The Jahn-Teller Center in Cadmium Halide Crystals (I)
— CdCl₂:CuCl₂ —

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The ESR spectra of a Cu²⁺ center in CdCl₂ have been studied at about 35 K, at liquid nitrogen temperature and at room temperature. The Cu²⁺ center in CdCl₂ is found to be composed of a central Cu²⁺ ion and six nearest neighbor Cl⁻ ions. The angular dependence of the spectra obtained at LNT will be explained in terms of the Jahn-Teller distortions, where the octahedron of Cl⁻ ions around a Cu²⁺ ion is elongated tetragonally. In addition, an axial distortion along the crystal c-axis was also observed at LNT. At 35 K, ten or thirteen sharp structures were observed at the high field part of the spectrum when the magnetic field was applied along or perpendicularly to the axis joining Cu²⁺ ion to one of the Cl⁻ ions, respectively. These are associated with superhyperfine structures due to the magnetic interaction of the unpaired electron spin with two or four Cl⁻ nuclei. At room temperature is observed a single broad ESR line with axial symmetry, which is interpreted in terms of the dynamical Jahn-Teller effect.

1. Introduction

It is well known that a Cu²⁺ ion has a 3d⁹ electronic configuration and the free ion has a ²D ground term. Thus, in the crystals, the Cu²⁺ impurity center is a typical hole center as well as the Ag²⁺ center. The ground ²D term of the free ion have the five-fold orbital degeneracy and split into an orbital doublet E₉ and an orbital triplet T₂g in a cubic crystal field. The ground state is the E₉ state which is lower than the T₂g state. Furthermore, by an effect of an additional trigonal field in the crystal, the T₂g state splits into an orbital singlet A₁g and another orbital doublet E₉ whereas the ground E₉ state does not split.

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Jahn and Teller\textsuperscript{1}) demonstrated in 1937 that any nonlinear complex in an orbitally degenerate state is unstable so that at least one asymmetric displacement of the nuclei will lift the electronic degeneracy and lower the energy. This phenomenon is well known as the Jahn-Teller (J-T) effect. In an electron spin resonance (ESR) study of Cu\textsuperscript{2+} in the zinc fluosilicate crystal, Bleaney and Ingram\textsuperscript{2}) found an anomalous spectrum which could not be explained from the standpoint of ordinary crystal field theory. Abragam and Pryce\textsuperscript{3}) explained this anomalous spectrum as a dynamic manifestation of the Jahn-Teller instability for the orbital doublet ground state of the Cu\textsuperscript{2+} ion. Thereafter, many studies concerning the J-T effect were carried out on the impurity centers in various crystals. For example, C. J. Delbecq et al.\textsuperscript{4}) found that the A\textsubscript{g}\textsuperscript{2+} complex center in KCl and NaCl crystals, an assembly of a central A\textsubscript{g}\textsuperscript{2+} ion and nearest neighboring six chlorine ions which form an octahedron, is elongated at liquid nitrogen temperature (LNT) along any one of three directions joining the central A\textsubscript{g}\textsuperscript{2+} ion to the Cl\textsuperscript{-} ions by the J-T effect. R. H. Borcherts et al.\textsuperscript{5}) also observed this effect in NaCl:Cu\textsuperscript{2+}.

The CdCl\textsubscript{2} crystal is a typical layer ionic crystal which belongs to CdCl\textsubscript{2} type structure. The symmetry of this crystal is D\textsubscript{3h}. In such a crystal, the Cd\textsuperscript{2+} ions are located on the center of the MX\textsubscript{6} type octahedral complex which consists of six surrounding nearest neighbor halogen ions. This octahedral complex is a little compressed along the c-axis and have the D\textsubscript{3d} symmetry. It is supposed that the Cu\textsuperscript{2+} ion may be substituted for Cd\textsuperscript{2+} ion in the crystal which contains Cu\textsuperscript{2+} ion as an impurity.

Since the ground E\textsubscript{g} state of a Cu\textsuperscript{2+} ion in the D\textsubscript{3d} crystal field has two-fold orbital degeneracy, the Cu\textsuperscript{2+} center is expected to be distorted by the J-T effect. Miyanaga et al.\textsuperscript{6}) investigated the ESR spectra of CdCl\textsubscript{2}:A\textsubscript{g}\textsuperscript{2+} in detail and found that the A\textsubscript{g}\textsuperscript{2+} center in CdCl\textsubscript{2} is distorted along the directions joining a A\textsubscript{g}\textsuperscript{2+} ion to one of the surrounding Cl\textsuperscript{-} ions by the J-T effect.

