sup> The transition probability  $A_{hk}$  at room temperature is determined by processes of Raman scattering of phonons.

In consequence of the fact that the energy of the phonons is on the average extremely large in comparison with the intervals between adjacent energy levels of the spin-system, the dependence of  $A_{hk}$  on the orientation of the field  $H$  should be weak. For isotropic paramagnets, the dependence of  $\rho$  on the field  $H$  is determined by the Van Vleck-Brons formula:

$$\rho = \rho_0 \frac{b/c + H^2}{b/c + pH^2}, \quad (1)$$

where  $\rho \approx 1$ , and for single crystals it will probably be the same. From all of the above, it follows that the anisotropy of the relaxation time at room temperature ought not to be large, but of the order of several per cent. However, experimental investigations that we have carried out show that the anisotropy of  $\rho$  in single crystals of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is much larger.

We have carried out measurements of the absorption coefficient  $\chi''$  in single crystals of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  and  $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  as a function of the magnitude and direction of the static magnetic field relative to the crystallographic axes. The constant  $b/c$  was determined by a measurement of  $\chi''$  at a frequency of  $6 \times 10^8$  cps. Measurements of the paramagnetic absorption, which is due to the spin-lattice interaction, were carried out at a frequency of 10.5 megacycles. For measurement, we made use of the grid current method of Zavoiskii.<sup>4,5</sup> The single crystals were prepared fresh from the mother solution.

### 2. RESULTS OF MEASUREMENT

1. For measurement of the constant  $b/c$ , we used an Esau circuit as an oscillator with a frequency of  $6 \times 10^8$  cps. The directions of the magnetic axes in the single crystals were determined in correspondence with published works.<sup>2,6</sup> The single crystal investigated was in the form of a sphere of diameter 8 mm.

According to Ref. 7, an individual cell in the single crystal  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  contains two ions of  $\text{Cu}^{++}$ .

Each ion is located in a field of tetragonal symmetry, where the tetragonal axes form angles of  $82^\circ$  with each other. The bisectrix of the acute angle between them will be denoted by  $\alpha$ , that of the obtuse angle by  $\beta$ , the normal to the  $(\alpha\beta)$  plane by  $\gamma$ . These three directions represent the three fundamental magnetic axes.<sup>8</sup> In Refs. 2 and 8 it was established that the magnetic static susceptibility  $\chi_0$  and the g-factor are also isotropic for directions lying in the  $(\alpha\beta)$  plane; these quantities differ markedly from their values in the  $(\alpha\beta)$  plane only in the  $\gamma$  direction. The Tutton salts  $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  have a structure similar to the structure of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .<sup>6,8</sup>

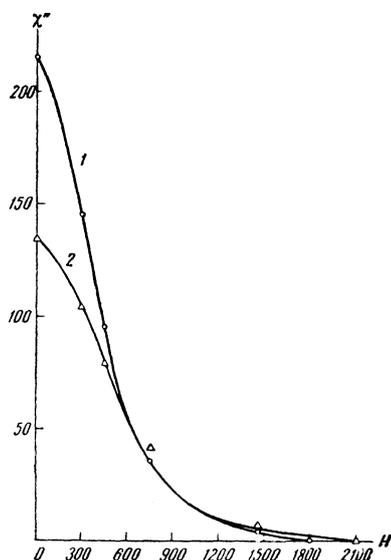
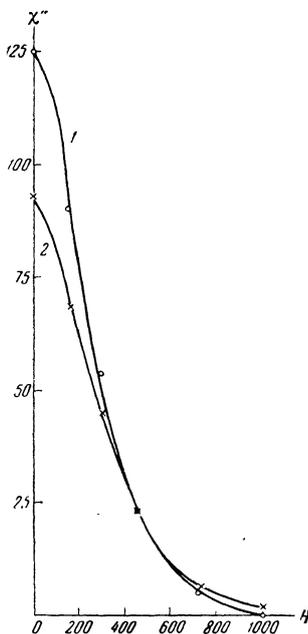


FIG. 1. Absorption curves in a single crystal of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  at a frequency of  $6 \times 10^8$  cps as a function of the direction of the magnetic axes  $\alpha$  and  $\gamma$  in relation to H.



Measurements of the paramagnetic absorption  $\chi''$  were carried out in their dependence of the magnitude and direction of H relative to the single crystal.\* The values of  $\chi''$  for each salt differ along the axes  $\alpha$  and  $\beta$  by not more than 5–10%. The values of  $\chi''$  along the  $\gamma$  axis are significantly less than the first two. We exhibit the results of measurement for the two directions:  $\alpha$  and  $\gamma$ .

