Electron Spin Resonance of Cu2+ Ion in CdWO4, ZnWO4, and MgWO4 Single Crystals

Z. Šroubek and K. Ždánský

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ideal fused-salt mixtures. In the latter case, in particular, the changes in kinematic viscosity with temperature and composition make it necessary to use the newly developed calculation.

CONCLUSION

In conclusion, the kinetic-energy correction factor does not vary with kinematic viscosity or flow rate in the range corresponding to Re from 50 to 1500. (At high flow rates, with an appreciable change in hydrostatic head during a determination, the maximum rather than average flow rate should be used to calculate the Re.) For precise work, the correction factor must be determined for each capillary whether it has trumpet-shaped or square-cut ends. In the construction of a viscometer, especially when the material is glass, it is often convenient to make the capillary with trumpet-shaped ends, in which case the geometric constants must be determined by calibration. For absolute viscosity determinations, the capillary should have square-cut ends to allow a reliable determination of the effective length.

Some recent work with square-cut capillaries,2 used in the determination of the viscosity of dense gases, was called to our attention by the referee for this paper. In that work, m was found to be constant over a wide range of kinematic viscosities and Reynolds numbers but deviated from the constant value at Re greater than 1600. This is entirely in agreement with our results since, under the conditions employed, there was no necessity for the hydrostatic-head calculation.

In viscometers in which all or part of the driving force is a varying hydrostatic head, it is necessary to use a calculation which includes a correction for the interaction of the hydrostatic-head and kinetic-energy effects. The more complicated calculation is especially important where the kinematic viscosities of the calibration and test materials are greatly different.

Although the exact equations, with the combined hydrostatic-head and KE corrections, are complex and require solution by a series of approximations, the need for more accurate viscosity data indicates a need for more work along this line. The accessibility of computers eliminates, to a large extent, the need for using approximate solutions to simplify the calculations. We plan to continue this work to develop exact expressions for other reservoir configurations and methods for handling the calculations more efficiently.

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THE JOURNAL OF CHEMICAL PHYSICS

Electron Spin Resonance of Cu$^{2+}$ Ion in CdWO$_4$, ZnWO$_4$, and MgWO$_4$ Single Crystals

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(Received 30 November 1965)

Paramagnetic resonance measurements have been carried out at 78° and at 4°K on Cu$^{2+}$ ions diluted in single crystals of CdWO$_4$, ZnWO$_4$, and MgWO$_4$. The g factors and the hyperfine interaction with the copper nucleus have been determined. From this experimental data the ground-state wave function of the Cu$^{2+}$ ion has been constructed. It has also been possible to calculate the relevant $I=2$ terms of the low-symmetry crystal-field components. Then in the framework of a simple $g$-factor theory the $g$-factor anisotropy has been calculated and compared with the measured anisotropy. The role of the distortion of the covalent $\pi$ bonds has also been examined. In the case of MgWO$_4$ and ZnWO$_4$ a distinct temperature-dependent $g$-factor shift and a temperature-dependent change of hyperfine interaction constants have been observed.

I. INTRODUCTION

The transition-metal complexes of the $3d^n$ configuration are of interest because they represent a relatively simple one-magnetic-hole system. By means of this system, it is hoped to obtain information about the electron wave functions even in a ligand field of low symmetry. In our case Cu$^{2+}$ is surrounded by a highly deformed octahedron, so that the orbital singlet is the ground state. The Jahn–Teller distortion, if it exists at all, is probably only an additional distortion superimposed on the already existing local distortion. The great anisotropy of the $g$ and $A$ factors, especially in CdWO$_4$, permit a quantitative determination of the appropriate ground-state wave function. The experimental observation of Cu$^{2+}$ in CdWO$_4$ with a preliminary description of the ground state was published by us as a Short Note. Using the determined wave function mixing coefficients we get the expression for the relevant crystal field. Then it is shown that the magnitude of the $g$-factor anisotropy can be deduced from simple crystal-field theory and can be compared with the experiment. The anisotropy of the spin–orbit coupling constant is also taken into account. Experimental data permit an estimate of the covalency and the spin–exchange polarization parameter $\kappa$ of Cu$^{2+}$ in all three crystals quantitatively.

