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PARAMAGNETIC LATTICE RELAXATION IN HYDRATED SALTS OF DIVALENT COPPER

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A theoretical calculation of the spin-lattice relaxation time in hydrated salts of divalent copper is carried out. The anisotropy of the relaxation time experimentally observed in $CuSO_4 \cdot 5H_2O$ crystals can be explained by taking into account the anisotropy of the spin-orbit interaction in the Cu^{++} ion due to partially covalent nature of the copper ion bonds in the crystal.

1. INTRODUCTION

HYDRATED salts of divalent copper form a group of paramagnets whose magnetic properties are comparatively well known: detailed examinations of the static susceptibility and paramagnetic resonance spectra have been carried out for a number of these salts, and experimental data on the spin-lattice relaxation are on hand. We shall dwell below on those results that have been utilized for our calculations.

In the crystals of hydrated copper salts the water molecules that surround a magnetic ion form, at the point where the magnetic ion is located, an electric field of cubic symmetry on which is superimposed a comparatively weak field of lower symmetry (tetragonal, trigonal, or rhombic). We shall now examine the Tutton's copper salts and the hydrated copper sulfate $CuSO_4 \cdot 5H_2O$. The unit cells of the crystals of the above salts contain two Cu^{++} ions each. The internal field is of tetragonal, almost cubic, symmetry. The angle between the tetragonal axes is 82° for two magnetic ions of a unit cell of the crystal.[1,2]

The basic state of the Cu^{++} ion is the ^2D state. The ground orbital level of the Cu^{++} ion is split up into a triplet and a doublet by the cubical field, the doublet lying lower. The orbital doublet is split up into two single levels by the tetragonal field. Since the spin is $S = \frac{1}{2}$, the lower level is
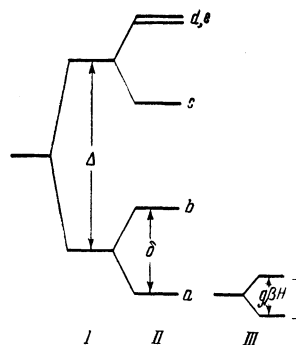
Scheme of the successive splitting of the ground level of a Cu^{++} ion under the influence of: I — an electric field of cubic symmetry; II — tetragonal symmetry; III — levels of the electron spin in the external magnetic field.

a Kramer doublet whose degeneracy is removed by the external magnetic field (see diagram). Optical examinations have shown that the magnitude Δ of the splitting due by the cubical component of the field is 12,300 cm^{-1} (references 1, 3, 4). Reliable data on the magnitude δ of the splitting due to the tetragonal component of the field are lacking. Following Owen's[4] calculations, we assume $\delta = 1400\ cm^{-1}$. In accordance with the diagram, we shall designate the two possible spin orientations in an external magnetic field H by + and − signs.

The paramagnetic-resonance spectra observed in crystals of Tutton's salts have been interpreted with g-factor values $g_{\parallel} = 2.4$ and $g_{\perp} = 2.1$ (Ref. 1).* Here $g_{\parallel}$ and $g_{\perp}$ characterize the

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*More exact values of the g-factor for different Tutton's salts are given in the paper by Bleany et al.[5]

splitting of the lower Kramer doublet by a magnetic field directed, respectively, parallel and perpendicular to the axis of symmetry of the internal crystal field. It follows from the theory of electron magnetic resonance spectra that a deviation of the g-factor value from the pure spin value is caused by the residual orbital magnetism of the lower orbital singlet of order $\lambda\beta/\Delta$, where λ is the spin-orbit interaction constant. However, calculations of corrections to the g-factor of the λ/Δ type have led to values of $g_\parallel$ and $g_\perp$ which differ from the measured ones. It was therefore assumed that the value of the constant λ in the crystals of Tutton's salts differs from its value for the free Cu^{++} ion ($\lambda = -829$ cm^{-1}) and equals -695 cm^{-1} (reference 1).

The measured g-factor values for the Cu^{++} ion in $CuSO_4 \cdot 5H_2O$ crystals are $g_\parallel = 2.47$ and $g_\perp = 2.06$. To explain the experimentally-obtained g-factor values it is necessary to assume the intensities of the tetragonal or rhombic components of the internal crystal field to be very great (of the same order as the cubical one)[2], an assumption not confirmed by the results of the optical investigations. Abe and Ono[3] offer another explanation. They assume that in the $CuSO_4 \cdot 5H_2O$ crystals the constant λ of the spin-orbit bond is an anisotropic quantity with components $\lambda_\parallel = -700$ cm^{-1} and $\lambda_\perp = -370$ cm^{-1}.

