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PARAMAGNETIC RELAXATION IN POTASSIUM CHROMIUM SULFATE AND AMMONIUM IRON SULFATE

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A phase transition in the interval from 90 to 300°K was detected by the paramagnetic relaxation method in single crystals of chromium potassium sulfate and ammonium iron sulfate.

THE author has shown earlier[1,2] that the 546-Mcs spin-spin absorption in parallel fields at room temperature diminishes monotonically in certain salts of Mn^{++} and Gd^{+++} with increasing constant magnetic field $H_{\parallel}$. The experimental curves obtained fit well the approximate formula

$$\chi''/\chi_0 = (1 - F)^2 \rho_s \nu, \quad F = \frac{b/c}{[(b/c) + H_{\parallel}^2]}, \qquad (1)$$

where ν is the frequency of the alternating magnetic field H_ν, and ρ_S is the isothermal spin-spin relaxation time, independent of $H_{\parallel}$. Formula (1) follows from the general theory of Shaposhnikov[3] provided $1/\rho_S < \nu < 1/\rho_L$. Formula (1) leads to a relation for b, the constant of the magnetic heat capacity of the spin system:

$$b = (1 + \sqrt{2})\, C\, (\Delta H_{\parallel})^2, \qquad (2)$$

where C is the Curie constant and $\Delta H_{\parallel}$ is the half-width of the absorption curve $\chi^{\parallel}(H_{\parallel})$. A good agreement between the Shaposhnikov theory and experiment was also reported in references 4 to 6.

1. MEASUREMENT PROCEDURE

A point-by-point measurement consumes much time and does not always disclose the details of complicated $\chi''(H_{\parallel})$ curves. In the present work we used, instead of a static magnetic field, a 50-cycle magnetic field of amplitude up to 2500 Oe. The $\chi''(H)$ curves were displayed on an oscillograph screen. The magnetic field was calibrated by resonance from the free radical of $\alpha\alpha$-diphenyl-β pycril-hydrazil at a frequency of 600 Mcs. The measurement procedure was described in detail in reference 7 and verified with Tutton's salt ($MnNH_4SO_4 \cdot 6H_2O$). The $\chi''(H_{\parallel})$ curve obtained for this salt in the frequency range from 600 to 300 Mcs and in the temperature interval from 300 to 90°K diminishes monotonically with increasing field $H_{\parallel}$. In this case $\Delta H_{\parallel}$ remains constant as the temperature is varied from 90 to 300°K. The experimental $\chi''(H_{\parallel})$ curve fits formula (1) with $\rho_S = \text{const}$ and $b/c = 0.61 \times 10^6$ Oe^2. At $T = 90$°K the intensity of $\chi''(H_{\parallel})$ is approximately three times the intensity at room temperature.

We used $CuCl_2 \cdot 2H_2O$ to verify that H_ν and $H_{\parallel}$ are parallel. In this salt, $T_1 = T_2 = 8.1 \times 10^{-10}$ sec, owing to the large exchange interactions in the perpendicular field, and the absorption $\chi''(H_{\parallel})$ is independent of $H_{\parallel}$ in parallel fields.[8]

When measuring the paramagnetic relaxation and the proton resonance in single crystals of the alums, the magnetic field $H_{\parallel}$ was oriented along one of the diagonals of the elementary cube.

2. MEASUREMENT RESULTS

$CrK(SO_4)_2 \cdot 12H_2O$

This salt was investigated in detail in a wide range of temperatures, using both the paramagnetic-relaxation method in parallel fields,[4,9,10] and the method of resonant absorption in the microwave band.[11-13]

Paramagnetic-resonance measurements[13] have shown that there is a phase transition in potassium chromium sulfate, and that therefore the initial splitting of spin doublets depends on the temperature (see Table I).

