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Angular variation of normal-type EPR intensities of V^{2+} in $CsMgCl_3$

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Abstract. EPR measurements have been made at room temperatures on a trigonal V^{2+} centre in $CsMgCl_3$ that was analysed as a substitutional centre by McPherson *et al* to second-order in perturbation theory. The spectrum has been described by direct diagonalization of a 32×32 -dimensional spin-Hamiltonian matrix using the computer software developed originally by us. The anisotropic parameters $g_{\parallel} - g_{\perp}$ and b_2^0 have opposite signs to each other contrary to the expectation from simple electrostatic theory. By rotating the sample while keeping the c -axis normal to the external magnetic field, signal intensities of low- and high-field fine-structure lines interchanged characteristically. From theoretical calculation the intensity variation has been ascribed to the variation of the transition probability. The intensity variation is considered to be the elementary process for the resonant field shift observed in magnetically concentrated materials. The uniaxial direction of a trigonal or tetragonal centre in a microwave cavity can be known from this type of intensity-variation measurement irrespective of the sign of the fine-structure parameter b_2^0 .

1. Introduction

Magnetic materials ABX_3 with $CsNiCl_3$ -like hexagonal structure are interesting in their characteristic relationship between magnetic ordering and crystal structure (Ackerman *et al* 1974). As seen from figure 1, the crystals are composed of alternating B and AX_3 layers along the crystalline c -axis, where A represents a monovalent cation, B a divalent cation and X a monovalent anion. Features of the structure are linear chains of face-sharing BX_6 octahedra along the c -axis and their arrangement in the form of a triangular lattice in the c -plane.

An electron paramagnetic resonance (EPR) study was carried out by McPherson *et al* (1970) for a magnetically diluted system with substitutional divalent vanadium ions in an isomorphous $CsMgCl_3$ crystal. They also studied the crystallographic structure of a pure $CsMgCl_3$ single crystal and found that the point symmetry at a Mg site is D_{3d} and the surrounding chlorine octahedron is elongated slightly along the trigonal c -axis. They described the spectrum using the second-order perturbation formula for the spin Hamiltonian derived by Bleaney (1951). In the presence of electronic–nuclear forbidden transitions, the angular variation of an EPR spectrum having both fine and hyperfine structures with non-cubic symmetry shows many lines as if there exist other low-symmetry centres. It may be cumbersome or difficult to use perturbation theory to confirm the existence of only one axial centre without superposition of

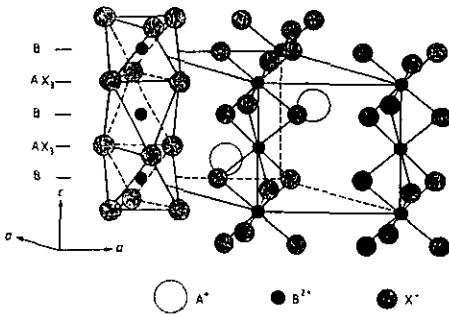


Figure 1. Structure of hexagonal ABX_3 -type crystal. The hexahedron shows a unit cell of the crystal and the octahedron shows a chlorine cage surrounding a B^{2+} ion.

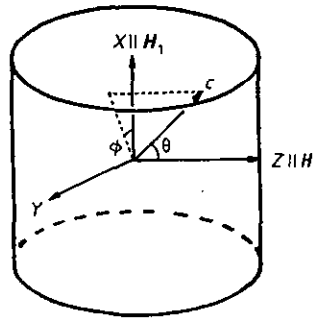


Figure 2. The TE_{011} -mode microwave cavity. The XYZ -coordinate system is fixed to the cavity with $Z \parallel H$ and $X \parallel H_1$. Polar coordinates θ and ϕ of the c -axis are defined with respect to the XYZ -coordinate system.

signals from other low-symmetric centres. We developed original computer software that can calculate all the allowed and forbidden EPR transitions of V^{2+} for any external field directions by diagonalizing the total electronic-nuclear spin-Hamiltonian matrix with 32×32 dimensions without any approximations. We examined the EPR spectra of $CsMgCl_3:V^{2+}$ accurately by the method of direct matrix diagonalization and determined the parameters for the substitutional centre including their absolute signs. By calculating the overall angular dependence of allowed and forbidden electronic-nuclear transitions, we confirmed there are no other low-symmetric centres within the sensitivity of our spectrometer.

