PARAMAGNETIC RELAXATION IN SINGLE CRYSTALS OF SALTS OF THE IONS Mn^{++}, Fe^{+++}, AND Cu^{++}AS A FUNCTION OF THEIR ORIENTATION IN A PARALLEL CONSTANT MAGNETIC FIELD AT ROOM TEMPERATURE

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The paramagnetic absorption curves of single crystals of salts of the ions Mn^{++}, Cr^{+++}, Fe^{+++}, and Cu^{++} in an oscillating field of frequency 10.5 Mc are given as a function of orientation in a constant magnetic field H. The results are reported of determinations of spin-lattice relaxation times in these single crystals. The Brons-Van Vleck formula is checked.

1. The spin-lattice relaxation time, ρ, is a function of b/C (where b is the magnetic thermal capacity constant and C is the Curie constant), the probability of a transition Ahk between energy levels of the spin system under the action of lattice vibrations. At room temperature the probability of a transition Ahk is determined by phonon Raman scattering processes [1]. Since the energy of the phonons is on the average very high in comparison with the intervals between neighboring energy levels of the spin system, ρ should depend to only a very slight extent on the orientation of the field H. For isotropic paramagnetic substances the relationship between the spin-lattice relaxation time, ρ, and the constant magnetic field, H, is given by the Brons-Van Vleck formula [2]:

$$\rho = \rho_0 \frac{b/C + H^2}{b/C + pH^2}, \tag{1}$$

where $p \leq 1$ and $p = \rho_0/\rho_\infty$, ρ_0 being the spin-lattice relaxation time when $H = 0$, and ρ_∞ the spin-lattice relaxation time when $H \to \infty$. The purpose of the present paper is to elucidate the Brons-Van Vleck formula for single crystals in respect of their orientation in a constant magnetic field.

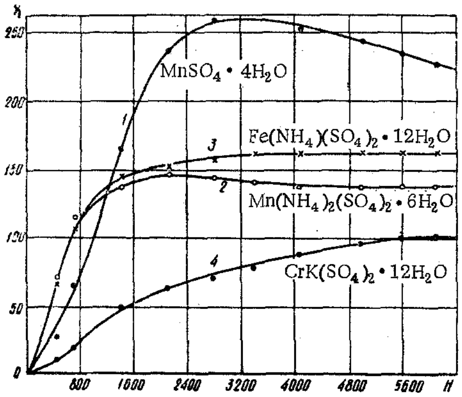

Fig. 1. Absorption curves for single crystals of salts of the ions Mn^{++}, Fe^{+++}, and Cr^{+++} at a frequency of 10.5 Mc as a function of the magnetic field.

Measurements were made of the coefficients of paramagnetic absorption, χ'', in single crystals of $MnSO_4 \cdot 4H_2O$, $Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O$, $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$, $CrK(SO_4)_2 \cdot 12H_2O$, $Cu(NH_4)_2(SO_4)_2 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$, $CuK_2(SO_4)_2 \cdot 6H_2O$, $CuCl_2(NH_4)_2Cl_2 \cdot 2H_2O$ as functions of the orientation of the crystals in a constant magnetic field. Measurements of $\chi''(H)$ at a frequency of 10.5 Mc by Zavoiskii's grid-current method [3] were carried out on a large number of fresh single crystals, taken directly from the mother liquor.

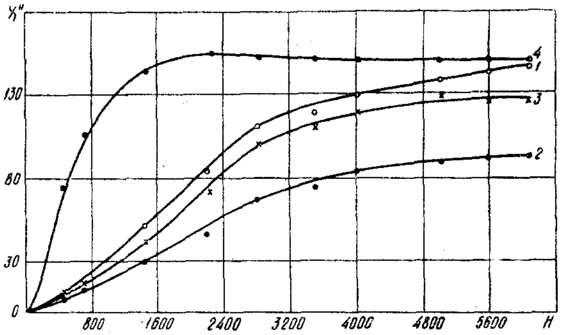

Fig. 2. Absorption curves for a single crystal of $Cu(NH_4)_2(SO_4)_2 \cdot 6H_2O$ at a frequency of 10.5 Mc in a constant magnetic field H as a function of the direction of the magnetic axes α and γ relative to the field. 1) Absorption along the α-axis; 2) absorption along the γ-axis; 3) absorption for a powder of the same substance; 4) absorption of the standard substance $Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O$.