In this paper will be reported the experimental results on the ESR spectrum of CdCl\textsubscript{2}:Cu\textsuperscript{2+} obtained at various temperature. The results will be analyzed by using a spin Hamiltonian of C\textsubscript{2h} symmetry, which includes the effect of J-T distortion.

2. Experimental Procedure

Single crystals of CdCl\textsubscript{2}:CuCl\textsubscript{2} used in this study was grown by the Stockbarger method from the melt of CdCl\textsubscript{2} containing CuCl\textsubscript{2} about 3 mole percent. Though most divalent copper ions are converted into
monovalent ones during the processes of crystal growth, some divalent ions are remained in the grown crystals which show yellow color\(^7\), and the ESR signal can be observed for as-grown CdCl\(_2\):CuCl\(_2\) crystals. Thus as-grown CdCl\(_2\):CuCl\(_2\) crystals was used in the present study.

The ESR measurements were made with X-band ESR spectrometer at room temperature (RT), at LNT and at about 35 K. The size of the specimen used in the measurements below LNT is about 2×2×2 mm\(^3\) and that used in the measurements at LNT and RT is about 2×2×10 mm\(^3\). The orientation of the crystal axes were determined from the Laue X-ray photograph. The direction of the static magnetic field is rotated in the plane containing the c-axis, the [111] axis, and the z-axis, the [001] axis. The intensity of the static magnetic field was measured by a proton meter.

3. Experimental Results and Analysis

3.1. The Model of The Cu\(^{2+}\) Center

It is supposed that the Cu\(^{2+}\) ion is located at the center of an octahedron composed of six nearest neighbor halogen ions as shown in Fig. 1. This octahedron is not regular but compressed along the crystal c-axis. Thus the symmetry of this center is D\(_{3d}\) with one three-fold axis and three two-fold axes.

It is convenient for the description of the experimental results to introduce two rectangular coordinate systems, which are illustrated in the figure as the (\(u,v,w\)) system and the (\(x,y,z\)) system. The origin of the (\(u,v,w\)) system is located at the center of the octahedron and the \(w\)-axis is taken parallel to the c-axis. The \(v\)-axis is in the direction of one of the two-fold axes in the plane of the cadmium ion layer. The \(u\)-axis is taken to be perpendicular to both the \(v\)- and \(w\)-
axis. The $(x,y,z)$ system is obtained by rotating the $(u,v,w)$ system with the Eulerian angle $\alpha = 0^\circ$, $\beta = -\cos^{-1}$1/$\sqrt{3}$ and $\gamma = -45^\circ$. In this rectangular coordinate system, the $u$-, $v$- and $w$-axis are located in the directions of [112], [110] and [111], respectively. Strictly speaking, the directions joining the Cu$^{2+}$ ion to the neighboring Cl$^-$ ions deviate a little from these of the $x$-, $y$- and $z$-axis. However, it may be said that the nearest neighbor Cl$^-$ ions lie on the $x$-, $y$- or $z$-axis when there is no confusion.

In the ESR experiments, the static magnetic field was rotated around the $v$-axis, i.e. in the $u$-$w$ plane as is mentioned in the previous section. It is noted that the $z$-axis lies in this $u$-$w$ plane. The direction of the static magnetic field, therefore, is expressed in the $(u,v,w)$ system by the variable zenith angle $\theta$ and the constant azimuth angle $\phi$.

### 3.2. Experimental Results

The ESR spectra of the CdCl$_2$:Cu$^{2+}$ crystal obtained at about 35 K are shown in Figs. 2 and 3. These spectra are attributed to the Cu$^{2+}$ center in CdCl$_2$ with an elongated distortion of the octahedron of Cl$^-$ ions along one of the cube axes as is shown later. The ESR spectrum
shown in Fig. 2 is obtained with the static magnetic field parallel to the \( z \)-axis. The four lines at low field side, with the splitting of 104 G, arise from the \( \text{Cu}^{2+} \) centers elongated along the \( z \)-axis (referred as the \( z \)-center in the following). The splitting is due to the hyperfine interaction of an unpaired electron spin with the copper nuclear spin \( (I = 3/2) \). At high field side of the spectrum are perceived ten lines, though three lines of which are not clearly resolved in the figure. These lines with the spacing of about 19 G are due to the \( \text{Cu}^{2+} \) centers elongated along the \( x \)- or \( y \)-axis (referred as the \( x \)- or \( y \)-center in the following). This spectrum is expected from the hyperfine interaction of unpaired electron spin with one copper nucleus and two chlorine nuclei \( (I = 3/2) \) on the \( z \)-axis assuming that the hyperfine constant of the copper and the chlorine are nearly equal in this magnetic field direction.