The difference between the value of λ in crystals and its value for the free Cu^{++} ion, and the anisotropic character of this value in $CuSO_4 \cdot 5H_2O$ crystals, can be attributed to the partially covalent character of the Cu^{++} ion bond with the nearest atoms of oxygen. A detailed analysis of the influence of covalent bonds in a crystal on the magnitude of the g-factor can be found in the works of Owen[4] and Stevens.[6]

It was established by Kronig[7] and Van Vleck[8] that in the hydrated salts of ions of the iron group the spin-lattice interaction is brought about chiefly by modulation of the internal crystal field by the thermal vibrations of the crystal lattice. Only the orbital motions of the electrons are directly influenced by the electric field. The interaction of the spin with the electric field is effected through the coupling of the spin with the orbit. The dependence of the spin-lattice relaxation time on the orientation of the crystal in the external magnetic field, found by Volokhova[9] in $CuSO_4 \cdot 5H_2O$ crystals, is therefore not unexpected. The anisotropic character of the constant λ is expected to entail an anisotropy of the relaxation time.

We have calculated the spin-lattice relaxation time ρ and determined that the anisotropy of ρ

detected in $CuSO_4 \cdot 5H_2O$ crystals can be explained by anisotropy of the constant λ. The expression obtained by us for ρ can also be applied to other salts of the Cu^{++} ion by assuming $\lambda_\parallel = \lambda_\perp$.

2. CALCULATION OF THE RELAXATION TIME

A system of orbital levels of the Cu^{++} ion in the electric field of the crystal with the above mentioned symmetry can be characterized by the following wave functions:[1,10]

$$\Psi_a = (\psi_2 + \psi_{-2})/\sqrt{2}, \quad \Psi_b = \psi_0, \quad \Psi_c = i(\psi_2 - \psi_{-2})/\sqrt{2},$$

$$\Psi_d = i(\psi_1 + \psi_{-1})/\sqrt{2}, \quad \Psi_e = (\psi_1 - \psi_{-1})/\sqrt{2}. \quad (1)$$

The indices a, b, c, d, e correspond to the diagram.

For a Hamiltonian that takes into account the interaction of the paramagnetic ion with the lattice vibrations we use the expression of Kronig,[7] which is the linear term of a series expansion of the electric potential of the crystal in terms of normal lattice vibrations. For the sake of convenience, we shall write it in a somewhat modified form and with different symbols:

$$\mathscr{H}^{(1)} = f[(3z^2 - r^2)f_1 + 2(x^2 - y^2)f_2$$
$$- 2xyf_3 - 2xzf_4 - 2yzf_5], \quad (2)$$

$$f = 8e\mu a^{-5}q\Phi, \qquad f_1 = u_z\lambda_z - {}^2/_3 u_x\lambda_x - {}^2/_3 u_y\lambda_y,$$
$$f_2 = u_x\lambda_x - u_y\lambda_y, \qquad f_3 = u_y\lambda_x + u_x\lambda_y,$$
$$f_4 = u_z\lambda_x + u_x\lambda_z, \qquad f_5 = u_z\lambda_y + u_y\lambda_z.$$

Here u_x, u_y, u_z and λ_x, λ_y, λ_z are cosines determining the directions of polarization and the velocities of elastic-wave propagation, respectively; q is the normal coordinate, μ is the effective dipole moment of the water molecule, $\phi = 2\pi a\nu/c$, c is the velocity of sound, a is the lattice constant; and e is the electron charge.

With the aid of the eigenfunctions (1) for matrix elements $\mathscr{H}^{(1)}$, we obtain the following expressions:

$$<a|b> = 4\sqrt{3}\alpha\bar{r}^2 ff_2,$$

$$<b|c> = 2\sqrt{3}\alpha\bar{r}^2 ff_3, \quad <a|c> = 0,$$

$$<a|d> = -\sqrt{3}<b|d> = -3\alpha\bar{r}^2 ff_5,$$

$$<a|e> = \sqrt{3}<b|e> = -3\alpha\bar{r}^2 ff_4,$$

$$(3)$$

where $\alpha = {}^2/_{21}$ and $\bar{r}^2$ is the mean square of the distance of the 3d-electron from the nucleus.

Choosing the direction of the magnetic field H as the axis of quantization of the electron spin, we write the operator of the spin-orbit coupling in the following form:

$$\mathscr{H}_{so} = \sum_{x'=x',y',z'} [\lambda_\perp (L_x l_{xx'} s_{x'} + L_y l_{yx'} s_{x'}) + \lambda_\parallel L_z l_{zx'} s_{x'}]. \quad (4)$$

Here $l_{xx'}$, $l_{xy'}$ ... are the cosines of the angles between the axes xyz and x'y'z', where xyz is the coordinate system connected with the symmetry axes of the internal crystal field, and the z' axis is parallel to H.