Investigations[10] of paramagnetic relaxation $T = 90$°K give a value $b/c = 0.64 \times 10^6$ Oe^2 and a spin-lattice relaxation time $\rho_L(H_{\parallel} = 0) = 2.5 \times 10^{-7}$ sec. Since ρ_L is on the order of 10^{-7} sec, the spin-spin relaxation plays the predominant role in the frequency range from 600 to 50 Mcs. The experimental $\chi''(H_{\parallel})$ curve (see Fig. 1a) which we obtained at 545 Mcs and $T = 90$°K, does not fit the theoretical $\chi''(H_{\parallel})$ curve, calculated with formula (1) for $\rho_S = \text{const}$ and $b/c = 0.64 \times 10^6$

TABLE I

$T°$ K	293	193	90	20
δ, cm^{-1}	0.12	0.055	$\left\{\begin{matrix}0.15\\0.26\pm0.01\end{matrix}\right.$	$\left\{\begin{matrix}0.15\pm0.01\\0.27\pm0.003\end{matrix}\right.$

Oe^2. In this case the theoretical curve for $H_{\|} \neq 0$ passes above the experimental $\chi''(H_{\|})$ curve. Our experimental $\chi''(H_{\|})$ curve also fails to fit formula (1) for $b/c = 0.79 \times 10^6$ Oe^2, determined from the structure of the microwave magnetic-resonance spectra[13,14] under the assumption that the potassium chromium sulfate contains approximately 80% Cr^{+++} ions with $\delta = 0.15$ cm^{-1} and 20% with $\delta = 0.27$ cm^{-1}.

When $\Delta H_{\|} = 370$ Oe relation (2) gives $b/c = 0.33 \times 10^6$ Oe^2. This low value of b/c is in contradiction with the b/c values given above. At 200°K and 545 Mcs, the $\chi''(H_{\|})$ curve (see Fig. 1b) corresponds to spin-lattice absorption. At this frequency, spin-lattice relaxation is observed only when ρ_L is on the order of 10^{-9} sec.

When the temperature is raised to room temperature (295°K) the spin-lattice absorption is seen to weaken and spin-spin absorption appears. It follows hence that the time ρ_L is on the order of 10^{-8} sec. Further increase of the temperature, to 320°K, increases the time further to an order of 5×10^{-8} sec. This is why spin-spin absorption plays a predominant role at this frequency, while the absorption due to the spin-lattice relaxation is vanishingly small. A maximum absorption is seen now in $\chi''(H_{\|})$ at $H_{\|} = 480$ Oe (see Fig. 1c). It is impossible to calculate b/c from relation (2), owing to the presence of a maximum on $\chi''(H_{\|})$.

At 75 Mcs and 90°K the maximum of $\chi''(H_{\|})$ in $CrK(SO_4)_2 \cdot 12H_2O$ occurs at $H_{\|} = 260$ Oe. An analogous $\chi''(H_{\|})$ curve was reported earlier in reference 14.

In efflorescent potassium chrom alum, which contains $5H_2O$, on the average, the phase transition disappears and at $\nu \sim 540$ to 75 Mcs, in the temperature range of approximately 320 to 90°K, one observes absorption which decreases monotonically with increasing $H_{\|}$. The pattern of the phase transition does not change when D_2O replaces H_2O in single crystals of potassium chrome alum.

$FeNH_4(SO_4)_2 \cdot 12H_2O$

Ammonium iron sulfate is the most thoroughly investigated salt.[4,9,15] Investigations[10] of paramagnetic relaxation in parallel fields at T = 90°K have yielded $b/c = 0.27 \times 10^6$ Oe^2 and $\rho_L(H_{\|} = 0) = 4 \times 10^{-8}$ sec.

The $\chi''(H_{\|})$ absorption curve, which we have for $\nu = 540$ Mcs and T = 90°K, corresponds to spin-spin relaxation (see Fig. 2a). Relation (2) for $\Delta H = 480$ Oe gives $b/c = 0.55 \times 10^6$ Oe^2. In view of this, the theoretical curve will be considerably below the experimental curve when ρ_S = const and $b/c = 0.27 \times 10^6$ Oe^2 for $H_{\|} \neq 0$.

At 200°K the $\chi''(H_{\|})$ absorption curve (see Fig. 2b) is due to the spin-lattice relaxation. It follows therefore that ρ_L is on the order of 10^{-9} sec. A further increase of the temperature to 295°K again results in a spin-spin absorption curve (see Fig. 2c), indicating a lengthening of ρ_L to approximately 10^{-8} sec.