The spectrum shown in Fig. 3 was obtained with the static magnetic field perpendicular to the \( z \)-axis. The four lines at low field side of the spectrum are due to the \( x \)- or \( y \)-centers. The splitting of 90 G is caused by the hyperfine interaction of an unpaired electron spin

![Fig. 3 The ESR spectrum of the \( \text{Cu}^{2+} \) center in CdCl\(_2\) at 34 K. The static magnetic field is perpendicular to the \( z \)-axis. The four broad lines at the low field side of the spectrum arise from the \( x \)- and \( y \)-center and the thirteen fine lines at the high field side are due to the \( z \)-center. The structures at the high field side are clearly resolved into only eleven lines. The other two lines are superposed on a broad line at the lower field side.](image-url)
with the copper nucleus. At high field side are perceived the thirteen lines, two of which are hidden in the highest field line of the low field spectrum. The splitting of about 14 G are expected from the superhyperfine interaction of the electron spin with four chlorine nuclei in the x-y plane. In this direction of the static magnetic field, the hyperfine interaction of the electron spin with the copper nucleus is supposed to be very weak and the splitting due to this interaction does not appear in the spectrum.

As shown in Figs. 2 and 3, the structures due to superhyperfine interaction with the chlorine nuclei are remarkable for their number and resolution when the static magnetic field is applied perpendicularly to the axes of the x-, y- or z-center, that is, these structures appear in the high field parts of the spectra. This suggests that the dominant mode of the static J-T distortion is that elongated along the tetragonal axis of each center.

In Fig. 4 are shown the ESR spectra of the Cu$^{2+}$ centers observed at LNT and RT with the magnetic field parallel to the z-axis. As shown in the upper part of the figure, each line becomes slightly broad and the resolved superhyperfine structures at high field part vanish at LNT. This change in the spectrum caused by the temperature rising may be associated with the change in the effect of the J-T distortion from the static to the dynamical one. This tendency become more and more remarkable as the temperature rises and the spectrum at RT becomes one broad line as shown in the lower part of Fig. 4.
The angular dependence of the spectra of the Cu$^{2+}$ center at LNT is shown in Fig. 5. The points denote the observed positions of each spectral line, and solid lines represent angular variation of the spectral positions calculated by using appropriate values of parameters described later. In this figure the angle $\theta \approx 125^\circ$ corresponds to the direction of the magnetic field parallel to the z-axis, and $\theta \approx 35^\circ$ corresponds to that perpendicular to the z-axis. It is seen in this figure that there is a strong axial symmetry along the x-, y- and z-axis. This axial symmetry may be brought about by the distortion due to the static J-T effect.

In Fig. 6 is shown the angular dependence of the $g$-value of the Cu$^{2+}$ center obtained at RT. The points denote the $g$-values obtained from observed spectral positions at each angle $\theta$. The solid line represents angular variation of the $g$-value calculated by the method described later. In this figure $\theta = 0^\circ$ and $180^\circ$ correspond to the magnetic field parallel to the c-axis. It is obvious in this figure that there is a conspicuous symmetry parallel to the c-axis. This axial symmetry may be caused mainly by the inherent $D_{3d}$ symmetry of the host CdCl$_2$ crystal.

![Fig. 5](image_url)
3.3. Analysis

The \( g \)-tensor of the \( \text{Cu}^{2+} \) center has an axial symmetry as is inferred from the angular dependence of the \( g \)-values shown in Fig. 6, that is, the axial field parallel to the \( c \)-axis is fairly strong and can not be neglected in treating the spectrum of the \( \text{Cu}^{2+} \) center in \( \text{CdCl}_2 \) crystals. Taking into account this axial field and the Jahn-Teller distortion along the \( x \)-, \( y \)- or \( z \)-axis, overall symmetry of the present \( \text{Cu}^{2+} \) center is \( C_{2h} \). Thus we must treat the \( g \)-tensor under the \( C_{2h} \) symmetry. Then the \( g \)-tensor for the \( \text{Cu}^{2+} \) center distorted along the \( z \)-axis (the \( z \)-center) is written in the \((u,v,w)\) system as

\[
g(u,v,w) = \begin{pmatrix} g_{uu} & 0 & g_{uw} \\ 0 & g_{vv} & 0 \\ g_{uw} & 0 & g_{ww} \end{pmatrix} \tag{1}
\]