Let us determine the matrix elements of $\mathcal{H}_{s0}$ needed for the subsequent computations:

$$< a\,|\,b > = < b\,|\,c > = 0,$$

$$< a\,|\,c > = 2i\lambda_{\parallel}\ (l_{zz'}S_{z'} + l_{zy'}S_{y'} + l_{zx'}S_{x'}),$$

$$< b\,|\,d > = \sqrt{3} < a\,|\,d >$$

$$= i\sqrt{3}\lambda_{\perp}\ (l_{xz'}S_{z'} + l_{xy'}S_{y'} + l_{xx'}S_{x'}),$$

$$< b\,|\,e > = -\sqrt{3} < a\,|\,e >$$

$$= i\sqrt{3}\lambda_{\perp}\ (l_{yz'}S_{z'} + l_{yy'}S_{y'} + l_{yx'}S_{x'}).$$

(5)

Let us examine the relaxation that results from the Raman scattering of phonons. This case is decisive even at comparatively low temperatures.

Since the splitting factors Δ and δ are sufficiently large (Δ, $\delta \gg$ kT), relaxation will take place only because of transitions between the two lower spin levels. To determine the probability of transition a, + → a, − due to Raman scattering of phonons, it is necessary to obtain for the perturbation energy a matrix element of the type $\mathcal{H}$(a, +, n, n'; a, −, n − 1, n' + 1) where n and n' are quantum numbers pertaining to the absorbed and emitted quanta of the elastic vibrations repectively. The latter may be obtained in the third approximation with the aid of expressions (2) and (4), which we will regard as a perturbation. It is necessary to take into consideration that $\Delta \gg \delta$ and for this reason we must choose from among all the terms of $\mathcal{H}'$ those in which the next nearest orbital level b is used as one of the intermediate states.

Taking this into account we obtain:

$$\mathcal{H}' = \sum_{\alpha=c,d,e} \left[\frac{P^+(n,n',\alpha)-P^-(n',n,\alpha)}{(-\Delta)(-\delta+h\nu)} + \frac{P^-(n',n,\alpha)-P^+(n,n',\alpha)}{(-\Delta)(-\delta-h\nu')} \right] + \frac{F^+(n,n',\alpha)-F^-(n',n,\alpha)}{(-\Delta+h\nu)(-\delta+h\nu)} + \frac{F^-(n',n,\alpha)-F^+(n,n',\alpha)}{(-\Delta-h\nu')(-\delta-h\nu')} \right],$$

$$P^\pm_{(n,n',\alpha)} = < a, +\,|\,\mathcal{H}_{s0}\,|\,\alpha, - > < \alpha, n\,|\,\mathcal{H}^{(1)}\,|\,b, n \mp 1 > < b, n'|\,\mathcal{H}^{(1)}|a, n' \pm 1 >,$$

(6)

$$F^\pm_{(n,n',\alpha)} = < a, n\,|\,\mathcal{H}^{(1)}\,|\,b, n \mp 1 > < b, +|\mathcal{H}_{s0}\,|\,\alpha, - > < \alpha, n'|\mathcal{H}^{(1)}|\,a, n' \pm 1 >.$$

We next take it into account that $h\nu \ll \delta$ and consider the frequencies ν and ν' of the emitted and absorbed phonons to be equal (this is permissible if $g\beta H \ll kT$).

The following expression is then obtained in the usual way[8] for the probability of relaxation:

$$A_{+-} = \tfrac{1}{2}AI_8\,[\lambda_{\parallel}^2 + \lambda_{\perp}^2 - (\lambda_{\parallel}^2 - \lambda_{\perp}^2)\,l_{zz'}^2],$$

$$A = 3.5\cdot 10^3\pi^4\,(h/D\Delta\delta^2)^2\,(e\mu\bar{r}^2/a^4)^4\left(c_l^{-5} + \tfrac{3}{2}\,c_t^{-5}\right)^2,$$

(7)

$$I_8 = \int_0^{h\Theta/h} \frac{\nu^8 e^{h\nu/kT}}{(e^{h\nu/kT}-1)^2}\,d\nu.$$

Here D is the crystal density, c_l and c_t the propagation velocities of longitudinal and transverse elastic waves and Θ the characteristic Debye temperature.