When $\Delta H = 300$ Oe, relation (2) yields $b/c = 0.22 \times 10^6$ Oe^2. The theoretical curve, calculated for $b/c = 0.27 \times 10^6$ Oe^2 for $H_{\|} \neq 0$ lies above the experimental curve of $\chi''(H_{\|})$ at T = 295°K. At 75 Mcs and 90°K, spin-spin absorption is observed with a maximum of $\chi''(H_{\|})$ at $H_{\|} = 600$ Oe. In efflorescent salts, containing $4H_2O$ on the average, the phase transition vanishes and an absorption maximum of $\chi''(H_{\|})$ is observed in the range

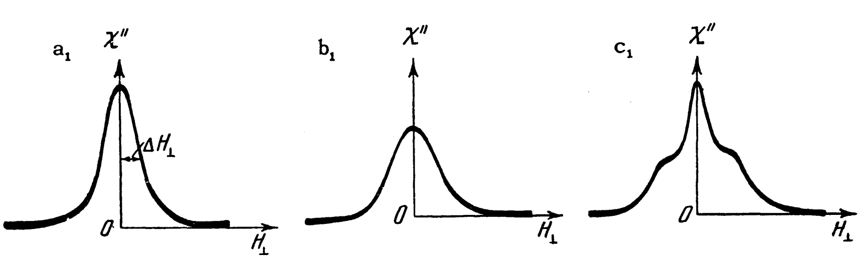

FIG. 1. $CrK(SO_4)_2 \cdot 12H_2O$; $\nu = 545$ Mcs; a, b, c) curves of $\chi''(H_{\|})$; a_1, b_1, c_1) curve of $\chi''(H_{\perp})$; χ'' in arbitrary units

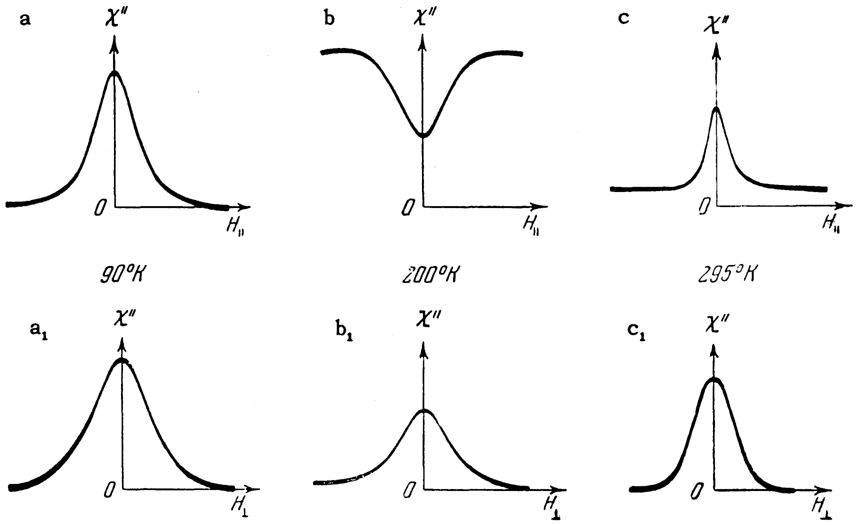

FIG. 2. $FeNH_4(SO_4)_2 \cdot 12H_2O$; ν = 540 Mcs; a, b, c) curves of $\chi''(H_{\parallel})$; a_1, b_1, c_1) curve of $\chi''(H_{\perp})$; χ'' in arbitrary units.

$\nu \sim$ 600 to 200 Mcs. The position of the maximum of $\chi''(H_{\parallel})$ is independent of the temperature and shifts towards the lower magnetic fields $H_{\parallel}$ with diminishing frequency of the alternating magnetic field H_{ν}.