At fairly low frequencies paramagnetic absorption in parallel fields is due only to spin-lattice relaxation and is described by the equation

$$\chi'' = \frac{\chi_0 mF \rho\nu}{1 + \rho^2\nu^2}, \tag{2}$$

where χ'' is the imaginary part of the complex magnetic susceptibility, χ_0 is the equilibrium susceptibility per unit mass, m is the mass of the sample, ν is the frequency of the oscillating field, ρ is the spin-lattice relaxation time, and F is some function of the constant magnetic field. The spin-lattice relaxation time was calculated from (2) by comparison with a standard crystal [4, 5]. The standard is a single crystal of $Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O$, for which all the parameters characterizing paramagnetic relaxation are known [1].

2. The paramagnetic absorption coefficients, $\chi''(H)$, of single crystals $MnSO_4 \cdot 4H_2O$, $Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O$, $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$, $CrK(SO_4)_2 \cdot 12H_2O$ was

Table 1

The Spin-lattice Relaxation Times in Single Crystals of Salts of the Ions Mn^{++}, Fe^{+++}, and Cr^{+++} in Relation to their Orientation in a Constant Magnetic Field H

Field (Oe)	Salt			
	$Mn(NH_4)_2(SO_4)_2\cdot 6H_2O$	$MnSO_4\cdot 4H_2O$	$Fe(NH_4)(SO_4)_2\cdot 12H_2O$	$CrK(SO_4)_2\cdot 12H_2O$
	$\rho\cdot 10^6$		$\rho\cdot 10^8$	
800	0.53	0.3	0.7	0.5
1600	0.66	0.4	0.8	0.7
2400	0.73	0.52	0.9	0.9
3200	0.75	0.65	1.00	1.1
4000	0.77	0.78	1.00	1.1
4800	0.79	0.90	1.00	1.1
5600	0.80	0.99	1.00	1.1
ρ_0	$0.4\cdot 10^{-6}$	$0.28\cdot 10^{-6}$	$0.4\cdot 10^{-8}$	$0.27\cdot 10^{-8}$
ρ_∞	$0.8\cdot 10^{-6}$	$2.0\cdot 10^{-6}$	$1.02\cdot 10^{-8}$	$1.1\cdot 10^{-8}$
$\rho = \frac{\rho_0}{\rho_\infty}$	0.5	0.14	0.4	0.25

Table 2

The Spin-lattice Relaxation Times, $\rho_0(H = 0)$ and $\rho\,\infty$ $(H \to \infty)$, for Single Crystals of Copper Salts as a Function of Their Orientation in a Constant Magnetic Field

Salt	Powder			Single Crystal					
				α-axis			γ-axis		
	$\rho_0\cdot 10^8$	$\rho_\infty\cdot 10^8$	p	$\rho_0\cdot 10^8$	$\rho_\infty\cdot 10^{+8}$	p	$\rho_0\cdot 10^8$	$\rho_\infty\cdot 10^8$	p
$CuSO_4\cdot 5H_2O$	0.34	3.4	0.10	0.34	4.25	0.08	0.34	2.6	0.13
$Cu(NH_4)_2(SO_4)_2\cdot 6H_2O$	0.30	1.46	0.22	0.30	1.50	0.20	0.30	1.33	0.20
$CuK_2(SO_4)_2\cdot 6H_2O$	0.26	1.04	0.25	Relaxation time almost independent of H					
$CuCl_2(NH_4)_2\cdot Cl_2\cdot 2H_2O$	0.8	3.20	0.25	0.8	4.00	0.20	0.60	3.00	0.20

measured at a frequency of 10.5 Mc at various orientations in a constant magnetic field. The curves obtained are reproduced in Fig. 1. The samples always had the same volume and were placed at the same point in the coil of the generator. From the results it was established that the paramagnetic absorption, $\chi''(H)$, and the spin-lattice relaxation times, ρ, in single crystals of salts of the ions Mn^{++}, Fe^{+++}, and Cr^{+++} are independent of the orientation of the crystals in the constant magnetic field. The values obtained for the spin-lattice relaxation times differed among themselves by less than 5%, and are listed in Table 1.

