

**SPIN-INVERSION LEVELS IN A MAGNETIC FIELD AND THE EPR SPECTRUM OF
OCTAHEDRAL Cu^{2+} ION COMPLEXES**

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With the octahedral Cu^{2+} ion complexes taken as an example, it is shown that by taking into account the inversion splitting previously investigated by the author, a system of spin-inversion (spin-electronic-vibrational) levels appears in a magnetic field. One of the features of the system is that some of the levels correspond to the same spin states. The transition probabilities between these states under the action of an electromagnetic perturbation depend significantly on the relation between the magnetic field strength and the magnitude of the inversion splitting. In this way one obtains a characteristic temperature transition from one type of EPR spectrum to another, which is confirmed by the available experimental data. An unusual frequency dependence of the spectrum and, in particular, the possibility of absorption in zero field is also deduced.

1. INTRODUCTION

In a previous paper [1] we considered the inversion splitting of the electronic-vibrational levels of an octahedral complex arising from the presence of several equivalent equilibrium configurations associated with the instability of the system in the configuration of a regular octahedron. The general splitting pattern, the wave functions of the inversion levels, and the magnitude of the inversion splitting were obtained. The last turned out to be of the order of magnitude of the quanta used in radiospectroscopy. Hence, it is reasonable to expect that inversion splitting should be an important consideration in electron paramagnetic resonance (EPR) problems and the like. In fact, the presence of a number of closely spaced levels, each of which for the case $S = 1/2$ is a Kramers doublet, should significantly alter the system of levels in a magnetic field compared to what would be expected for a single doublet with no inversion splitting.

On the other hand, not all experimental facts from EPR spectra in the systems considered find satisfactory explanations. Even the most simple and most studied (see [2]) example of the spectrum of Cu^{2+} remains unclear. In particular, a satisfactory interpretation has not yet been given for the temperature transition from one type of spectrum to another (see below) that is observed in some of its compounds. Hence, the investigation of the effect of inversion splitting on EPR spectra

began naturally with octahedral complexes of the Cu^{2+} ion. It was expected that taking inversion splitting into account would lead to a satisfactory explanation of the most important experimental peculiarities of the spectra of these systems, in particular, the temperature dependence. As will be seen below, these expectations were fulfilled.

The present paper sets forth the general method of obtaining the system of levels of octahedral complexes of transition metals in a magnetic field, with account taken of inversion splitting and spin-orbit interaction, and applies it to the case of Cu^{2+} . The characteristics of the set of spin-inversion levels obtained can be important for the establishment of a system with a large negative effective temperature.

2. INVERSION LEVELS WITH SPIN-ORBIT INTERACTION

In the octahedral Cu^{2+} complex there are two inversion levels [1]: the ground level A_{1g} and an excited, doubly degenerate level E_g . The wave functions corresponding to them have the form¹⁾:

$$\begin{aligned}\Psi_{1x} &= [3(1 - \gamma_x)]^{-1/2} (\Phi_{1x} + \Phi_{2x} + \Phi_{3x}), \\ \Psi_{2x} &= [3(2 + \gamma_x)]^{-1/2} (2\Phi_{1x} - \Phi_{2x} - \Phi_{3x}), \\ \Psi_{3x} &= [2 + \gamma_x]^{-1/2} (\Phi_{2x} - \Phi_{3x});\end{aligned}\quad (1)$$

¹⁾These functions differ from those in [1] by the specification of normalization constants.

$$\Phi_{ix} = \psi_i(q) \chi_{ix}, \quad \chi_{ix} = \prod_{\alpha=1}^p \chi_{n_\alpha} (Q_\alpha^{(i)}), \quad i = 1, 2, 3, \\ \gamma_x = \int \chi_{ix} \chi_{jx} dQ_\alpha, \quad i \neq j. \quad (2)$$

Here $\psi_i(q)$ is the electronic function of the missing 3d electron in the 3d¹⁰ shell, $\chi_{n_\alpha}(Q_\alpha^{(i)})$ is the wave function of the n_α -th excited state of the harmonic oscillator corresponding to the normal coordinate Q_α in the i -th equilibrium configuration, and κ is shorthand for the set of quantum numbers n_1, \dots, n_p characterizing the vibrational state of the complex.