The interesting problem of spin–lattice relaxation times for Cu$^{2+}$ ion in distorted lattices has also been

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ESR OF Cu\textsuperscript{2+} ION IN CdWO\textsubscript{4}, ZnWO\textsubscript{4}, AND MgWO\textsubscript{4}

briefly examined in the case of CdWO\textsubscript{4} between 77\degree and 300\degree K. The spin–lattice relaxation is much longer in this case than in the MgWO\textsubscript{4} crystals and can be deduced from line broadening. The temperature-dependent g-factor shift has been observed in MgWO\textsubscript{4} and ZnWO\textsubscript{4} crystals in the temperature region between 4\degree and 77\degree K.

II. EXPERIMENT

Crystals of CdWO\textsubscript{4}, ZnWO\textsubscript{4}, and MgWO\textsubscript{4} were grown from flux containing a small amount (0.1\%) of CuO. The crystals grow in a very-well-defined form with the crystallographic c axis along the growth axis. The crystals were aligned by cleaving them in the (010) plane. The y susceptibility axis was taken to be along the b crystallographic axis, perpendicular to the (010) cleavage plane, in agreement with Peter. The positions of the x and z susceptibility axes of Cu\textsuperscript{2+} were fixed with respect to the well-defined Fe\textsuperscript{3+} magnetic axes and crystal c axes. It has been found that the Cu\textsuperscript{2+} z axis very nearly coincides with the Cu\textsuperscript{2+}–O\textsuperscript{2−} connecting line in the (010) plane. In CdWO\textsubscript{4}, for example, the magnetic s axis is rotated from the crystalline +a axis towards the crystalline +c axis by 57±1 deg (see Fig. 1). From the x-ray data\textsuperscript{4} for the isostructural NiWO\textsubscript{4} the angle between the +a axis and the Cu\textsuperscript{2+}–O\textsuperscript{2−} connecting line is 58 deg.

The observed paramagnetic spectra of all three crystals resemble each other and can be fitted to the spin Hamiltonian

\[ \mathcal{H} = \sum_{\mu \sigma} \left( g_{\mu} \mathbf{H} \cdot \mathbf{S} + A_{\mu} \mathbf{S} \cdot \mathbf{I} + P_{\mu} \mathbf{I}^{2} \right), \]

where \( g_{\mu} \) is the Bohr magneton and \( S = \frac{1}{2}, I = \frac{3}{2} \). The g and nuclear spin operators, respectively.

No evidence was found to suggest that the g tensor and hyperfine tensor have different principal axes. The large difference in the angular dependence of the effects produced by the two tensors could mask a small displacement of the axes.

![Fig. 1. Positions of oxygens surrounding Cu\textsuperscript{2+} ion in CdWO\textsubscript{4} projected along h = ey axis. Magnetic and crystallographic axes are denoted x, y, z and a, b, c, respectively. Open circles are oxygens, solid circle is copper.](image)

Due to the lack of resolution the magnitude of \( P_{\mu} \) cannot be measured precisely. As we see later, the ground-state wavefunction is predominantly \( |3z^{2} - r^{2}\rangle \).

We therefore rewrite the quadrupole part of (1) in the simplified axial form \( P[I_{z}^{2} - \frac{1}{3}(I + 1)] \) and take \( P = -(11±1) \times 10^{-4} \text{ cm}^{-1} \). This value of \( P \) was obtained by Bleaney et al.\textsuperscript{5} in the case of \((\text{Mg, Cu})_{2} \text{La}_{2}(\text{NO}_{3})_{12} \cdot 2\text{D}_{2} \text{O} \).

Quadrupole interaction plays an important role in the \( x \) direction in CdWO\textsubscript{4} and in the \( y \) direction in ZnWO\textsubscript{4} and MgWO\textsubscript{4}. For example, the spectrum of \((\text{Zn, Cu})\text{WO}_{4}\) in the \( y \) direction at 78\degree K has the form shown in Fig. 2. If the value of \( P \) is known, \( A_{\mu} \) can be numerically calculated.

The parameters obtained by fitting the EPR data are presented in Table I. The tabulated values of \( A_{\mu} \) are in units of \( 10^{4} \text{ cm}^{-1} \) and refer to the mean of the values for the two isotopes \( ^{64}\text{Cu} \) and \( ^{65}\text{Cu} \), weighted in proportion to their natural abundance.

