

*THE DYNAMICAL CHARACTER OF THE JAHN-TELLER EFFECT AND ITS INFLUENCE  
ON THE PARAMAGNETIC RESONANCE OF  $\text{Cu}^{2+}$*

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We consider copper complexes  $\text{Cu}^{2+}\text{Y}_6$  for which there are, in contradistinction to other paramagnetic complexes, in first approximation an infinite number of geometries within a certain manifold corresponding to the minimum energy, instead of one well-defined geometry. Using crystal field theory we establish the connection between the geometry of the complex and the electron density distribution of the  $\text{Cu}^{2+}$  ion. "Geometrical degeneracy" leads to the result that the latter may experience finite (permanent) distortions; it is shown that the changes in the "crystalline" field corresponding to these distortions should lead to oscillations of the electron cloud of the  $\text{Cu}^{2+}$  ion relative to the nucleus. We also consider the influence of the interactions which lead to a partial stabilization of the complex. It is shown that even when these interactions are taken into account the electron cloud continues to oscillate but at a lower frequency, and the frequency depends on the mass of the corner atoms. We have considered the influence of the effect considered on the hyperfine structure and  $g$ -factors in free complexes.

## 1. INTRODUCTION

It is well established that in copper salts in which the crystalline electrical field at the position of the  $\text{Cu}^{2+}$  ion has a symmetry higher than a tetragonal one<sup>1</sup> and, as an exception, in copper Tutton salts<sup>2</sup> where the crystalline field is tetragonal, the magnitudes of the  $g$ -factors and of the hyperfine-structure (hfs) constants are temperature dependent: they are strongly anisotropic at low temperatures and become isotropic at high temperatures, while the hfs constant is considerably decreased at high temperatures. Aqueous solutions of copper salts have a peculiar behavior.

The behavior of a  $\text{Cu}^{2+}$  ion in salts with a trigonal (or higher) symmetry was explained by the dynamic character of the Jahn-Teller effect which occurs in these salts.<sup>3</sup> The behavior of a copper ion in Tutton salts<sup>2</sup> and also in aqueous solutions<sup>4,5</sup> has not yet been adequately explained.

There are grounds for assuming that the Jahn-Teller effect is also responsible for the decrease and isotropy of the hfs constant in aqueous solutions of copper salts (and, apparently, as an exception, in Tutton salts). This is indicated by the fact that both in a free  $\text{Cu}^{2+}\text{Y}_6$  complex and also in the complex situated in a force field with trigonal symmetry, the ground state of the  $\text{Cu}^{2+}$  ion is two-fold degenerate, if the Jahn-Teller effect

is not taken into account, while in both cases the degeneracy is lifted thanks to the Jahn-Teller effect. Since the Jahn-Teller effect in  $\text{Cu}^{2+}\text{Y}_6$  complexes in a trigonal field has a dynamic character, it follows from the above analogy that it must also have a dynamic character in free complexes.

It is the aim of the present paper to consider from the same point of view all peculiarities of paramagnetic resonance of copper ions which, according to one consideration or another, may be ascribed to the dynamical character of the normal Jahn-Teller effect.

General considerations about the nature of the effect are given in Sec. 2. A theory of the phenomenon in free (not fixed in a lattice)  $\text{Cu}^{2+}\text{Y}_6$  complexes is offered in Sec. 3. A general discussion is given in Sec. 4 of the influence of the effect on the paramagnetic resonance of  $\text{Cu}^{2+}$  in complexes with different corner atoms  $\text{Y}$ .

## 2. THE JAHN-TELLER EFFECT IN FREE COPPER COMPLEXES

The Jahn-Teller theorem<sup>6</sup> applied to  $\text{XY}_6$  complexes proves that the octahedral configuration formed by such complexes is unstable, if the atom (ion)  $\text{X}$  is in a degenerate state.