In the course of the experiment, we found a characteristic variation of the signal intensities for three fine-structure lines with the azimuthal angle ϕ formed by the c -axis with the microwave magnetic field H_1 when the c -axis is kept normal to the external magnetic field H in a conventional TE_{011} -mode microwave cavity. Recently, Parent and Marshall (1986) reported that the EPR signal intensities of the transitions $M = \frac{3}{2} \leftrightarrow \frac{1}{2}$ and $M = -\frac{3}{2} \leftrightarrow -\frac{1}{2}$ observed for the tetragonal $Cr^{3+}-V_{Mg}$ centre in MgO are different to each other when the axial direction is nearly normal to the external field, and they were the first to make a primitive analysis of the ratio of transition probabilities among a few signals using perturbation theory. We performed a strict theoretical calculation with the expectation that the characteristic angular variation of signal intensities observed in our experiment can be explained by ϕ -dependence of the transition probability for three fine-structure lines. It will be shown in section 3 that the $\cos 2\phi$ -dependence of the intensity variation obtained from our strict calculation is in good agreement with the angular dependence observed.

The variation of signal intensity found in our experiment for the diluted system shows a similar ϕ -dependence to that of the resonant field shift known in low-dimensional magnetic materials (Natsume *et al* 1980). In section 4, we will propose that the resonant field shift in magnetic materials is ascribed to the elementary ϕ -dependence of the signal intensity of the individual ions.

2. Experimental procedure

Single crystals doped with a V^{2+} ion with a nominal concentration of 1 mol% were grown using the Bridgman technique. The crystals obtained were transparent and had a pale greenish colour and were easily cleaved in the planes parallel to the c -axis. The measurements were made at room temperature using an X-band EPR spectrometer with 100 kHz field modulation. A cleaved plane of the sample was pasted on the face of a two-axis goniometer with silicon grease to be rotated in the cylindrical microwave cavity with the TE_{011} mode as shown in figure 2. The external magnetic field H is applied parallel to the horizontal Z -axis and the microwave magnetic field H_1 is parallel to the vertical X -axis at the sample position in the XYZ -coordinate system fixed to the sample cavity. Microwave frequencies were measured directly by a frequency counter. The magnetic fields at the sample position were obtained by correcting the measured values using the shielding factor determined with DPPH (α, α' -diphenyl- β -picryl hydrazyl), because a trace of possible magnetic impurities within the cavity material may partially shield the external magnetic field that is measured by the NMR probe. The numerical computations were performed at the Computation Centre of Nagoya University.

3. Results

Three typical recorder traces of EPR signals are shown in figure 3. Each chart consists of three fine-structure groups of signals with eight-line hyperfine structure, showing effective electronic spin $S = \frac{3}{2}$ and nuclear spin $I = \frac{7}{2}$. This is characteristic of a V^{2+} ion in an axial crystalline field with external magnetic field parallel or perpendicular to the axial field. As the c -axis is declined from the external field direction, many signals appear and recorder traces become very complicated.

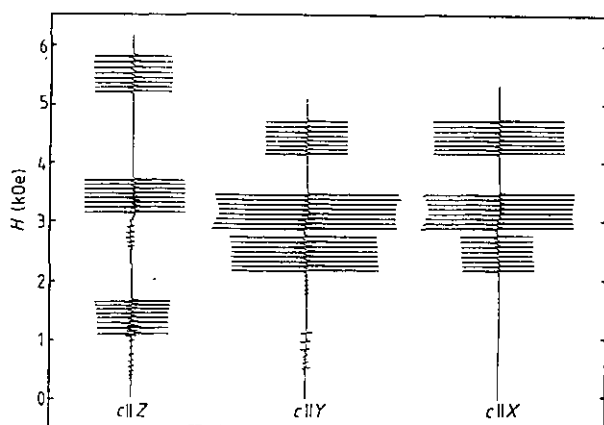


Figure 3. EPR spectra of the trigonal V^{2+} centre in $CsMgCl_3$ observed at 302 K when $c \parallel Z$, $c \parallel Y$ and $c \parallel X$. In the $c \parallel Z$ recorder trace, some forbidden transitions are observed because of the slight intentional misdirection of the external field.