All the measurements were carried out at 4\degree and at 78\degree K by means of an X-band spectrometer employing 960-kHz modulation of the magnetic field. At 78\degree K the resonance curves of Cu\textsuperscript{2+} in MgWO\textsubscript{4} broaden appreciably. In CdWO\textsubscript{4} and ZnWO\textsubscript{4} the resolution is about the same at 78\degree K as at 4\degree K. An apparent broadening exists only above a temperature higher 100\degree K.

III. DYNAMICAL EFFECTS

In the region above 78\degree K the electron spin–lattice relaxation time of Cu\textsuperscript{2+} in CdWO\textsubscript{4} (\( H \parallel y \)) has been measured. From 95\degree to 300\degree K the relaxation time

\[ \text{Table I. Spin-Hamiltonian parameters for Cu\textsuperscript{2+} ion in CdWO\textsubscript{4}, ZnWO\textsubscript{4}, MgWO\textsubscript{4}} \]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CdWO\textsubscript{4}</th>
<th>ZnWO\textsubscript{4}</th>
<th>MgWO\textsubscript{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{\mu} )</td>
<td>( 15±2 )</td>
<td>( 0 )</td>
<td>( 0 )</td>
</tr>
<tr>
<td>( A_{\mu} )</td>
<td>( 18±1 )</td>
<td>( 0 )</td>
<td>( 18±1 )</td>
</tr>
<tr>
<td>( A_{\mu} )</td>
<td>( 2.302±0.002 )</td>
<td>( 2.343±0.002 )</td>
<td>( 2.334±0.002 )</td>
</tr>
<tr>
<td>( \xi_{a} )</td>
<td>( +82±2 )</td>
<td>( +76.5±2 )</td>
<td>( +76±2 )</td>
</tr>
<tr>
<td>( \xi_{a} )</td>
<td>( 2.496±0.002 )</td>
<td>( 2.379±0.002 )</td>
<td>( 2.385±0.003 )</td>
</tr>
<tr>
<td>( \xi_{a} )</td>
<td>( 2.012±0.001 )</td>
<td>( 2.000±0.001 )</td>
<td>( 2.013±0.001 )</td>
</tr>
</tbody>
</table>

\textsuperscript{6} M. Peter, Phys. Rev. 113, 801 (1959).

vanes as $T^{-2}$, as is characteristic of relaxation dominated by Raman processes at temperatures higher than the Debye temperature. The $T^{-2}$ dependence has been deduced from the variation of the EPR inflection of the mental setup employed.

The initial linewidth of liquid helium an obvious g-factor shift has been found. The g-factor shift is probably caused by dependent mixing of the first excited state really has been observed (see Table II).

Between the temperature of liquid nitrogen and the effect can be easily detected, and 4°K. The tabulated values of the effect can be seen to be smaller than in ZnW2.. The measured value of $\rho_{\text{exptl}}$ in solid state is smaller than $\rho_{\text{free ion}}$. To obtain $\rho_{\text{exptl}}$ we must multiply $\rho_{\text{free ion}}$ by the probability of the electrons actually being in the 2D state around the copper ion, i.e.,

$$\rho_{\text{exptl}} = \rho_{\text{free ion}} \times \alpha^2 \rho_{H^1}.$$

The orbital contribution to $A_s$ in (4) is equal to $\rho \Delta g$ and is actually equal to $\rho_{\text{free ion}} \Delta g$, because the covalency reduction effect is already contained in $\Delta g$. The form of Eq. (3), modified by covalency, is then

$$A_s = \rho_{\text{exptl}} (-\alpha^2 + \Delta g_2 + \frac{1}{2} \Delta g_2) + \alpha^2 (\Delta g_2/2 + \Delta g_2/2) + \Delta g_2/2 + \Delta g_2/2).$$

In consequence of our supposition $\beta<1$, we neglect in (6) the terms quadratic in $\beta$. The value of the $p_{\text{exptl}}$ is taken for the state of the free Cu2+ ion and is equal to 0.036 cm$^{-1}$. The signs of $A_s$ are not known from experiment but fortunately one of the cases is equal to zero and the other is positive unambiguously. The solution of (6) is straightforward, with the results shown in Table III.

The tabulated values of $A_s$ and $\rho_{\text{exptl}}$ are in units of 10$^{-4}$ cm$^{-1}$. The correct sign of $A_s$ in Table III, with the X-band spectrometer used, cannot be determined unambiguously. The small observed asymmetry of the resonance curves (see Fig. 2), which has the same character for ZnW2O4 and MgWO4, suggests $A_s = 18$ for these two crystals. For the same reason $A_s = 15$ for CdWO4 is somewhat more probable. On the other hand, the theoretical conclusions given below are in favor of the other choice: $A_s = 18$ for ZnWO4, MgWO4, and $A_s = 15$ for CdWO4. The possible reason for such a disagreement is discussed in the conclusion.