The electronic functions in the approximation considered are expressed by the usual hydrogen d-functions φ_4 and φ_5 , the angular parts of which are respectively $3z^2 - r^2$ and $x^2 - y^2$ in Cartesian coordinates. For the case of tetragonal distortion in the equilibrium configurations consisting of an elongation along one axis of the octahedron,

$$\psi_1 = \varphi_5, \quad \psi_2 = -\frac{1}{2}\varphi_5 + \frac{\sqrt{3}}{2}\varphi_4, \quad \psi_3 = -\frac{1}{2}\varphi_5 - \frac{\sqrt{3}}{2}\varphi_4. \quad (3)$$

For shortened octahedra the ψ_i are similar and can be obtained from (3) by exchanging φ_4 and φ_5 . The expression for the magnitude of the inversion splitting and the numerical values for certain cases were given in [1].

Each of the inversion states (1) is a spin doublet [$S = 1/2$; the states corresponding to projections of the spin on the Oz axis are symbolized by (+) and (-)]. These states are not coupled by the spin-orbit interaction, but are subjected to the influence of the nearest excited state T_{2g} , described by the electronic d-functions [1] φ_1 , φ_2 , and φ_3 , the angular parts of which equal respectively xy , xz , and yz . Choosing the expression for the spin-orbit interaction in the form $\lambda \hat{L} \cdot \hat{S}$ where λ is the spin-orbit coupling constant, and symbolizing the separation between the terms E_g and T_{2g} by Δ , it is possible to obtain the following expressions for the wave functions of the Kramers doublets of Cu^{2+} ion in a free octahedral complex by first-order perturbation theory (equilibrium configurations—elongated octahedra):

$$\Psi_{1x}^{(\pm)'} = \Psi_{1x}^{(\pm)} + \frac{\lambda}{\Delta} [3(1 - \gamma_x)]^{-1/2} \\ \times \left\{ -i \left(\chi_{3x} - \frac{1}{2} \chi_{2x} - \frac{1}{2} \chi_{1x} \right) \varphi_3^{(\mp)} \left(\chi_{2x} - \frac{1}{2} \chi_{1x} - \frac{1}{2} \chi_{3x} \right) \right. \\ \left. \times \varphi_2^{(\mp)} \mp i \left(\chi_{1x} - \frac{1}{2} \chi_{2x} - \frac{1}{2} \chi_{3x} \right) \varphi_1^{(\pm)} \right\}, \\ \Psi_{2x}^{(\pm)'} = \Psi_{2x}^{(\pm)} + \frac{\lambda}{\Delta} [3(2 + \gamma_x)]^{-1/2} \left\{ i \left(\chi_{1x} + \chi_{3x} - \frac{1}{2} \chi_{2x} \right) \varphi_3^{(\mp)} \right. \\ \left. \mp \left(\chi_{1x} + \chi_{2x} - \frac{1}{2} \chi_{3x} \right) \varphi_2^{(\mp)} \right. \\ \left. \mp i \left(2\chi_{1x} + \frac{1}{2} \chi_{2x} + \frac{1}{2} \chi_{3x} \right) \varphi_1^{(\pm)} \right\},$$

$$\Psi_{3x}^{(\pm)'} = \Psi_{3x}^{(\pm)} + \frac{\lambda}{\Delta} [4(2 + \gamma_x)]^{-1/2} \left\{ i \left(\chi_{2x} + 2\chi_{3x} \right) \varphi_3^{(\mp)} \right. \\ \left. \pm (2\chi_{2x} + \chi_{3x}) \varphi_2^{(\mp)} \pm i \left(\chi_{2x} - \chi_{3x} \right) \varphi_1^{(\pm)} \right\}. \quad (4)$$

Similar expressions can be obtained for the case when the equilibrium octahedra are tetragonally flattened out (shortened along a diagonal).