As shown in figure 4, with a V^{2+} ion at the body centre, the ζ -axis is chosen to be parallel to the $c \parallel [111]$ direction and the ξ -axis parallel to the $[11\bar{2}]$ direction of the cubic axes system for an assumed regular octahedron. In the figure six chlorine ions

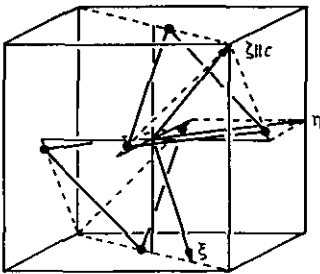


Figure 4. Principal $\xi\eta\zeta$ -axes of the spin Hamiltonian with respect to an elongated chlorine octahedron along the c -axis drawn parallel to the [111] direction of the cubic axis system for an assumed regular octahedron.

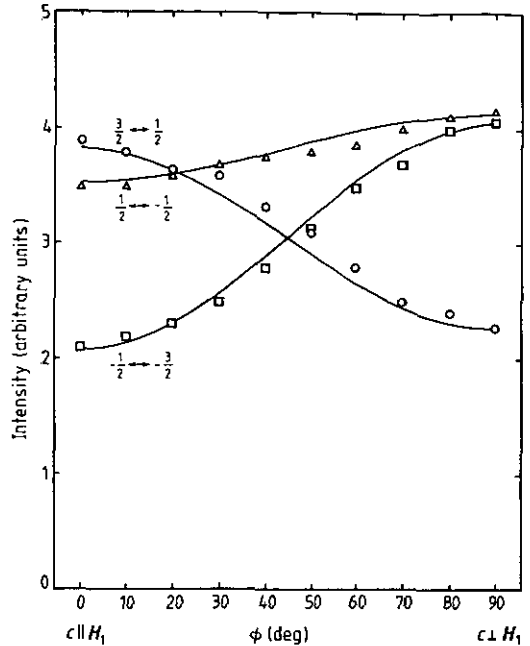


Figure 5. Angular variation of intensities of three fine-structure signals from $c \parallel H_1$ to $c \perp H_1$ in the $c \perp H$ plane. Full curves are calculated ones using equation (5).

in an elongated-octahedral configuration are shown by closed circles. The spectrum was described by the following spin Hamiltonian

$$\mathcal{H} = g_{\parallel} \beta S_{\zeta} H_{\zeta} + g_{\perp} \beta (S_{\xi} H_{\xi} + S_{\eta} H_{\eta}) + \frac{1}{3} b_2^0 O_2^0 + A S_{\zeta} I_{\zeta} + B (S_{\xi} I_{\xi} + S_{\eta} I_{\eta}) \quad (1)$$

where $S = \frac{3}{2}$, $I = \frac{7}{2}$ and β is the Bohr magneton. To equation (1), we added the expression for the $S^3 I$ terms that can be obtained in our coordinate system by changing the signs of the terms in U'_{\parallel} and U'_{\perp} of the expression by Brisson and Manogian (1980).