---

### Table II. Temperature dependence of $\Delta g_s = g_s - 2.0023$ and of the hyperfine interaction constant $A_s$ for Cu2+ ion in CdWO4, ZnWO4, MgWO4

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$\Delta g_s$ (78°K $-$ 4°K)</th>
<th>$A_s$ (10$^{-4}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdWO4</td>
<td>+0.011 +0.009</td>
<td>79 82</td>
</tr>
<tr>
<td>ZnWO4</td>
<td>+0.010 -0.002</td>
<td>72 76</td>
</tr>
<tr>
<td>MgWO4</td>
<td>+0.020 +0.010</td>
<td>69 76</td>
</tr>
</tbody>
</table>

---

Calculation of the $g_x - g_z$ Difference of Cu$^{2+}$ in CdWO$_4$

In this chapter the calculation of $g$ factors is performed within the simple crystalline-field framework, using the Cu$^{2+}$ ion in CdWO$_4$ as an example. The role of the distortion of covalent bonds is examined. We start with the well-defined ground-state wavefunction (3) which for CdWO$_4$ takes two possible forms ($\beta = -0.138, \beta = -0.081$)

$$\begin{align*}
(0.8)^4(5z^2-r^2)-0.138 \cdot (x^2-y^2)), \\
(0.85)^4(5z^2-r^2)-0.081 \cdot (x^2-y^2)).
\end{align*}$$

(7)

Now it is possible to calculate the difference $g_x - g_z = \delta g$ and compare the calculated $\delta g$ with the experimental one.

The $\delta g$ is caused by

(A) mixing the $|x^2-y^2\rangle$ orbital with the $|3z^2-r^2\rangle$ orbital;

(B) the energy splitting of the $|xz\rangle$ and $|yz\rangle$ states (the $|xz\rangle$ state determines $\Delta g_x$, the $|yz\rangle$ state determines $\Delta g_y$);

(C) different covalency of the $|xz\rangle$ and the $|yz\rangle$ states;

(D) mixing the $|yz\rangle$ orbital with the $|xy\rangle$ orbital of the first excited state.

(A) Bleaney et al.$^5$ have derived the expressions for $g_0$, assuming the general orbital wavefunction of the ground state

$$\frac{1}{2}(5)^4(f(r)(ax^2+by^2+cz^2))$$

(8)

with the conditions

$$a+b+c=0, \quad a^2+b^2+c^2=6.$$ 

Neglecting the splitting of the $|xz\rangle$ and $|yz\rangle$ states,

**Table III. Microscopic parameters for Cu$^{2+}$ in CdWO$_4$, ZnWO$_4$, and MgWO$_4$.**

| Parameter | CdWO$_4$ | ZnWO$_4$ | MgWO$_4$
|-----------|----------|----------|----------|
| $\rho_{\text{exp}} (10^4 \text{ cm}^{-3})$ | $290 \pm 30$ | $260 \pm 281$ | $256 \pm 280$
| $\beta$ | $0.219 \pm 0.238$ | $0.210 \pm 0.237$ | $0.71 \pm 0.78$
| $\kappa$ | $0.08 \pm 0.85$ | $0.72 \pm 0.78$ | $0.72 \pm 0.78$
| $\alpha^2$ | $0.8 \pm 0.85$ | $0.72 \pm 0.78$ | $0.72 \pm 0.78$

$^a$ Calculated from Eq. (6) using all possible parameters of Table I.

the $g_x$ and $g_y$ values, correct to the first order, are

$$g_x = 2.0023 + \Delta g_x = 2.0023 + A(b-c)^2,$$

$$g_y = 2.0023 + \Delta g_y = 2.0023 + A(c-a)^2,$$

(9)

$A$ is a constant.

Comparing (8) and (3), we see that in our case ($\beta < 1$)

$$\begin{align*}
a &= -(1-\sqrt{3})\beta, \\
b &= -(1+\sqrt{3})\beta, \\
c &= 2.
\end{align*}$$

(10)

From (9) to (10) we obtain

$$\delta g = g_x - g_z = -12.4\sqrt{3}\beta = -\Delta g(4\sqrt{3})\beta,$$

(11)

where $\Delta g = \frac{1}{2}(\Delta g_x + \Delta g_y)$. As $\delta g_{\text{exp}}$ is positive, $\beta$ must be negative, in agreement with experiment.