Results of measurement have been plotted in Figs. 1 and 2 for the salts  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , respectively (the curves for  $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  have not been

FIG. 2. Absorption curves in a single crystal of  $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  at a frequency of  $6 \times 10^8$  cps as a function of the direction of the magnetic axes  $\alpha$  and  $\gamma$  relative to H.

plotted). In each figure, curve 1 corresponds to the direction  $\alpha$ , curve 2 to the direction  $\gamma$ . It is evident from the drawings that the zero field absorption along the  $\gamma$  axis is less than along the  $\alpha$  axis; the half width  $\delta$  along the  $\gamma$  axis is greater in comparison with the half width along the  $\alpha$  axis. These curves are well described by Shaposhnikov's formula:<sup>9</sup>

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

where  $F = H^2 / ((b/c) + H^2)$ ,  $\rho_s$  is the isothermal spin-spin relaxation time, which does not depend on H, and  $\nu$  is the frequency of the variable field.

The experimental points lie along the theoretical curve. If we assume that  $\rho_s$  does not depend on the field, then we obtain a relation for b/c from Eq. (2):<sup>10</sup>

$$b/c = (1 + \sqrt{2}) \rho^2. \quad (3)$$

The resultant values of the quantity b/c, expressed in oersteds, are given in Table I. It is seen from this table that the value of b/c for each salt is, with some approximation, inversely proportional to the magnetic static susceptibility  $\chi_0$ .† Along the axis of magnetic symmetry  $\gamma$ , the quantity b/c is significantly larger than in the direction perpendicular to this axis. This direction lies in the  $(\alpha\beta)$  plane. The results obtained for powders agree with Refs. 3 and 11. The values of b/c computed from  $\chi''$ , and obtained for different oscillator frequencies of the same order, agree with each other to within 5%.

\*  $\chi''$  is expressed in relative units, H in oersteds.

† The static susceptibility  $\chi_0$  for powders was measured by the authors by the method of Gouy. The values of  $\chi_0$  for single crystals have been obtained on the basis of these results.<sup>2,8</sup>

TABLE I

Material	Powder		Single Crystal			
			$\alpha$ axis		$\gamma$ axis	
	$b/c \cdot 10^{-4}$	$\chi_0 \cdot 10^4$	$b/c \cdot 10^{-4}$	$\chi_0 \cdot 10^4$	$b/c \cdot 10^{-4}$	$\chi_0 \cdot 10^4$
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	0.47	6.1	0.40	6.60	0.60	5.50
$\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	0.16	3.8	0.16	4.50	0.22	3.75
$\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	0.12	3.3	0.11	3.62	0.15	3.03

Investigations of the paramagnetic relaxation in the single crystals  $\text{Mn}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  and  $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  give values for  $b/c$  of  $6.3 \times 10^6$ ,  $0.64 \times 10^6$ ,  $0.28 \times 10^6$ , and  $0.65 \times 10^6$ , respectively. These agree with the data of Gorter.<sup>3</sup> Here, within the limits of experimental error (5%) no dependence of  $b/c$  on the orientation of the single crystal in a magnetic field was observed.

2. The results of the measurement of the absorption coefficient in its dependence on the magnitude and direction of the external magnetic field  $H$  relative to the crystallographic axes, carried out at a frequency of 10.5 megacycles in single crystals of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  have been plotted in Fig. 3. Curves 1 and 2 correspond to the directions  $\alpha$  and  $\gamma$  for  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , curve 3, to powders of this same salt; curves 5 and 6 correspond to the directions  $\alpha$  and  $\gamma$  for  $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ; curve 4, as a standard.

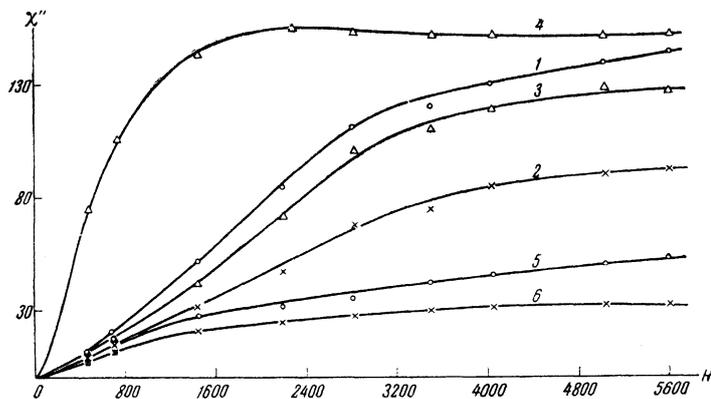


FIG. 3. Absorption curves in single crystals of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  at a frequency of 10.5 megacycles as a function of the direction of the magnetic axes  $\alpha$  and  $\gamma$  relative to the field  $H$ .