The Hamiltonian leading to a Jahn-Teller effect can be written in the form<sup>7,8</sup>

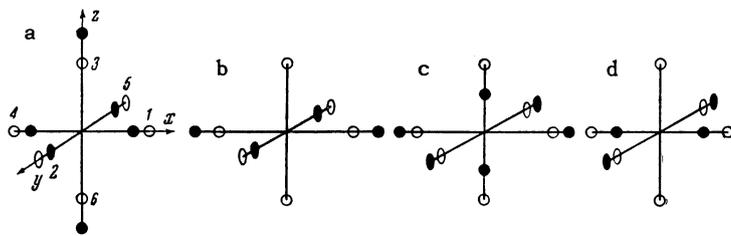


FIG. 1. Static distortions of an octahedral complex of symmetry  $Q_3$  and  $Q_2$  (a: for  $\theta = 0$ , b: for  $\theta = \pi/2$ , c: for  $\theta = \pi$ , d: for  $\theta = 3\pi/2$ ). ● — initial geometry, ○ — structure arising due to the static Jahn-Teller effect

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{\text{cub}} + (\hat{V}_2 Q_2 + \hat{V}_3 Q_3) + \frac{1}{2} k (Q_2^2 + Q_3^2). \quad (1)$$

The term  $\hat{\mathcal{H}}_{\text{cub}}$  is the energy of the ion in a crystalline field of cubic symmetry and is considered as the unperturbed Hamiltonian; the second and third terms are perturbations. For our purpose it is sufficient to consider only the influence of the perturbation on the lowest orbital cubic doublet (for the sake of brevity we indicate by this term the lowest two-fold degenerate orbital state of the  $\text{Cu}^{2+}$  in the field of cubic symmetry).

The Jahn-Teller effect as such is connected with the term linear in  $Q_2$  and  $Q_3$ , where

$$\hat{V}_3 = 18C(3z^2 - r^2)/\sqrt{3}, \quad \hat{V}_2 = -18C(x^2 - y^2)$$

are operators with matrix elements

$$\langle \psi_1 | \hat{V}_3 | \psi_1 \rangle = -\langle \psi_2 | \hat{V}_3 | \psi_2 \rangle$$

$$= \langle \psi_1 | \hat{V}_2 | \psi_2 \rangle = \langle \psi_2 | \hat{V}_2 | \psi_1 \rangle = -a,$$

and  $\mathbf{r}(x, y, z)$  is the radius vector taken from the nucleus to the electron of the incomplete shell of the  $\text{Cu}^{2+}$  ion. If the corner atoms Y are electric dipoles with moment  $\bar{\mu}$ ,  $C = e'\mu/R^5$  where  $e'$  is the electron charge and R the equilibrium distance between  $\text{Cu}^{2+}$  and Y in a regular octahedral complex.

For our further calculations we put  $Q_3 = \rho \cos \theta$ ,  $Q_2 = \rho \sin \theta$ . The notation of the variables  $Q_2$  and  $Q_3$  in (1) is the same as the notation for the two-fold degenerate vibrational coordinates of a regular octahedral complex  $\text{XY}_6$  (of the type  $E_g$ ), although they characterize in the given case static distortions of the complex. These variables can be expressed as follows in terms of displacements in a Cartesian system of coordinates (see Fig. 1):

$$Q_3 = [z_3 - z_6 - \frac{1}{2}(x_1 - x_4 + y_2 - y_5)]/\sqrt{3},$$

$$Q_2 = \frac{1}{2}(x_1 - x_4 - y_2 + y_5).$$

Expression (1) determines the energy of the  $\text{Cu}^{2+}$  ion as a function of the geometrical parameters  $Q_2$  and  $Q_3$  (or  $\rho$  and  $\theta$ ). On the other hand, the energy of the  $\text{Cu}^{2+}\text{Y}_6$  "molecule" as a function of the same variables is equal to\*

\*Since we are interested in the connection between the geometry of the complex and the electron density distribution we have omitted from Eq. (1a) third order displacement terms caused by the interaction between the corner atoms Y and the effective charge of the  $\text{Cu}^{2+}$  nucleus.

$$\hat{\mathcal{H}} = U_0 + V_2 Q_2 + V_3 Q_3 + \frac{1}{2} k (Q_2^2 + Q_3^2), \quad (1a)$$

where  $U_0$  is the potential energy of the  $\text{Cu}^{2+}\text{Y}_6$  "molecule" when it has the symmetry of a regular octahedron.

In order to find the stable geometry it is necessary first to diagonalize (1a) and then to impose a minimum condition.<sup>7</sup> We get (see Fig. 2)

$$E = -a^2/2k, \quad \Delta E = 2a\rho_0,$$

$$\rho_0 = (Q_2^2 + Q_3^2)^{1/2} = |a|/k. \quad (1b)$$

The eigenfunctions of the  $\text{Cu}^{2+}$  ion are of the form

$$\varphi_1 = \{(1 + \cos \theta)^{1/2} \psi_1 + (1 - \cos \theta)^{1/2} \psi_2\}/\sqrt{2}, \quad (2a)$$

$$\varphi_2 = \{(1 - \cos \theta)^{1/2} \psi_1 - (1 + \cos \theta)^{1/2} \psi_2\}/\sqrt{2}, \quad (2b)$$

where  $\psi_1$  and  $\psi_2$  are the functions of the lowest orbital cubic doublet of the copper ion.