3. SPLITTING IN A MAGNETIC FIELD; g FACTORS

Since the splitting in an external magnetic field can turn out to be of the same order as the inversion splitting, its effect should be calculated at the same time as the interaction between the equivalent configurations of the complex U. [1] The complete perturbation of these configurations therefore has the form

$$U + \lambda(\hat{L}, \hat{S}) + \beta(\hat{L} + 2\hat{S}, \mathbf{H}). \quad (5)$$

The matrix elements of this expression are determined rather easily if we start with the functions (4), in which basis the matrix $U + \lambda \hat{L} \cdot \hat{S}$ is diagonal. We obtain a sixth-order secular equation to find the energy levels $\epsilon_{i\kappa}$. Its solution for arbitrary direction of the field is difficult. We shall first consider the direction $\mathbf{H} \parallel \text{Oz}$. For this we find

$$\epsilon_{1x}^{\pm} = -\frac{1}{6} \delta_x \pm \left[1 - \frac{\lambda}{\Delta} \left(\frac{5}{2} + \frac{3}{4} \gamma_x \right) \right] \beta H \\ - \frac{1}{2} \left\{ \left[\delta_x \mp \frac{\lambda}{\Delta} \left(1 + \frac{3}{2} \gamma_x \right) \beta H \right]^2 + \frac{8\lambda^2}{\Delta^2} \left(1 - \frac{3}{4} \gamma_x \right)^2 \beta^2 H^2 \right\}^{1/2}, \\ \epsilon_{2x}^{\pm} = -\frac{1}{6} \delta_x \pm \left[1 - \frac{\lambda}{\Delta} \left(\frac{5}{2} + \frac{3}{4} \gamma_x \right) \right] \beta H \\ + \frac{1}{2} \left\{ \left[\delta_x \mp \frac{\lambda}{\Delta} \left(1 + \frac{3}{2} \gamma_x \right) \beta H \right]^2 + \frac{8\lambda^2}{\Delta^2} \left(1 - \frac{3}{4} \gamma_x \right)^2 \beta^2 H^2 \right\}^{1/2}, \\ \epsilon_{3x}^{\pm} = \frac{1}{3} \delta_x \pm \left[1 - \frac{\lambda}{\Delta} \left(1 - \frac{3}{2} \gamma_x \right) \right] \beta H. \quad (6)$$

The dependence of these levels on magnetic field intensity is shown in the figure. We see that as a consequence of the interaction of the levels 1⁺ and 2⁺, 1⁻ and 2⁻, two regions of differing behavior of the levels in the magnetic field arise, separated by a certain interval (indicated in the figure by the dashed lines) in which there is a mixing of the levels. The position of this interval depends on the ratio between δ_K and βH . In the region to the right of it $\lambda \beta H / \Delta \gg \delta_K$; this we call the high-frequency region for short. There is significant probability for three transitions here, as indicated in the figure by arrows. The g factors corresponding to these transitions are

$$g_1 = 2 - \frac{8\lambda}{\Delta},$$

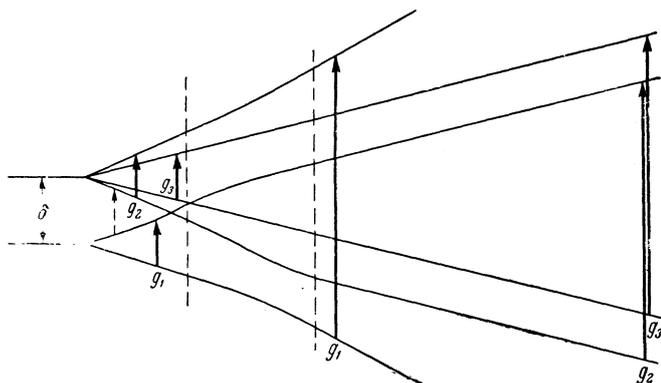
$$g_2 = 2 - \frac{\lambda}{\Delta} (2 + 3\gamma_x), \quad g_3 = 2 - \frac{\lambda}{\Delta} (2 - 3\gamma_x). \quad (7)$$

In the low-frequency region, where $\lambda\beta H/\Delta \ll \delta_\kappa$, three other transitions are allowed, with g factors:

$$g_1 = 2 - \frac{4\lambda}{\Delta},$$

$$g_2 = 2 - \frac{\lambda}{\Delta} (6 + 3\gamma_\kappa), \quad g_3 = 2 - \frac{\lambda}{\Delta} (2 - 3\gamma_\kappa). \quad (8)$$

In the intermediate region the probabilities of the low-frequency transitions decrease with increasing field and become vanishingly small at its right edge. The high-frequency transitions disappear at the left boundary.