TABLE II

Material	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$				$\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$			$\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$		
	Powder $\rho \cdot 10^6$	$\alpha$ axis $\rho_\alpha \cdot 10^6$	$\beta$ axis $\rho_\beta \cdot 10^6$	$\gamma$ axis $\rho_\gamma \cdot 10^6$	Powder $\rho \cdot 10^6$	$\alpha$ axis $\rho_\alpha \cdot 10^6$	$\gamma$ axis $\rho_\gamma \cdot 10^6$	Powder $\rho \cdot 10^6$	$\alpha$ axis $\rho_\alpha \cdot 10^6$	$\gamma$ axis $\rho_\gamma \cdot 10^6$
800	1.0	1.0	1.0	0.8	0.8	0.8	0.8	0.8	0.8	0.8
1600	1.5	1.5	1.4	1.2	1.0	1.2	1.0	9.9	0.9	0.9
2400	2.0	2.5	2.3	1.7	1.2	1.3	1.1	1.0	1.0	0.9
3200	2.5	3.0	2.7	2.0	1.3	1.4	1.2	1.0	1.0	0.9
4000	2.8	3.3	3.0	2.2	1.4	1.5	1.3	1.0	1.0	0.9
4800	3.0	3.5	3.2	2.3	1.4	1.5	1.3	1.0	1.0	0.9
5600	3.1	3.6	3.3	2.4	1.4	1.5	1.3	1.0	1.0	0.9

where a small anisotropy was observed, the results are given for the three axes  $\alpha$ ,  $\beta$ ,  $\gamma$ . The data of Table II show that in the copper sulfates, the relaxation time  $\rho$  is a function of the anisotropy. The dependence of  $\rho$  on the direction of the external magnetic field  $H$  is most clearly demonstrated in the crystals of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . It is also of interest that where there is a large anisotropy of the relaxation time, the dependence of it on the magnitude of the applied external field  $H$  is also significant.

The results obtained for powders are described approximately by the relation  $\rho = \frac{1}{3}(2\rho_\alpha + \rho_\gamma)$ .

A theoretical account of these results has been given by Bashkirov.<sup>13</sup>

\* The previously published preliminary communication<sup>12</sup> contained inaccuracies connected with the determination of the magnetic axes.

If as seen from the drawings that the values of  $\chi''$  along the axis are much smaller than in the  $\gamma$  direction, for  $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , these values differ by 1.4–1.5 times, while in the case of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , they differ by 1.6–1.7 times (in strong fields).

Measurements were carried out by a comparison method<sup>10,11</sup> with a single crystal of  $\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  as a standard. Furthermore, a check was made on the results by comparison with the effect on a single crystal of  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ .

Measurements of  $\chi''$  as a function of  $H$  for the salts  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  and  $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  show that the absorption does not depend on the orientation of the single crystal in the static field  $H$ . The experimental errors in all cases did not exceed 4%.

On the basis of the results of measurement of  $\chi''$  at a frequency of 10.5 megacycles, and of the values of  $b/c$  obtained in Sec. 1, we determined the spin-lattice relaxation times in the copper sulfates. The calculation of  $\rho$  was carried out by the formula of Casimir and DuPre,<sup>3</sup> which coincides at the given frequency with the formula of Shaposhnikov:<sup>9</sup>

$$\chi'' = \chi_0 F m \frac{\rho v}{1 + \rho^2 v^2} \quad (4)$$

The results of the calculation for  $\rho$  are shown in Table II.\* For  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,

## CONCLUSIONS

1. The constant  $b/c$  was measured as a function of the orientation of the magnetic field relative to the crystal, and is approximately inversely proportional to the static susceptibility.

2. In copper sulfates, an anisotropy was discovered in the spin-lattice relaxation time. In this case, the relaxation time is shortest when the magnetic field is directed parallel to the  $\gamma$  axis.

3. The anisotropy of  $\rho$  in crystals of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is much greater than in the two copper sulfates  $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .

4. In single crystals of  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ,  $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , no dependence of the values  $b/c$  and  $\rho$  on the orientation of the external magnetic field was observed.

The author expresses his deep gratitude to S. A. Al'tshuler for suggestion and direction of the work, and also to B. M. Kozyrev and K. P. Sitnikov for their interest in the work.

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Translated by R. T. Beyer

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SOVIET PHYSICS JETP

VOLUME 6 (33), NUMBER 4

APRIL, 1958

*A GROUP-THEORETICAL CONSIDERATION OF THE BASIS OF RELATIVISTIC QUANTUM MECHANICS. I.*

*THE GENERAL PROPERTIES OF THE INHOMOGENEOUS LORENTZ GROUP*

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Submitted to JETP editor May 17, 1956

J. Exptl. Theoret. Phys. (U.S.S.R.) **33**, 861-872 (October, 1957)

This paper is the first of a series in which the possibilities of relativistic quantum mechanics are investigated on the basis of group theory, without the use of any specific form of the equations of motion. In the present paper we discuss some of the general properties of group representations as well as some of the specific properties of the representations of the inhomogeneous Lorentz group.

1. INTRODUCTION

THE requirements of invariance of quantum mechanics with respect to some group of transformations of space-time impose quite rigid restrictions on possible wave functions (state vectors): The wave function must transform according to one of the linear representations of the particular group. The most