It is clear from (1b) that neither the energy of the  $\text{Cu}^{2+}$  ion (the eigenvalues of the ground-state energy and the magnitude of the level splitting) nor the energy of the  $\text{Cu}^{2+}\text{Y}_6$  "molecule" (equal to  $U_0 - E$ ) depend on the parameter  $\theta$ , which characterizes the geometry of the complex and the form of the eigenfunction of the ground state of the  $\text{Cu}^{2+}$  ion.

The fact that the energy of the complex is independent of the deformation (within the limits  $Q_2^2 + Q_3^2 = \rho_0^2 = \text{const}$ ) leads to a situation where the usual Jahn-Teller effect has a dynamic character. The complex can, namely, go over freely (as long as we do not take into account interactions leading

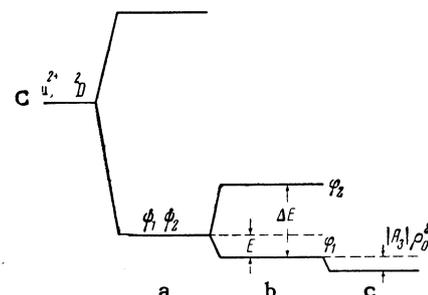


FIG. 2. Energy level splitting for the ion: a — in a field of cubic symmetry, b — thanks to the Jahn-Teller effect, c — thanks to the Jahn-Teller effect, taking the third order approximation in the displacements of the corner atoms Y from the position corresponding to a regular octahedral configuration into account.

to a suppression of the effect, see Sec. 3) from one geometrical arrangement to another one with a sufficiently high frequency, determined by external conditions; the latter is caused by the fact that all these arrangements correspond to the same energy.

We shall now consider what influence is exerted by this phenomenon on the electron density distribution of the  $\text{Cu}^{2+}$  ion. The external force changes the geometry of the complex, causing a change in the distribution in the electron cloud of the magnetic ion (and a change in the ground-state eigenfunction of  $\text{Cu}^{2+}$ ). This explains the fact that although there are no nondiagonal perturbation matrix elements which can be responsible for a mixing of the cubic eigenfunctions of the ion, nevertheless, in this complex, the eigenfunctions of the ground state of the ion are superpositions of the eigenfunctions of the orbital cubic doublet with, generally speaking, arbitrary coefficients that are subject to the conditions of orthogonality and normalization [see (2a), where  $\theta$  is arbitrary].

The geometry of a complex with a degenerate ion in a solid is determined by the crystal lattice, so that the distribution of the electron cloud of the magnetic ion is fixed, thanks to the stability of the complex. The given effect can therefore take place in a solid containing a copper complex only in the special cases mentioned above (Sec. 1).

To elucidate the influence of the dynamic character of the Jahn-Teller effect in free complexes with other paramagnetic ions we need a special consideration. We can point here, however, to the essential difference between the copper ion and the other ions in that not one of the latter possesses the aforementioned degeneracy with respect to the geometry of the complex (with the exception of  $\text{Cr}^{2+}$  and  $\text{Mn}^{3+}$ , which have an even number of electrons).

The first to introduce the idea of the dynamic nature of the Jahn-Teller effect in copper complexes were Abragam and Pryce<sup>3</sup> in order to explain the small magnitude and the isotropy of the hyperfine structure constant and the isotropy of the  $g$ -factor in copper salts with trigonal symmetry. In accordance with the dynamic character of the effect, they used in their calculations eigenfunctions of the ground state of  $\text{Cu}^{2+}$  in the form  $\varphi = \psi_1 \cos \theta + \psi_2 \sin \theta$ , and assumed that  $\theta$  was a cyclic coordinate. After averaging over  $\theta$  they obtained  $g$ -factors and hfs constants that agreed with experiment. The ideal case where the energy of the complex is independent of the character of the deformation (within the limits  $Q_2^2 + Q_3^2 = \text{const}$ ) is, however, in actual fact not realized. It has been