In terms of the elements of this tensor, the effective \( g \)-value of the Zeeman term in the spin Hamiltonian is given for the \( \text{Cu}^{2+} \) center as

\[
g = \frac{1}{2} \left( (g_{uu}^2 + g_{ww}^2) \sin^2 \theta \cos^2 \phi + g_{vv}^2 \sin^2 \theta \sin^2 \phi + (g_{uw}^2 + g_{ww}^2) \cos^2 \theta + 2g_{uw}(g_{uu} + g_{ww}) \sin \theta \cos \theta \cos \phi \right) \tag{2}
\]

where \( \phi \) is zero for the \( z \)-center and is \( 120^\circ \) for the \( x \)- and \( y \)-center.

The ESR spectrum of the \( z \)-center is fitted to the spin Hamiltonian

\[
H = gB\hbar M_s + A I_z S_z + B(I_x S_x + I_y S_y) + B'((I_x^1 + I_x^2) S_x + (I_y^1 + I_y^2) S_y), \tag{3}
\]

where \( g \) is the effective \( g \)-value given by eq. (2), \( B \) is the Bohr magneton, \( H \) is the intensity of the static magnetic field, \( M_s \) is the magnetic quantum number of the electron spin, \( I(=3/2) \) is the copper nucleus spin and \( I_1, I_2, I_3 \) and \( I_4(=3/2) \) are spins of chlorine nuclei.
at the site 1, 2, 3 and 4 shown in Fig. 1, respectively. The spin Hamiltonian for the other two equivalent centers, the \(x\)- and \(y\)-center, is obtained from the same eq. (3) by substituting \(\phi = 120^\circ\). The best fitted values of parameters with experiments at LNT are

\[
\begin{align*}
g_{xx} &= 2.075 \pm 0.003, & g_{zz} &= 2.335 \pm 0.004, \\
g_{xy} &= -0.019 \pm 0.002, & g_{xz} &= 0.011 \pm 0.002, \\
g_{uu} &= 2.227 \pm 0.004, & g_{vv} &= 2.094 \pm 0.003, \\
g_{ww} &= 2.164 \pm 0.003, & g_{uw} &= -0.137 \pm 0.002, \\
A &= (117.5 \pm 1.4) \times 10^{-4} \text{ cm}^{-1}, \\
B &= (13.1 \pm 0.1) \times 10^{-4} \text{ cm}^{-1}, \\
B' &= (20 \pm 1.3) \times 10^{-4} \text{ cm}^{-1}.
\end{align*}
\]

The spectrum of the \(\text{Cu}^{2+}\) center observed at RT is fitted to an axial \(g\)-tensor with

\[
g_w = 2.173 \pm 0.002, \quad g_u = g_v = 2.148 \pm 0.002. \quad (8)
\]

The solid line in Fig. 6 shows the average value calculated using the \(g\)-tensor element,

\[
\begin{align*}
g_{uu} &= 2.210 \pm 0.001, & g_{vv} &= 2.080 \pm 0.001, \\
g_{ww} &= 2.170 \pm 0.001, & g_{uw} &= -0.137 \pm 0.001,
\end{align*}
\]

namely \(g = (g_x + g_y + g_z)/3\), where the \(g_x\), \(g_y\) and \(g_z\) are the \(g\)-values of the \(x\)-, \(y\)- and \(z\)-center, respectively. This curve well agree with the experimental results at RT. The difference of the \(g\)-tensor elements at RT from that at LNT may arise from the anisotropic thermal expansion of the \(\text{CdCl}_2\) crystal\(^8\).

4. Discussion

It is seen in Fig. 5 that the angular variation of the observed positions of each spectral structure well agrees to that calculated by using the values given in eqs. (4) or (5), (6) and (7). As recognized in eq. (5), the \(g\)-tensor with reference to the \((u, v, w)\) system has fairly large off-diagonal elements, which indicates that the symmetry of the \(\text{Cu}^{2+}\) center in \(\text{CdCl}_2\) deviates considerably from that of \(\text{D}_{3d}\) expected at the \(\text{Cd}^{2+}\) ion site in this crystal. On the other hand, the off-diagonal elements in the \(g\)-tensor with reference to the \((x, y, z)\) system are very small as are given in eq. (4). These facts indicate that the symmetry of the \(\text{Cu}^{2+}\) center in \(\text{CdCl}_2\) can be approximated by the tetragonal one, \(\text{D}_{4h}\). As is mentioned in the previous section, this change of symmetry of the center from \(\text{D}_{3d}\) to \(\text{D}_{4h}\) is due to the J-T distortion of \(\text{Cu}^{2+}\) center which elongate each center
along the \( x \), \( y \) or \( z \)-axis.