In a second series of experiments the paramagnetic absorption coefficients of single crystals of the copper salts $CuSO_4 \cdot 5H_2O$, $Cu(NH_4)_2(SO_4)_2 \cdot 6H_2O$, $CuK_2(SO_4)_2 \cdot 6H_2O$, and $CuCl_2(NH_4)_2Cl_2 \cdot 2H_2O$ were measured for various orientations of the constant magnetic field, H, relative to the magnetic axes, α, β, γ of the single crystal [6]. From the results it was found that in copper salts the coefficient of paramagnetic absorption $\chi''(H)$, the spin-lattice relaxation time, ρ, and the constant b/C are all anisotropic (cf [7]). The absorption curves for single crystals of the salts $Cu(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and $CuK_2(SO_4)_2 \cdot 6H_2O$, are shown in Figs. 2 and 3.

In the case of the Tulton salt $CuK_2(SO_4)_2 \cdot 6H_2O$ the character of the relationship between the absorption coefficient, χ'', and the strength of the constant field, H, differs from that of other copper salts in that for fields above ~1500 Oe the paramagnetic absorption is independent of the magnetic field. For all the copper-salt single crystals investigated, it appears that the paramagnetic absorption along the γ-axis is 1.7-times less than absorption in the $(\alpha\beta)$-plane; χ''_α differs from χ''_β by approximately 5–10%. From our results it was found that

$$\chi'' = \frac{1}{3}(\chi''_\alpha + \chi''_\beta + \chi''_\gamma), \qquad (3)$$

where χ'' refers to the powder, and χ''_α, χ''_β, χ''_γ to the magnetic axes of the single crystal. A similar equation was obtained for the spin-lattice relaxation times:

$$\rho = \frac{1}{3}(\rho_\alpha + \rho_\beta + \rho_\gamma), \qquad (4)$$

where ρ is the spin-lattice relaxation time for the powder, and ρ_α, ρ_β, and ρ_γ are the times for the α, β, and γ axes of the single crystal.

3. The results obtained for the spin-lattice relaxation times in single crystals of salts of the ions Mn^{++}, Cr^{+++} and Cu^{++} (see Table 1 and [7]) for various orientations in a parallel constant magnetic field at room temperature were used to verify the Brons-Van Vleck formula. The calculation (Table 2) showed that:

1) The formula is satisfactory for all orientations of single crystals of salts of Mn^{++}, Fe^{+++}, and Cr^{++}, and χ'' and ρ are independent of the orientation in a constant magnetic field.

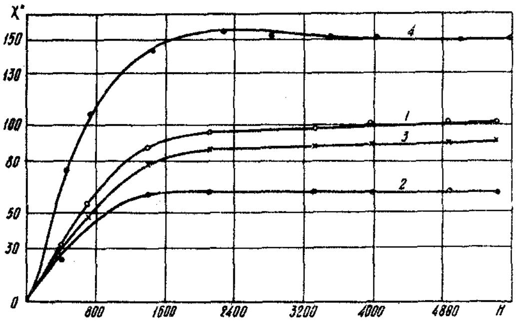

Fig. 3. Absorption curves for single crystals of $CuK_2(SO_4)_2 \cdot 6H_2O$ at a frequency of 10.5 Mc in a constant magnetic field H as a function of the direction of the magnetic axes α and γ relative to the field. 1) Absorption along the α-axis; 2) absorption along the γ-axis; 3) absorption for a powder of the same substance; 4) absorption of the standard substance $Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O$.

2) For $CuSO_4 \cdot 5H_2O$, the value of ρ_0 (see Table 2) for H = 0 is independent of the orientation of the single crystal (scatter less than 4%), and the value of the relaxation time ρ_∞ for $H \to \infty$ along the α-axis differs from that along the γ-axis by a factor of 1.6.

3) For double salts of copper the spin-lattice relaxation time ρ_0 is independent of the orientation of the single crystal (but the scatter in the calculation may reach 20%), and the value of ρ_∞ along the α-axis is 1.2 times greater than that along the γ-axis.

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