established (see, for instance, reference 8) that in reality the  $\text{Cu}^{2+}\text{Y}_6$  complexes have structures with a  $D_{4h}$  symmetry. The change in potential energy of the complex is equal to  $A_3 \rho^3 \cos 3\theta$  ( $A_3 \sim \text{const}$ ,  $|A_3| \rho^3 \sim 600 \text{ cm}^{-1}$ ,  $A_3 < 0$ )<sup>9</sup> (see Fig. 2), if we use polar coordinates  $\rho$ ,  $\theta$  in the  $Q_2$ ,  $Q_3$  plane. Thus, there is no free "rotation" of the complex in the  $Q_2$ ,  $Q_3$  plane. All the same, experiment shows that in some cases the hfs constant is averaged, and this averaging cannot be ascribed to exchange interactions.<sup>5</sup> It is therefore expedient to consider the connection between the Jahn-Teller effect and the vibrational motion of the complex.

### 3. THE JAHN-TELLER EFFECT, TAKING THE THIRD ORDER APPROXIMATION IN THE DISPLACEMENTS INTO ACCOUNT

If one considers the energy of the  $\text{Cu}^{2+}$  ion as a function of the parameters  $Q_2$  and  $Q_3$  which characterize the change in the geometry of the complex, the Hamiltonian of the problem becomes

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{\text{cub}} + \hat{V}_2 Q_2 + \hat{V}_3 Q_3 + \frac{1}{2} k (Q_2^2 + Q_3^2) + A_3 \rho^3 \cos 3\theta. \quad (3)$$

Its eigenvalues are

$$E = \pm a\rho'_0 + \frac{1}{2} k\rho'_0{}^2 + A_3 \rho_0^3 \cos 3\theta. \quad (4a)$$

From this we get, from the requirement that the energy of the system be a minimum,

$$E_1 = -a\rho'_0 + \frac{1}{2} k\rho'_0{}^2 + A_3 \rho_0^3, \quad \Delta E = 2a\rho'_0, \\ \rho'_0 = (k - \sqrt{k^2 - 12a|A_3|}) / 6|A_3|, \quad (4b)$$

where  $E_1$  is the energy eigenvalue of the  $\text{Cu}^{2+}$  ion corresponding to the ground state. At the same time,  $E_1$  characterizes the change in potential energy of the  $\text{Cu}^{2+}\text{Y}_6$  complex, considered as a molecule, when the complex goes over from an unstable octahedral configuration to a stable bipyramidal one. Thanks to the presence of a term linear in  $Q_2$  and  $Q_3$  in the Hamiltonian (3), the regular octahedral configuration of the  $\text{Cu}^{2+}\text{Y}_6$  is therefore again unstable, but now both the energy of  $\text{Cu}^{2+}$  and the energy of  $\text{Cu}^{2+}\text{Y}_6$  as a molecule depend on the angle  $\theta$ , and their minimum is realized at  $\theta = \theta_0 = 0, 2\pi/3, \text{ and } 4\pi/3$ .

Our problem will now consist of establishing the dependence of the electron density in  $\text{Cu}^{2+}$  on the vibrations of the deformed complex. To do this we consider  $\text{Cu}^{2+}\text{Y}_6$  as a vibrational system. The Hamiltonian of the problem has in that case the form

$$\hat{\mathcal{H}} = U_0 + \hat{V}_2 Q_2 + \hat{V}_3 Q_3 + \frac{1}{2} k (Q_2^2 + Q_3^2) + A_3 \rho^3 \cos 3\theta, \quad (5)$$

where  $U_0$  is the potential energy of a complex that has octahedral symmetry. Before we evaluate the normal vibrations of the system, the Hamiltonian of which is given by (5), it is necessary to find the form of the potential function of the complex when it has the symmetry corresponding to the energy minimum.

Let  $Q_j$ ;  $Q_2, Q_3$  ( $j = 1, \dots, 13$ ) be the displacements of the regular octahedral complex, which have the symmetry of the vibrational coordinates  $\tilde{Q}_j, \tilde{Q}_2, \tilde{Q}_3$ . The potential function of the bipyramidal complex can in these variables be written in the form

$$U(Q_j^0 = 0; Q_2^0, Q_3^0) = U_0 - E, \quad (6)$$

where  $Q_2^0$  and  $Q_3^0$  are the displacements of the corner atoms Y. Expanding (6) in a Taylor series in the vicinity of  $Q_j = Q_2 = Q_3 = 0$  we get

$$U(Q_j^0 = 0; Q_2^0, Q_3^0) = U(0) + \sum_n U_{Q_2}^{(n)}(0) Q_2^{0n} / n! + \sum_n U_{Q_3}^{(n)}(0) Q_3^{0n} / n!, \quad (7)$$

where  $U(0) = U_0$  is the potential function of the regular octahedral complex. The function  $U(Q_j^0 = 0; Q_2^0, Q_3^0)$  expressed in this form is identical with

$$U(Q_j^0 = 0; \rho_0, \theta) = U_0 + U(\rho_0, \theta), \quad (8)$$

where  $U(\rho, \theta)$  is (4a).