With the experimental $\beta = -0.138$ we get

$$\delta g = +0.125,$$

which is smaller than the experimental value $\delta g_{\text{exp}} = +0.194$. For $\beta = -0.081$ we obtain an even smaller value $\delta g = +0.075$. Points (B), (C), and (D) must therefore be taken into account.

(B) To calculate the splitting of the $|xz\rangle$ and $|yz\rangle$ states we must find the expression for the relevant part of the low-symmetry crystal field. The general low-symmetry crystal field in the Cu$^{2+}$ position in CdWO$_4$ is described by

$$V_L = Cy^2 + Dx^2 + Exz.$$  (12)

To make the problem tractable we neglect higher-order terms. The relevant part of $V_L$, necessary for further calculation, is only $Cy^2$. In estimating $C$ we are helped by the fortunate circumstance that only $Cy^2$ mixes the $|3z^2-r^2\rangle$ and the $|x^2-y^2\rangle$ states. As the mixing coefficient $\beta$ is well established, $C$ can be calculated from the second-order perturbation calculation. The coefficient $\beta$ in terms of $Cy^2$ is given by

$$\beta = -\langle 3z^2-r^2 | Cy^2 | x^2-y^2 \rangle/E_1.$$  (13)

$E_1$ is the energy difference between the $|x^2-y^2\rangle$ and $|3z^2-r^2\rangle$ states. The $|x^2-y^2\rangle$ state belongs to the same representation of the cubic group as the $|xz\rangle$ and $|yz\rangle$ states and therefore all three states have the same energy in the first approximation.

The calculation of (13) is straightforward, giving

$$\beta = - NC2\sqrt{3}/E_1.$$  (14)

$N$ is a constant. The energy splitting $\delta E$ of the $|yz\rangle$ and $|xz\rangle$ states is

$$\delta E = \langle yz | Cy^2 | yz \rangle - \langle xz | Cy^2 | xz \rangle = 6NC.$$  (15)

From (14) and (15) we get

$$\delta E = -\sqrt{3}BE_1.$$  (16)
The anisotropy of the $g$ factor due to this energy splitting is given by

$$
\delta g = g_e - g_s = \frac{K}{E_1 - \frac{1}{2}(\delta E)} - \frac{K}{E_1 + \frac{1}{2}(\delta E)}
$$

$$
\approx \frac{K}{E_1} \left( \frac{\delta E}{E_1} \right) = \Delta g \frac{\delta E}{E_1} = - \Delta g \gamma_3. \quad (17)
$$

With $\beta = -0.138$ we get $\delta g = +0.095$ and with $\beta = -0.081$ we get $\delta g = +0.056$. Summing the contributions of Points (A) and (B) we obtain

$$
\delta g = 0.220 \quad \text{for} \quad \beta = -0.138
$$

$$
\delta g = 0.130 \quad \text{for} \quad \beta = -0.081.
$$

(C) The problem proceeds to the stage of taking into account the contribution due to the distortion of the covalent $\pi$ bonds. The discussion has, of course, only a qualitative character.

With the LCAO method we can write the two antibonding orbitals

$$
\phi_{\pi s} = (N_{\pi s})^{-1} (\psi_{\pi s} - \rho_{\pi s} \rho_{\pi s}),
$$

$$
\phi_{\pi s} = (N_{\pi s})^{-1} (\psi_{\pi s} - \rho_{\pi s} \rho_{\pi s}), \quad (18)
$$

where the $\psi_{\pi s}$ and $\psi_{\pi s}$ refer to the $\pi$ wavefunctions of the Cu$^{2+}$ ion, $\rho_{\pi s}$ and $\rho_{\pi s}$ are suitable linear combinations of $\sigma^*$ atomic orbitals. $N_{\pi s}$ and $N_{\pi s}$ are normalization constants. In the simple LCAO approach the coefficients $\rho_{\pi s}$ and $1/N_{\pi s}$ are approximately expressed in the form

$$
\rho_{\pi s} = l_{\pi s} / (E_{\pi s} - E_{\pi s}), \quad (i = x, y),
$$

$$
1 / N_{\pi s} = 1 / \left[ l_{\pi s} / (E_{\pi s} - E_{\pi s}) \right]^2 \approx 1 - \left( l_{\pi s} / (E_{\pi s} - E_{\pi s}) \right)^2, \quad (19)
$$

where $E_{\pi s}$ and $E_{\pi s}$ are energy levels of a single $\pi$s electron on the Cu$^{2+}$ ion and of a single $\rho\pi$ electron on the attached oxygen ion, respectively; $l_{\pi s}$ are resonance integrals between the appropriate $\pi$ and $\rho\pi$ electrons.