A small but apparent difference is perceived in Fig.5 between the angle where the \( g \)-value of the \( z \)-center becomes maximum and that where the \( g \)-value of the \( x \)- or \( y \)-center becomes minimum; the former is \( \alpha = 130^\circ \) and the latter \( \alpha = 125^\circ \). This difference in angles indicates that the principal axes of \( g \)-tensor is deviated from the \( x \)-, \( y \)- or \( z \)-axis towards the \( c \)-axis by about 2.5\(^\circ\), which corresponds to the presence of off-diagonal elements in \( g \)-tensor with reference to the \((x,y,z)\) system. Although the positions of \( \text{Cl}^- \) ions deviate from those on the \( x \)-, \( y \)- and \( z \)-axis in the regular \( \text{CdCl}_2 \) crystal, this deviation is opposite to that of the principal axes of the \( g \)-tensor. Therefore the deviation is not explained by the regular crystal structure of \( \text{CdCl}_2 \). The same deviation of the principal axes of the \( g \)-tensor have been also observed in \( \text{CdCl}_2:\text{Ag}^{2+} \) by one of the present authors and his co-workers\(^6\). They proposed a plausible explanation for this deviation by taking account of mixing of excited \( E_g(T_{2g}) \) state to the ground \( E_g(E_g) \) state. This mixing gives rise to another mode of the \( J-T \) distortion which makes the Cl\(^-\) ions deviate along the \( c \)-axis. This explanation may be accepted for the present case of the \( \text{Cu}^{2+} \) center in \( \text{CdCl}_2 \).

In eq. (10) are given the \( g \)-values for a 3\( d \) hole on the \( E_g \) ground state of the three equivalent centers, the \( x \)-, \( y \)- and \( z \)-center, which is assumed to be distorted along each axis by the static \( J-T \) effect which reduced the symmetry of the centers from \( O_h \) to \( D_{4h} \).

\[
\begin{align*}
g_x &= 2 - \frac{2\xi}{\Delta} \left( \cos^2 \frac{\theta}{2} + \sqrt{3}\sin^2 \frac{\theta}{2} \right)^2, \\
g_y &= 2 - \frac{2\xi}{\Delta} \left( \cos^2 \frac{\theta}{2} - \sqrt{3}\sin^2 \frac{\theta}{2} \right)^2, \\
g_z &= 2 - \frac{8\xi}{\Delta} \cos^2 \frac{\theta}{2}, \quad (10)
\end{align*}
\]

where \( \xi \) is the spin-orbit interaction constant, \( \Delta \) is the energy difference between the \( E_g \) and \( T_{2g} \) states and \( \theta \) is the azimuth angle from the \( Q_3 \) axis. By using this angle \( \theta \), the normal coordinates of distortions of ligand ions in the Van Vleck's notation are expressed as \( Q_3 = \rho \cos \theta \) and \( Q_2 = \rho \sin \theta \). In the case of the elongated tetragonal \( J-T \) distortion, \( \theta = 0^\circ \), these \( g \)-values are reduced to

\[
\begin{align*}
g_1 &= g_x = g_y = 2 - \frac{2\xi}{\Delta}, \\
g_v &= g_z = 2 - \frac{8\xi}{\Delta}. \quad (11)
\end{align*}
\]

Then, the values of \( g_1 \) and \( g_v \) satisfy the relation, \((g_v - 2)^4(g_1 - 2)\).
It is easy to show that this relation between \( g_1 \) and \( g_y \) is approximately satisfied by using the experimental values of \( g_1 = g_{xx} = g_{yy} \) and \( g_z = g_{zz} \) given in eq. (4). This fact supports a conclusion that the Cu\(^{2+}\) centers are elongated along one of \( x\)-, \( y\)-, and \( z\)-axis, which have been reduced in the previous section from the fact that the superhyperfine structures appear clearly in the spectrum when the static magnetic field is applied perpendicularly to the tetragonal axis of each center.