We do not consider it our task to calculate the normal vibrations of the deformed bipyramidal complex and to discuss at the same time the peculiar nature of the vibrations which may occur in this case because the metallic ion is not in an S-state. Our aim is to show that among the normal vibrational coordinates of the bipyramidal complex there will be coordinates of the kind  $q = \rho_0 - \rho$  and  $\gamma = \theta_0 - \theta$  which will have the symmetries  $\tilde{Q}_3$  and  $\tilde{Q}_2$  respectively; this follows from the relations  $\rho = (Q_2^2 + Q_3^2)^{1/2}$ ,  $\theta = \arctan(Q_2/Q_3)$  if we take into account that  $Q_2^0 = 0$  and  $Q_3^0 = \rho_0$ . We shall in particular be interested in vibrations of the type  $\gamma$ , because they influence essentially the electronic density of  $\text{Cu}^{2+}$ .

Expanding (8) in  $q$  and  $\gamma$  in the neighborhood of  $\rho_0, \theta_0$  we get

$$U(\rho, \theta) = U(\rho_0, \theta_0) + \frac{1}{2}(k - 6|A_3|\rho_0 \cos 3\theta_0)q^2 + \frac{1}{2}(k + 9|A_3|\rho_0^3 \cos 3\theta_0)\gamma^2. \quad (9)$$

Apart from this, we must take into account the contribution from the linear term.<sup>9</sup> We have

$$E^{(2)} = -|\langle \varphi_1^0 | \hat{V}_2 Q_2 + \hat{V}_3 Q_3 | \varphi_2^0 \rangle|^2 / \Delta E,$$

where  $\Delta E$  is the magnitude of the shift of the lowest orbital doublet of  $\text{Cu}^{2+}$  (see Fig. 2); one must take the matrix element with respect to the unperturbed wave functions of the copper ion  $\varphi_1^0 = \varphi_1(\theta_0)$  and  $\varphi_2^0 = \varphi_2(\theta_0)$  [(2a), (2b)].

If we consider  $E^{(2)}$  as a correction of the second order to the energy of the ion, we must take the matrix element with respect to wave functions of  $\text{Cu}^{2+}$ , where the complex is in the vibrational ground state. One sees easily that  $E^{(2)} = 0$ , since

$$\langle \varphi_1(\theta) | \hat{V}_2 \rho \sin \theta + \hat{V}_3 \rho \cos \theta | \varphi_2(\theta) \rangle = 0$$

for the values  $\rho_0$  and  $\theta = 0$ . We are, however, interested in the contribution of the linear term to the vibrational energy of the complex and not to the energy of the  $\text{Cu}^{2+}$  ion, i.e., we must find

$$U'(q_2, q_3) = E^{(2)}(Q_2^0 + q_2, Q_3^0 + q_3) - E^{(2)}(Q_2^0, Q_3^0),$$

where  $Q_2^0$  and  $Q_3^0$  are the values of  $Q_2$  and  $Q_3$  at the minimum of the potential energy of the deformed complex, and  $q_2 = \tilde{Q}_2$ ,  $q_3 = \tilde{Q}_3$  are the vibrational coordinates. The calculation shows that

$$U'(q_2, q_3) \approx -\frac{1}{2} k q_2^2 = -\frac{1}{2} k \rho_0^2 \gamma^2,$$

so that

$$U(\rho, \theta) = U(\rho_0, \theta_0) + \frac{1}{2}(k - 6|A_3|\rho_0 \cos 3\theta_0)q^2 + \frac{9}{2}|A_3|\rho_0^3 \cos 3\theta_0 \cdot \gamma^2. \quad (9a)$$

It is necessary to note that vibrations of the type  $\gamma$  possess a peculiar spatial degeneracy: in some fixed system of coordinates identical vibrations may occur when the complex is stretched along the x, y, or z axis; it is essential for this that for the transition, let us say from x to y, the system must overcome a relatively high potential barrier (see Fig. 3).