In this molecular orbital picture the energy difference $\delta E$ [Eq. (15)] is expressed by

$$
\delta E = \left[ l_{\pi s}^2 / (E_{\pi s} - E_{\pi s}) \right] - \left[ l_{\pi s}^2 / (E_{\pi s} - E_{\pi s}) \right]. \quad (20)
$$

We take here the difference $\delta E$ with opposite sign, in contrast to (15), because we now calculate electron and not hole energy levels. According to the simple $g$-factor calculation in the MO approach

$$
\delta g = \frac{K}{N_{\pi s}} (E_1 - \frac{1}{2}(\delta E)) - \frac{K}{N_{\pi s}} (E_1 + \frac{1}{2}(\delta E)), \quad (21)
$$

where $K$ is a constant and $E_1$ is the same as in (17). Using (19) and (20) we obtain the approximate expression

$$
\delta g = \Delta g \delta E \left[ 1 / (E_1) - \left[ 1 / (E_{\pi s} - E_{\pi s}) \right] \right]. \quad (22)
$$

The first term in (22) describes the effect of the energy-level splitting and is similar to (17). The second term describes the effect of the covalent distortion. To obtain rough quantitative information, we suppose that the energy splitting is due only to the covalency. Then, for $\beta = 0.138$, the first term in (22) is equal to 0.094 [Contribution (B)]. For reasonable values

$$
E_1 = 1.5 \text{ eV}, \quad E_{\pi s} - E_{\pi s} = 6 \text{ eV},
$$

the second term [Covalency Contribution (C)] is equal to

$$
- \Delta g \delta E / (E_{\pi s} - E_{\pi s}) = -0.027.
$$

Adding all the contributions (A), (B), (C) we find $\delta g = 0.194$ in good agreement with experiment.

(D) Up to now we have neglected the term $E_{\pi s}$ in (12). This term can mix the $|xy\rangle$ state in the first excited state $|xy\rangle$, enlarging $\Delta g$, slightly and diminishing $\delta g$. Consequently this contribution has the same effect on $\delta g$ as the covalency distortion.

**Calculation of the $g_z$ Factor of Cu$^{2+}$ in CdWO$_4$**

In the pure $|3z^2-r^2\rangle$ ground state $\Delta g_s$ should be very small and negative. From the theory\(^4\) it is expected that

$$
\Delta g_s = -0.02.
$$

Table I shows that Cu$^{2+}$ in CdWO$_4$ has $\Delta g_s > 0$. In this case the positive $\Delta g_s = 0.010$ can be explained if we take into account the mixing of $|x^2-y^2\rangle$ in the ground state. If the separation between the ground state and the first excited state $|xy\rangle$ is $E_0$, the change of $g_z$ is

$$
\Delta g_s = 2a^2\beta\lambda (|x^2-y^2| L_s |xy\rangle |E_0\rangle). \quad (23)
$$

The required $\Delta g_s = 0.03$ is obtained for

$$
E_0 = 3400 \text{ cm}^{-1} \quad (\beta = -0.138),
$$

$$
E_0 = 1150 \text{ cm}^{-1} \quad (\beta = -0.081). \quad (24)
$$

It is possible that an important contribution to $\Delta g_s$, even at low temperature, is due to the vibrational mixing of the $|xy\rangle$ state into the ground state.\(^7\)