For directions of H along the Ox or Oy axes the energy level spectrum is the same as (6). However, in intermediate directions, not along the coordinate axes (the tetragonal axes of the octahedron), the levels approach each other in such a way that the differences in the g factors decrease, and in the trigonal axis direction all g values are the same and equal to $g = 2 - 4\lambda/\Delta$, both in the low-frequency and also in the high-frequency spectrum.

The general picture of the high-frequency spectrum is as if there were three paramagnetic ions absorbing at the same time, each situated in a nearly tetragonal field (the terms containing γ_κ are in fact second-order corrections, with the directions of the tetragonal axes of these ions mutually orthogonal. In the low-frequency spectrum there is one completely isotropic transition g_1 , corresponding to the ground inversion state, and two anisotropic transitions located symmetrical on both sides of the isotropic line. The latter are at their maximum separation from the isotropic transition when the magnetic field is along the tetragonal axes of the octahedron and are closest to it when the field is along the trigonal axes.

In the case when the equilibrium configurations of the complex are (flattened) octahedra that are shortened along a diagonal, the spectral pattern is

in principle similar to that obtained above; however, instead of (7), we have for the g factors of the high-frequency spectrum:

$$g_1 = 2, \quad g_2 = 2 - \frac{\lambda}{\Delta} (6 + 3\gamma_\kappa), \quad g_3 = 2 - \frac{\lambda}{\Delta} (6 - 3\gamma_\kappa). \quad (9)$$

4. TEMPERATURE DEPENDENCE OF THE SPECTRUM. EXPLANATION OF THE TEMPERATURE TRANSITION OBSERVED IN THE CRYSTALLINE STATE.

An interesting peculiarity of this spectrum is its temperature dependence. This shows up in the magnitude of the inversion splitting δ_κ , which is determined by the vibrational state κ and grows exponentially with temperature (even for a free complex). Temperature dependence via the parameter γ_κ is less effective, since it enters only in terms of the second order, as has already been noted.

As δ increases, the transition region of the spectrum shifts to the right (see the figure), i.e., the upper limit of the low-frequency spectrum and the lower limit of the high-frequency spectrum become higher. For a constant (and sufficiently high) frequency of absorbed electromagnetic radiation, the following temperature dependence should be observed. At low temperatures, the spectrum corresponds to the high-frequency system of lines, given by the g factors of (7) [or (9)]. As the temperature is increased, a point corresponding to the right boundary of the transition region is reached; here the intensity of the high-frequency spectrum begins to fall off and the low-frequency lines begin to appear. With further increase of temperature, the left boundary is reached; the spectrum is the low-frequency spectrum and is determined by the g factors of (8).

It is obvious that the direct observation of this temperature dependence is possible only in complexes within crystals. In fact, in the liquid and gaseous states the observed spectrum is averaged over all directions. The complication in the spectrum brought about by the inversion splitting is manifested only indirectly, in the line width and its temperature and frequency dependence. The investigation of this question will be the subject of a separate communication.

In order to observe the spectrum described above in the crystalline state, at least two conditions must be fulfilled: (1) The symmetry of the surroundings of the given complex must not remove the E_g degeneracy of its electronic ground state (this will stabilize one of the three equivalent

Experimental data on the temperature transition in the EPR spectrum of the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex in salts of trigonal symmetry

Crystal	Region of the temperature transition, ° K	Low-temperature spectrum			High-temperature spectrum, g_1
		g_1	g_2	g_3	
(Cu,Zn) $\text{SiF}_6 \cdot 6\text{H}_2\text{O}$	~12—50	2,46	2,10	2,10	2,22
(Cu,Zn) $(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$	~ < 7—35	—	—	—	2,22
(Cu,Mg) $_3\text{La}_2(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$	33—45	2,47	2,10	2,10	2,22
(Cu,Mg) $_3\text{B}_2(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$	~20—90	2,45	2,10	2,10	2,22
$\text{Cu}_3\text{La}_2(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$	~170—270	2,41	2,10	2,10	2,22

configurations of the tetragonally distorted octahedron), i.e., must not remove the inversion splitting, and (2) the effect of these surroundings must be sufficiently small, so that the distortion of the octahedron in the equilibrium configuration and the height of the barrier between these configurations remain sufficiently large; otherwise, the criterion of applicability of the theory of inversion splittings [1] is not fulfilled.