The \( g \)-values at RT are obtained by averaging those in eq. (10) with respect to \( \theta \). The results are equal to \( (g_x + g_y + g_z)/3 \). This guarantees the justification of the method used in the previous section to analyze the angular dependence of the \( g \)-values obtained at RT. It is likely that the tunnelling or the motional averaging among the equivalent three distortions become more and more remarkable with rising temperature and finally at RT the distortions are completely averaged out. As is shown in Fig. 6, the principal axis of the \( g \)-tensor becomes nearly parallel to the \( c \)-axis at RT.

For a 3\textit{d} hole on a transition metal ion in a tetragonal crystal field, the hyperfine constant \( A \) and \( B \) are given by\(^{10} \)

\[
A = (-K - \frac{4}{7} + g_{1\mu} - 2) \times 2 \gamma \beta N r^{-3}
\]

\[
B = (-K + \frac{2}{7} + g_{1\mu} - 2) \times 2 \gamma \beta N r^{-3}
\]

where \( K \) is a numerical factor representing the admixture of configuration with unpaired \( s \)-electron, \( \gamma \) is the nuclear gyromagnetic factor in unit of \( e/2 M_c \) and \( \beta N \) is the nuclear magneton. The estimated values, \( K \) and \( r^{-3} \), using the values of \( g_{xx} \) and \( g_{zz} \) given in eq.(4) and of \( A \) and \( B \) given in eq. (6) are

\[
K = 0.30, \quad r^{-3} = 2.03 \times 10^{25} \text{ (cm}^{-3})
\]

At low temperature of about 35 K, ten or thirteen sharp lines are resolved in the region of high magnetic field of the ESR spectra as shown in Figs. 2 and 3. These lines are associated with the superhyperfine structures arising from the magnetic interactions of the unpaired electron spin with the Cl\(^-\) ion nuclei. In the case of the magnetic field parallel to the \( z \)-axis (Fig.2), the unpaired electron spin on the \( x \)- or \( y \)-centers may interact magnetically with one Cu\(^{2+}\) nucleus and two Cl\(^-\) nuclei on the \( z \)-axis. When the hyperfine constant of copper is nearly equal to that of the chlorine in this magnetic field direction, the intensity ratios of these lines are expected to be 1 : 3 : 6 : 10 : 12 : 10 : 6 : 3 : 1. These ratios are con-
sistent with those observed in the spectrum in Fig.2. In the case of the magnetic field perpendicular to the z-axis (Fig. 3), the unpaired electron spin on the z-center may interact with four Cl⁻ nuclei. If the hyperfine splitting due to the Cu²⁺ nucleus is negligibly small in this magnetic field direction, the intensity ratios are expected to be 1 : 4 : 10 : 20 : 31 : 44 : 40 : 31 : 20 : 10 : 4 : 1, which seems to correspond to those observed in the spectrum in Fig.3. As shown in Fig. 4, the calculated splitting due to the hyperfine interaction with the Cu²⁺ nuclei is not zero even in the case of the magnetic field perpendicular to the z-axis (i.e. θ = 35°). This may owe to the slight error in the values given in eqs. (4), (5) and (6).

Similar sharp lines have been also found in the ESR spectra of the Cu²⁺ centers in NaCl[5] and AgCl[11]. They were interpreted, however, as those due to the nuclear electric quadrupole effect of the copper ion. But it is not the case in the present system of the CdCl₂:Cu²⁺. It would be most plausible explanation that the observed sharp structures are the superhyperfine structures in the elongated J-T centers as described above.

5. Conclusion

The Cu²⁺ center in CdCl₂ has been found to the MX₆ type octahedral complex composed of the central Cu²⁺ ion and six nearest neighbor chlorine ions. The angular variation of the ESR spectrum of this center can be fitted by using a g-tensor of C₂ᵥ symmetry. By analyzing the anisotropic g-tensor obtained at low temperature, it was found that the Cu²⁺ centers are elongated along the each of the three mutually perpendicular fourfold axes of MX₆ complex by the static J-T effect. In addition to this tetragonal distortion, an effect of a small axial distortion along the c-axis is also discerned in the angular dependence of spectral positions observed at LNT. At low temperature of about 35 K, ten or thirteen sharp structures are resolved in the region of high magnetic field of the ESR spectra when the magnetic field is applied in parallel or perpendicularly to the z-axis, respectively. these structures are well explained as the superhyperfine structures arising from the magnetic interactions of the unpaired electron spin of Cu²⁺ ion with two or four ligand Cl⁻ ion nuclei. At room temperature, the three equivalent tetragonal J-T distortions are averaged out completely (the dynamical J-T effect) and the ESR signal shows only one broad spectral line. The angular variation of the g-value is fitted to an axial g-tensor of D₃d symmetry.
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