3. PHASE TRANSITION IN PERPENDICULAR FIELDS

In perpendicular fields, the phase transition in undiluted potassium-chrome (see Figs. $1a_1$, $1b_1$, and $1c_1$) and iron-ammonium (Figure $2a_1$, $2b_1$, and $2c_1$) alums is also accompanied by a change in the shape of the absorption curves $\chi''(H_{\perp})$ in the temperature range from 90 to 300°K (see Table II).

TABLE II

Substance	$\Delta H_{\perp}$, Oe		
	90° K	200° K	295° K
$CrK(SO_4)_2 \cdot 12\ H_2O$	400	500	—
$FeNH_4(SO_4)_2 \cdot 12\ H_2O$	730	670	520

In single crystals of $CrK(SO_4)_2 \cdot 12H_2O$ and $FeNH_4(SO_4)_2 \cdot 12H_2O$, diluted respectively by $AlK(SO_4)_2 \cdot 12H_2O$ and $AlNH_4(SO_4)_2 \cdot 12H_2O$ in a ratio of 1 : 10, fine-structure spectra corresponding to intermediate fields ($\delta \gtrsim h\nu$) are observed at 540 Mc and 90 and 295°K. The spectra at 90°K differ from those at room temperature, and in the vicinity of the phase-transition point, T ~ 200°K, the fine-structure peaks spread out, leaving one broad line.

An unsuccessful attempt was also made to study the phase transition in dilute chromium-potassium and iron-ammonium phosphates and in pure aluminum-potassium and aluminum-ammonium sulfates with the aid of proton resonance. At 15 Mcs we obtained temperature-independent fine-structure proton lines consisting of four components for potassium sulfates and five components for ammonium sulfates.

4. DISCUSSION OF THE RESULTS

In one of the first investigations devoted to the absorption maxima in parallel fields, Gorter and Frijer[14] suggested that this maximum in $CrK(SO_4)_2 \cdot 12H_2O$ at 20°K is due to relaxation between two spin systems ("second spin-spin relaxation"). They observed furthermore that at liquid-air temperature the second relaxation in the spin system of $CrK(SO_4)_2 \cdot 12H_2O$ does not permit exact determination of b/c from measurements of paramagnetic dispersion and absorption.

During phase transitions in chromium-potassium and iron-ammonium sulfates, conditions are apparently set up for the appearance of second relaxation in the spin system. This second relaxation causes the half-width $\Delta H_{\parallel}$ of the $\chi''(H_{\parallel})$ curves that result from spin-spin relaxation to broaden in iron-ammonium sulfates at 90°K and ~ 540 Mcs and to narrow down in chromium-potassium sulfates at the same temperature. The second relaxation is sometimes the cause of the maxima that appear on these curves.

We now proceed to a discussion of the results obtained in perpendicular fields. Since the line width in a perpendicular field is determined, in the case of dilute single crystals, by the spin-lattice interactions, then the short time ρ_L at 200°K leads to such a strong broadening of the lines that the peaks of the fine structure spread out at 540 Mcs, leaving a single broad line. On the other hand, in undiluted single crystals the widths of the lines are determined by magneticdipole interactions and therefore the shortening of ρ_L of 200°K barely affects the width $\Delta H_\perp$ of the $\chi''(H_\perp)$ curve.

5. PRINCIPAL RESULTS

1. The paramagnetic-relaxation method was used for the first time to observe the phase transition in the iron-ammonium sulfate in the temperature range from 90 to 300°K.
2. The same method was used to confirm the existence of a phase transition in chromium-potassium sulfates.
3. The phase transition in both alums is accompanied by variations in ρ_L, $\Delta H_\perp$, $\Delta H_{||}$ and b/c. Here ρ_L becomes shorter as the temperature drops from 300 to 200°K and reaches a value $\rho_L \sim 10^{-9}$ sec at $T \sim 200$°K. Upon further cooling ρ_L again lengthens, as expected.
4. The shortest time ρ_L corresponds to the minimum value of δ for $CrK(SO_4)_2 \cdot 12H_2O$. To reconcile this result with the Van Vleck theory[16] it is natural to assume that the variation in the splitting of the orbital levels in a cubic field, resulting from the phase transition, has a greater effect on the relaxation time ρ_L than the variation in the initial splitting of the spin sublevels.

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