It is proper to mention at this point that in a crystal the height of the barrier between equivalent equilibrium configurations of a complex really depends also on the state of interaction of its ligands with the external surroundings (on their mobility) and, consequently, depends strongly on temperature (on the excitation of vibrations of the crystal as a whole). Hence the inversion splitting δ should be expected to be a strong function of the temperature independently of the population of the vibrational states of the complex.²⁾

The hydrated salts of copper with trigonal symmetry best fulfill the requirements set forth above. In these salts the ionic sites are occupied by the hydrated complex $\text{Cu}(\text{H}_2\text{O})_6^{2+}$, and the surrounding field, having trigonal symmetry, does not remove the inversion splitting in this complex. It is necessary to compare our results with the EPR measurements on these compounds.

Some experimental EPR data [3-6] on a group of similar crystals are presented in the table. In all cases a temperature transition from one type of spectrum to another is observed. Thorough studies [5,6] have shown that at low temperatures the observed spectrum corresponds to the presence of three types of Cu^{2+} ions in the crystal, each of which is situated in a tetragonal field, with the three tetragonal axes mutually perpendicular and forming the edges of a cube (or the diagonals of an

octahedron), the trigonal axis of which coincides with the crystal axis. As the temperature is raised, the intensity of this spectrum begins at a certain point to diminish to zero, and, at the same time, a new type of spectrum consisting of a single isotropic line begins to appear with increasing intensity. The limits of the region of the temperature transition are indicated approximately in the table. The g factors corresponding to the field directed along the tetragonal axis of one of the Cu^{2+} ions are given for the low-temperature spectrum.

It is easy to see that the general picture presented here of the observed spectrum and its temperature dependence is in good agreement with the theory. The g factors of the low-temperature spectrum correspond to Eq. (7), which pertains to elongated (along a diagonal) octahedra in the equilibrium configurations (this again confirms that elongated octahedra are more stable than shortened ones, see [7]). In the intermediate region the correspondence between theory and experiment is also complete. The isotropic line with $g = 2.22$ observed in the high-temperature spectrum corresponds to a transition between the sublevels of the ground inversion state with $g_1 = 2 - 4\lambda/\Delta$. Even such a detail as a certain diminution in the value of g_1 with an increase in temperature near the upper limit of the transition region [$g = 2.235 \pm 0.005$ at $T = 45^\circ\text{K}$ and $g = 2.218 \pm 0.003$ at $T = 90^\circ\text{K}$ for $(\text{Cu}, \text{Mg})_3\text{La}_2(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ [6]] also follows directly from the temperature dependence of the energy levels in a magnetic field given in (6) (see the figure; an increase in temperature corresponds to a shift along the spectrum from right to left). However, transitions corresponding to excited inversion levels in the high-temperature spectrum have as yet not been clearly observed. It is known only that some additional weak lines whose origin is unclear have been observed. [3] It is possible that more careful experimental investigation will permit a positive identification of

²⁾Any kind of accurate calculations of the barrier height and its temperature dependence are scarcely possible or convenient here, since they involve the complete calculation for the crystal as a whole.

these transitions.³⁾ One can expect to observe them more easily at low temperatures and respectively lower frequencies.

Thus, the temperature transition observed in these systems is naturally explained within the framework of the inversion splitting theory. Likewise it is clear that this transition does not have its origin in the properties of the crystal as a whole and in particular in any kind of phase transition, as has been proposed by Ingram,^[8] but is a property of the octahedral complex. The entire spectrum arises from one complex ion, and the presence of three unequivalent ions in the crystal at low temperatures is not required for its explanation. The crystalline state, by stabilizing the directions of the axes of the octahedral complex in space, only makes the observation of the spectrum easier.⁴⁾

It also follows from the explanation presented that the temperature transition from one spectrum to the other should be higher, the higher the frequency of the absorbed electromagnetic radiation.