**V. CONCLUSION**

The theoretical analysis shows that the magnetic orbital wavefunction of Cu$^{2+}$ in CdWO$_4$, ZnWO$_4$, and MgWO$_4$ is mainly of the $|3z^2-r^2\rangle$ type. The stabilization of the complex by Jahn–Teller distortion is probably of minor importance, because this stabilization usually prefers the $|xy\rangle$ magnetic state. The transition to the dynamic Jahn–Teller effect has not been observed up to 300 K. At higher temperatures the spectra are not observable because of great linewidth. Small changes of the $g$ and $A$ parameters with the temperature can be explained by vibrational mixing of the first excited state with the ground state. The theoretical analysis has revealed the possibility of calculating the important components of the low-symmetry crystal field in CdWO$_4$. The complete calculation of the $g$-tensor anisotropy is then given and the calculated $\Delta g$ values can be compared with the experiment. For $A_s = 15(10^{-4} \text{ cm}^{-1})$ we obtain very good agreement. For the other choice, $A_s = 15(10^{-4} \text{ cm}^{-1})$, the agreement

is not so good. As the $g$-factor analysis seems to be complete, any disagreement with the experiment could probably only be explained by the inadequacy of the expression (12) for the low-symmetry potential. If the higher-order terms $(l=4)$ play an important role, the simple relation between $\langle t | V_L | e \rangle$ and $\langle t | V_L | t \rangle$ is disturbed. The mixing coefficient $\beta \sim \langle t | V_L | e \rangle$ can be smaller and the $t$-orbitals splitting $\delta E \sim \langle t | V_L | t \rangle$ greater than those given by the relation (16) and higher $\delta g$ is obtained for smaller $\beta$.

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Theory of the Width and Shift of Molecular Spectral Lines in Gases

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(Received 6 December 1965)

A theory is developed for linewidths and line shifts in molecular spectra of gases. A semiclassical method is used, which does not make the approximations of perturbation theory and a straight-line trajectory upon which previous work has been based. General formulas are given for linewidths and line shifts in microwave, infrared and Raman spectra of linear molecules. Numerical application of the results is made to the widths of a number of spectra, and the results are in good agreement with both the magnitude and $J$ dependence of the experimental values.

1. INTRODUCTION

The study of pressure broadening and shifts of molecular spectral lines in gases should be a valuable probe of intermolecular torques and of molecular collision processes in gases. Considerable experimental data on linewidths and shifts has been gathered by the techniques of microwave, infrared, and Raman spectroscopy. This information has been interpreted mainly through the method developed by Anderson, in which the relative translational motion is treated by classical mechanics, while the rotational motion is described by quantum-mechanical perturbation theory carried to second order. While there are systems, such as $\text{H}_2$, in which the intermolecular torques are weak enough for such a perturbation treatment to be reasonably accurate, in most molecular collisions rotation and translation are strongly coupled. Therefore a somewhat uncertain extrapolation procedure must be employed to estimate the effect of strong collisions. Another limitation of the usual interpretation of line broadening is the approximation of the collision trajectory by a straight line at an average velocity. Because of these two approximations, perturbation theory and the straight-line path, once can hardly hope to use Anderson's theory to understand line broadening in systems with strong, short-range intermolecular torques. Another shortcoming of the perturbation theory is its failure to give $J$-dependent line shifts which have been observed experimentally.

The purpose of the present paper is to develop a theory for the width and shift of molecular spectral lines in gases, which does not employ the assumptions of perturbation theory and a straight-line path, either in the formal theory or in the numerical calculations. We use a semiclassical description of both the rotational and translational motion. Three distinct physical effects of a collision are found to contribute to the broadening and shift of a line:

1. Interpretation of the radiation by rotationally inelastic collisions.
2. Phase shifts of the rotation (and of the vibration in a rotation–vibration spectrum) produced by a collision
3. Amplitude modulation of the effective radiating dipole due to reorientation by collisions which transfer angular momentum but not energy. The first two effects are well known in line-broadening theory, but this reorientation effect has not been distinguished previously.

If a perturbation expansion of the present theory is made, it is shown that Anderson's perturbation theory may be rearranged into a form which corresponds exactly to the present results. It is also shown that intuitive attempts to generalize Anderson's treatment beyond the perturbation limit are in error because the reorientation effect was neglected.

The magnitude of these three contributions to the width and shift are calculated by classical dynamics followed by application of the correspondence principle

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3 A. Ben-Reuven has kindly brought to my attention his treatment of another reorientation effect [J. Chem. Phys. 42, 2037 (1965)] due to collisions adiabatic about a rotating quantization axis [cf., H. Margenau and H. C. Jacobson, J. Quant. Spectry. Radiative Transfer 3, 35 (1963); H. Margenau, ibid., p. 445]. A comparison of these effects has been added to Sec. 8 of the present paper.