We shall now consider the connection between the vibrations of the complex of the type  $\gamma$  and the form of the eigenfunctions of the copper ground state. If the complex is in the vibrational ground

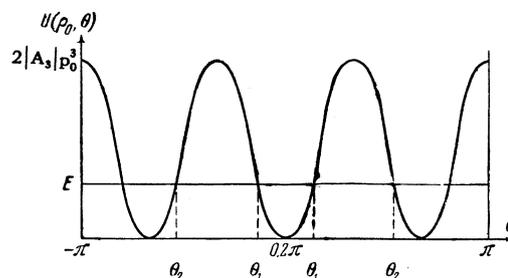


FIG. 3. Curve of the potential energy  $U(\rho, \theta)$  of the complex.

state as far as the coordinate  $\gamma$  is concerned, the eigenfunction  $\varphi_1^{(1)}$  of the copper ground state is a pure  $\psi_1$  [see (2a) and (2b)]. The combinations  $\varphi_1^{(2,3)} = \frac{1}{2}\psi_1 + (\sqrt{3}/2)\psi_2$  correspond to a change in the configuration of the complex; in some fixed system of xyz coordinates, namely, the functions  $\varphi_1^{(2)}$  and  $\varphi_1^{(3)}$  may be the eigenfunctions of the  $\text{Cu}^{2+}$  ion when the complex is stretched along the x and the y axis respectively, if  $\varphi^{(1)}$  is defined relative to the z axis.

If the complex performs vibrations of type  $\gamma$  with some frequency, the cubic eigenfunction  $\psi_2$  will be mixed with the same frequency into the eigenfunction  $\varphi_1$  of the ground state of the ion. The amplitude with which  $\psi_2$  is present in the superposition  $\varphi_1(\psi_1, \psi_2)$  is determined by the expression  $(1 - \cos \theta)^{1/2}/\sqrt{2}$  [see (2a)].

The interdependence of the eigenvibrations of the complex and the form of the function  $\varphi_1$  of the ground state of  $\text{Cu}^{2+}$  is a consequence of the connection, already noted by us, of the geometry of the complex and the distribution of the electron cloud of the magnetic ion. In the equilibrium state of the complex at a temperature T, the eigenfunction  $\psi_2$  will be present in  $\varphi_1$  with some average intensity  $\alpha^2 = \frac{1}{2} \langle (1 - \cos \theta) \rangle_{\text{av}}$  (time average) so that the eigenfunctions will be of the form\*

$$\varphi_1 = (1 - \alpha^2)^{1/2} \psi_1 + \alpha \psi_2. \quad (10)$$

An arbitrary physical quantity L obtained by quantum mechanical averaging over the ground state of the system (such as the g-factor, the hfs constants, and so on) will therefore be of the form

$$L = L_1 - \alpha^2(L_1 - L_2), \quad L_1 = \langle \psi_1 | \hat{L} | \psi_1 \rangle, \\ L_2 = \langle \psi_2 | \hat{L} | \psi_2 \rangle. \quad (11)$$

This mechanism was considered by us. It gives a qualitatively correct dependence of the g-factors and the hfs constants on the temperature, but under the given conditions it is not unique and is, apparently, not the main mechanism.

Indeed it is well known<sup>10</sup> that if a quantum particle with momentum p is in a potential well U(x) of the form depicted in Fig. 4, while U(x) satisfies the condition for quasi-classical behavior:  $m\hbar F/p^3 \ll 1$ ,  $F = -\partial U/\partial x$ , the probability (per unit time) for the overcoming of the barrier is equal to

\*The eigenfunctions  $\psi_1$  and  $\psi_2$  taken by us in the LMSS<sub>z</sub> representations are arbitrary spin and orbital functions. This is connected with the fact that  $\langle \psi_1 | \lambda(\mathbf{L} \cdot \mathbf{S}) | \psi_2 \rangle = 0$ , where  $\lambda(\mathbf{L} \cdot \mathbf{S})$  is the spin-orbit interaction.

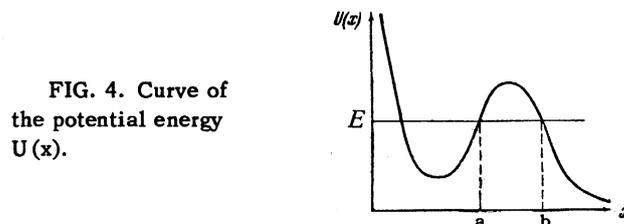


FIG. 4. Curve of the potential energy U(x).

$$w = (\omega_0/2\pi) \exp \left[ -2\hbar^{-1} \left| \int_a^b p dx \right| \right],$$

since during a unit time interval a particle performing classical vibrations inside the well impinges  $\omega_0/2\pi$  times on the barrier.