5. FREQUENCY DEPENDENCE OF THE SPECTRUM. POSSIBLE ABSORPTION IN ZERO FIELD.

Another interesting property of the investigated spectrum is its frequency dependence. The character of the dependence of the spectrum on the frequency of the electromagnetic radiation at constant temperature is similar to the temperature dependence at constant frequency with the only difference that the changes in the spectral pattern with increasing frequency (moving from left to right in the figure) correspond to the changes in the spectrum with diminishing temperature. A detailed description of the expected low-frequency and high-frequency spectra and their changes in the intermediate region was given above. At low frequencies one can hope to see the g_2 and g_3

lines, which cannot be distinguished clearly in the high-temperature spectrum. Experiments to study the frequency dependence of the spectrum in the aspect considered above have not been carried out, to our knowledge.

Besides the usual allowed transitions of which we are speaking, there is in this spectrum also the possibility of transitions the matrix elements of which arise only from excited orbital states and the spin-orbit interaction and are of order λ/Δ in the magnetic dipole approximation. This also includes zero-field transitions between inversion levels. The magnitude of the absorption quantum corresponding to these transitions equals the inversion splitting δ , which can be determined approximately by comparing the theoretical data on the temperature dependence of the energy levels [from Eqs. (6)] with the experimental data (results of approximate calculations of δ are in ^[1]). Knowing the size of the quantum being used $h\nu = g\beta H$, it suffices to determine that value of δ , in relation to which $\lambda\beta H/\Delta$ in (6) becomes negligibly small, that corresponds to the temperature of the left boundary of the transition interval. Similarly, the value of δ for the right boundary of this interval can be found. For $(\text{Cu, Mg})_3\text{La}_2(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$, on which detailed measurements have been made,^[6] it is easy to find that for $T = 33^\circ\text{K}$, $\delta \sim 100$ Mc/sec, and for $T = 45^\circ\text{K}$, $\delta \sim 100$ Mc/sec, and for $T = 45^\circ\text{K}$, $\delta \sim 10^5$ Mc/sec. Approximately the same values of δ for other crystals will be attained at other temperatures, as can be seen from the table. In view of the strong temperature dependence of δ the corresponding absorption is best sought at constant frequency by means of varying the temperature.

Other transitions with approximately the same probability could be 1^+-2^- , 1^+-3^- , 1^--2^+ , 1^--3^+ in the low-frequency spectrum (the transition 1^+-2^- is indicated by the broken arrow in the figure) and analogously in the high-frequency spectrum. A characteristic property of these further transitions is that, in contradistinction to all the other transitions, they do not disappear (more correctly, they do not combine with the main lines) for field direction along the trigonal axis of the octahedron. Just such lines were observed by Bleaney and Ingram.^[3] For their further identification it is necessary to keep in mind that along the trigonal axes the lines 1^+-2^- and 1^+-3^- come together and are at a distance $H_1 - H_2 = (1/g_1\beta)(\delta - 2h\nu)$ from the main line g_1 , where $h\nu$ is the magnitude of the absorbed quantum. Knowing the position of the additional line and the frequency, one can estimate the magnitude of the inversion splitting from

³⁾It is possible that the difficulty in observing these lines is above all due to the fact that at high temperatures δ is large; this can lead to a violation of the criterion of applicability of the theory of inversion splitting,^[1] and, consequently, to the disappearance of the excited inversion levels. It is also probable that the width of these levels is large on account of relaxation transitions to lower inversion states not associated with a change in spin state.

⁴⁾It should be noted that, in principle, correct qualitative proposals as to the origin of the temperature transition in the spectrum were in fact made earlier^[9,10] (see also ^[11]), but they could not be regarded as convincing. An explanation for the isotropic low-temperature line in the spectrum was first proposed by Abragam and Pryce.^[12]

this relation.⁵⁾ It is also easy to see that the position of this line, as well as the frequency, depends also on the temperature.

Further experimental tests of the results of this paper would be of great interest.

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