According to the Casimir and Du Pre thermodynamic theory of paramagnetic relaxation,[11] the relaxation time is $\rho = 2\pi C_H/\alpha$, where C_H is the heat capacity of the spin system in the presence of a constant magnetic field H, while α is the coefficient of thermal conductivity between the spin system and the lattice. Using for C_H and α the relations given by Al'tshuler[12] and averaging over the internal magnetic fields with account of the anisotropy of the g-factor, we obtain:

$$\rho = \frac{2\pi}{AI_8}\,\frac{g_0^2 H_0^2 + g_i^2 H_i^2/2}{[\lambda_{\parallel}^2 + \lambda_{\perp}^2 - (\lambda_{\parallel}^2 - \lambda_{\perp}^2)\cos^2\varphi]\,g_0^2 H_0^2 + \tfrac{2}{3}\,(\lambda_{\parallel}^2 + 2\lambda_{\perp}^2)\,g_i^2 H_i^2},$$

$$g_0^2 = g_{\parallel}^2\cos^2\varphi + g_{\perp}^2\sin^2\varphi,\quad g_i^2 = \tfrac{1}{3}(g_{\parallel}^2 + 2g_{\perp}^2),\quad (8)$$

where H_i is the effective internal magnetic field, H_0 the intensity of the external magnetic field, and φ the angle between H_0 and the symmetry axis of the electric field of the crystal z.

To illustrate the obtained angle dependence, we shall determine the numerical value of ρ for a $CuSO_4 \cdot 5H_2O$ crystal.

Let us evaluate the constants in (8). The values of Δ, δ, $\lambda_{\parallel}$, $\lambda_{\perp}$ have been given in the first part of this paper. Assuming $\mu = 2 \times 10^{-18}$ cgs esu and using the formula[4] $\Delta = 25e\mu\bar{r}^4/3a^6$, we obtain $a = 2.1 \times 10^{-8}$ cm. We then assume $c_l = c_t = 2.5 \times 10^5$ cm/sec and $\Theta = 100°$ K.

Let us determine the values of ρ for the directions of the external magnetic field that correspond to the angles $\varphi_\alpha = 41°$, $\varphi_\beta = 49°$ and $\varphi_\gamma = 90°$ (principal magnetic axes of the crystal) at T = 290°K. In strong magnetic fields ($H_0^2 \gg H_i^2$) we have*

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*Considering that the values of the constants are only approximately known, it is sensible to speak only of the order of magnitude of ρ. Exact values of ρ are given as illustration of the angle dependences obtained.

$\rho_\alpha = 0.5 \cdot 10^{-8}$, $\rho_\beta = 0.45 \cdot 10^{-8}$, $\rho_\gamma = 0.34 \cdot 10^{-8}$ sec.

In weak fields ($H_0^2 \ll H_i^2$) we get $\rho = 0.2 \cdot 10^{-8}$ sec. For a polycrystalline specimen

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

The resulting dependence of the relaxation time on the orientation of the $CuSO_4 \cdot 5H_2O$ crystal in an external magnetic field H_0 agrees very well with the experimental results obtained by Volokhova.[9] With a certain approximation the dependence of ρ on the absolute value of H_0 also agrees with the results obtained by Volokhova. The temperature dependence of ρ is determined by the integral I_8.

If the constant λ is isotropic, then the probability of the relaxation transition A_{+-} (7) will also be isotropic. The anisotropy of ρ will be determined in this case by the anisotropy of the g-factor only. With $g_\parallel = 2.4$ and $g_\perp = 2.1$ the computed values of ρ for H_0 directed along the three magnetic axes of the crystal differ by no more than 4%, i.e., it is difficult to attribute to the anisotropy of the g-factor even a comparatively small (10 to 20%) anisotropy of ρ as observed in the crystals of Tutton's copper salts.[9] It may be presumed that the constant λ of the spin-orbit coupling is also anisotropic here, the more so since these salts are similar to $CuSO_4 \cdot 5H_2O$ in their crystalline structure.

In conclusion, the author wishes to thank S. A. Al'tshuler for suggesting this work and for valuable advice.

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KINETIC THEORY OF THE FLOW OF A GAS THROUGH A CYLINDRICAL TUBE

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By introducing a certain "anisotropy function" a good description of the flow of a gas can be obtained, even at pressures at which only empirical formulas have been used hitherto. Furthermore, the term corresponding to the slipping of the gas relative to the walls is obtained automatically, without any additional hypotheses; the same is true of the minimum rate of flow at intermediate pressures. Our final formula is qualitatively correct at all pressures, including intermediate ones.

IT is well known that hydrodynamics cannot provide the solution of the problem of the flow of gases at low pressures. Knudsen[1] succeeded in establishing the correct laws of flow at such pressures by using kinetic theory. In an intermediate range of pressures, however, neither hydrodynamics nor