The considerations given here are applicable in our case to vibrations of type  $\gamma$  if the condition for quasi-classical behavior is satisfied for the potential curve  $U(\rho_0, \theta)$  (see Fig. 3). Calculation shows that the condition for quasi-classical behavior is satisfied for  $U(\rho_0, \theta)$  so that we get

$$w(E) = (\omega_0/\pi) \exp \left[ -2\hbar^{-1} \left| \int_{\theta_1}^{\theta_2} M(\theta) d\theta \right| \right], \quad (12a)$$

where

$$U(\rho_0, \theta) = U_0(1 - \cos 3\theta), \quad U_0 = |A_3| \rho_0^3,$$

and  $M(\theta)$  is found from the equation

$$M^2/2J + U(\rho_0, \theta) = E.$$

J is the moment of inertia for the "rotation" of the complex along the circle  $Q_2^2 + Q_3^2 = \text{const}$ ; for the hydrated complex  $J \sim 7.8 \times 10^{-40} \text{ g-cm}^2$  (for  $\rho_0 = 0.3 \times 10^{-8} \text{ cm}$ );<sup>9</sup> E is the energy.

It is clear that if the vibrations have large amplitudes they will no longer be harmonic, but for  $2|A_3| \rho_0^3 \gg E$  we can restrict ourselves to the harmonic-oscillator approximation for a rough estimate of the frequency  $\omega_0$  of the vibrations. For hydrated complexes  $\omega_0 \approx 5 \times 10^{13} \text{ sec}^{-1}$  ( $\hbar\omega_0 \approx 300 \text{ cm}^{-1}$ ).

Since  $J\omega_0^2 = 9|A_3| \rho_0^3$ ,

$$w(E) = \frac{\omega_0}{\pi} \exp \left[ -\frac{2U_0}{\hbar\omega_0} \left| \int_{\delta_1}^{\delta_2} \sqrt{2[E/U_0 - (1 - \cos \delta)]} d\delta \right| \right]. \quad (12b)$$

It is unfortunately difficult to perform the thermodynamic averaging (12b) and to find  $\tilde{w}(T; M, U_0)$  explicitly (M is the mass of the corner atoms Y, and  $2U_0$  the height of the potential barrier). Indeed, for such an averaging it is assumed that E changes from 0 to  $\infty$ . For a sufficiently large increase of E the theory of small vibrations becomes, however, inapplicable so that  $\omega_0 = \omega_0(E)$ .

It is well known that an exchange interaction of the order of  $I \sim 1 \text{ cm}^{-1}$  ( $I/\hbar = \omega_{\text{exch}} \sim 2$

$\times 10^{11} \text{ sec}^{-1}$ ) leads practically to a complete removal of hfs in copper. The given mechanism will thus be essential for the averaging of the hfs and  $g$ -factor, only if the frequency of the "rotation" of the electron density  $2\pi\tilde{\omega} \sim 10^{11} \text{ sec}^{-1}$ .

In addition to the tunnel effect, another factor contributing to the "rotation" of the electron density is the classical mechanism of overcoming the potential barrier through energy fluctuations. This mechanism is not considered in the present paper.

#### 4. DISCUSSION

The decrease in the hfs constant, which is observed in a number of cases in solid salts of elements of the iron group and in particular in copper salts, is usually explained either by exchange interactions or by a partial covalent bond between the magnetic ion and the corner atoms.

We propose still another mechanism for solutions of copper salts, which under well defined conditions may lead to both isotropy and a decrease of the hfs constants and at the same time to isotropy of the  $g$ -factor; this mechanism predicts, generally speaking, a temperature dependence of the hfs constants and of the  $g$ -factors.

If there occurs a "rotation" of the electron density, as discussed in Sec. 3, the eigenfunction of the ground state can be written in the form

$$\varphi_1 = [1 - \alpha^2(\tilde{\omega})]^{1/2} \psi_1 + \alpha(\tilde{\omega}) \psi_2,$$

$$\alpha(\tilde{\omega}) = (1 - \cos 2\pi\tilde{\omega}t)^{1/2} / \sqrt{2},$$

and the magnitude of  $L$  is equal to the time average

$$L = \langle \varphi_1 | L | \varphi_1 \rangle_{\text{av}} = L_1 - \langle \alpha^2(\tilde{\omega}) \rangle_{\text{av}} (L_1 - L_2).$$

For such an average the ratio of  $2\pi\tilde{\omega}$  and the frequency of the Larmor precession  $\omega_{\text{res}}$  is an important quantity. If the barrier is sufficiently low so that  $2\pi\tilde{\omega} \gg \omega_{\text{res}}$  one may put the period  $T$  equal to  $2\pi/\omega_{\text{res}}$ . We have then

$$\langle \alpha^2(\tilde{\omega}) \rangle_{\text{av}} = 1/2, \quad \tilde{L} = \frac{1}{2} (L_1 + L_2).$$

This corresponds to a complete averaging of the quantity  $L$ .

In the other extreme case, when the barrier is so high that  $2\pi\tilde{\omega} = \omega_{\text{res}}$ , one cannot average the quantity  $L$  by taking the overcoming of the barrier into account. Only the eigenvibrations of the complex can in that case influence the magnitude of  $L$ ; however, calculation shows that the influence of these vibrations is unimportant.

When  $2\pi\tilde{\omega} \sim \omega_{\text{res}}$  the magnitude of  $L$  will be temperature dependent. As was mentioned already

it is difficult to get an explicit expression for this dependence.

In hydrated complexes  $\text{Cu}^{2+}(\text{H}_2\text{O})_6$  in solutions and also in copper salts with a trigonal symmetry, complete averaging apparently does take place. Bearing in mind that\*

$$g_x^{(1)} = g_y^{(1)} \approx 2.28, \quad g_z^{(1)} \approx 2.0,$$

$$|A^{(1)}| = 85 \cdot 10^{-4} \text{ cm}^{-1}, \quad |B^{(1)}| = 78 \cdot 10^{-4} \text{ cm}^{-1};$$

$$g_x^{(2)} = g_y^{(2)} \approx 2.11, \quad g_z^{(2)} \approx 2.46,$$

$$|A^{(2)}| \approx 110 \cdot 10^{-4} \text{ cm}^{-1}, \quad |B^{(2)}| \approx 30 \cdot 10^{-4} \text{ cm}^{-1},$$

we get

$$\tilde{g}_x = \tilde{g}_y \approx 2.19, \quad \tilde{g}_z \approx 2.23,$$

$$|\tilde{A}| \approx 17 \cdot 10^{-4} \text{ cm}^{-1}, \quad |\tilde{B}| \approx 24 \cdot 10^{-4} \text{ cm}^{-1}.$$

In evaluating  $|\tilde{A}|$  and  $|\tilde{B}|$  we have taken into account the theoretical considerations about the signs of the constants  $A$  and  $B$ .<sup>11</sup>

In the framework of the given theory there is also an explanation for the experimental fact that some copper complexes, as a rule with heavy corner atoms,<sup>12</sup> have a hyperfine structure. Indeed, the theoretical considerations involve the three parameters  $J$ ,  $\omega_0$ , and  $|A_3| \rho_0^3$  which are connected by the relation  $J\omega_0^2 = 9|A_3| \rho_0^3$ . A change in the corner atoms may lead both to a change in  $|A_3| \rho_0^3$  and to a change in  $J$  due to a change in the effective mass of the complex ( $J \approx \frac{1}{2} M \rho_0^2$ ): one must understand by  $M$  not the total mass of the corner atoms, but some effective mass, since the corner atoms  $Y$  do not take part in the vibrations of the complex as a whole. If we assume that  $|A_3| \rho_0^3$  does not change appreciably when we make a substitution of the corner atoms, we obtain all the same an important dependence of  $\tilde{\omega}$  on the mass of the corner atoms, as follows from Eq. (12b) ( $\omega_0 = \sqrt{9|A_3| \rho_0^3 / J}$ ). We have not enough data about the character of the change of the quantities mentioned at our disposal to make concrete calculations.

In conclusion the author expresses his deep gratitude to B. M. Kozyrev for a discussion of his results and to S. A. Al'tshuler for his interest in the work.

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\*The data are taken for Tutton salts of copper<sup>2</sup> where the ground state (in the LMSS<sub>z</sub> representation) is  $\psi_1 = \psi_{2,0} \psi_\alpha(S_z)$  and for the fluorosilicate of copper (at  $T = 20^\circ \text{K}$ )<sup>1</sup> where the ground state is  $\psi_2 = \psi_\alpha(S_z)(\psi_{2,2} + \psi_{2,-2})/\sqrt{2}$ .

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