Accurate measurements were made with the field in the best-set ζ - and ξ -axis directions. The total electronic-nuclear spin Hamiltonian was fitted to the 48 hyperfine line positions observed for the allowed transitions by direct diagonalization of the 32×32 -dimensional matrix using our original software on a computer. Values obtained for the parameters are listed in table 1, where those reported by McPherson *et al* (1970) and the values for the cubic V^{2+} centres in $KMgF_3$ and MgO are also listed for comparison. The anisotropies of the \mathbf{g} and \mathbf{A} tensors are determined accurately by our experiment. We select negative signs for the hyperfine parameters A and B in the same way as those chosen for the cubic V^{2+} centre in $KMgF_3$ by Davies *et al* (1972), since the dominant isotropic part of the central hyperfine interaction arises from the Fermi contact interaction with the nucleus through the core-polarization mechanism. The root-mean-square error was about 40 times larger for the negative sign of b_2^0 than for the positive one. This result shows that the positive

sign of b_2^0 is reasonable. No higher-order hyperfine terms greater than experimental errors were detected. ^{51}V -ENDOR measurements may be needed to detect the small higher-order hyperfine terms. By calculating the angular variation of the resonant fields for all the allowed and electronic–nuclear forbidden transitions using the matrix-diagonalization software, we confirmed that the complicated spectrum observed can be ascribed to only one kind of substitutional V^{2+} centre.

Table 1. Experimental values of the spin-Hamiltonian parameters for the V^{2+} centres. b_2^0 , A , B , and U are in units of 10^{-4} cm^{-1} .

Crystal	CsMgCl_3^a	CsMgCl_3^b	KMgF_3^c	MgO^d
T (K)	302	300	4.2	4.2
g_{\parallel}	1.9729(1)	1.9730(6)	1.9720(2)†	1.9806(4)
g_{\perp}	1.9747(2)	1.9750(6)	1.9720(2)†	1.9806(4)
b_2^0	965.0(1)	941(4)	—	—
A	-76.18(8)	75.9(4)	-86.172(2)	-74.3237(2)
B	-74.50(7)	73.8(9)	-86.172(2)	-74.3237(2)
U	0.01(5)	—	0.037(2)	0.0300(2)
Symmetry	Trigonal	Trigonal	Cubic	Cubic

^a Present work.

^b McPherson *et al* (1970).

^c Takeuchi *et al* (1979).

^d de Wijn and Schrama (1968).

† From EPR measurements at 77 K by Davies *et al* (1972).

When a conventional TE_{011} -mode cavity is used, the angular variation of the EPR spectrum is observed in most cases by keeping the external field H in the horizontal plane of the cavity. Intensity-variation measurements where the ζ -axis or the c -axis is rotated in a plane normal to the external field (the $c \perp H$ sample rotation) are rare for cubic or layer-shaped crystals. This is because for cubic crystals the normal-type signal from a defect centre is usually the superposition of signals from equivalent magnetic ions different only in their axial directions that are mutually orthogonal. For layer-shaped crystals the rotation of the sample c -axis from the vertical to the horizontal direction is not natural in the measurements even with a two-axis goniometer.

However, for a single crystal with cleaved plane parallel to the c -axis it is easy to observe the intensity variation in normal-type signals by the use of a two-axis goniometer. Accordingly, the EPR observation of this type of sample rotation can be performed naturally for the CsMgCl_3 crystal. We observed the EPR spectrum in rotating the c -axis from the $c \parallel X$ to the $c \parallel Y$ direction and found a characteristic variation of signal intensities, as shown in figure 5. The intensity variation was measured keeping the resonant fields constant. The open circles, triangles and squares represent the intensities observed for the fourth hyperfine lines from the high-field sides of the $M = \frac{3}{2} \leftrightarrow \frac{1}{2}$, $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ and $-\frac{1}{2} \leftrightarrow -\frac{3}{2}$ electronic transitions, respectively. The intensities for the low-field fine-structure group (squares) and high-field one (circles) vary rapidly and interchange with each other, and those for the mid-field group (triangles) vary slowly.

Here, we try to explain the intensity variation of the normal-type signals. The transition probability between the states ψ_n and ψ_m is proportional to $|\langle \psi_m | \mathbf{h} \cdot \mathbf{g} \cdot S | \psi_n \rangle|^2$, where \mathbf{h} is a unit vector along the direction of the time-varying

microwave field H_1 with linear polarization (Orton 1968). For simplicity, our analysis uses only the electronic spin Hamiltonian

$$\mathcal{H}_e = g_{\perp} \beta S_z H + b_2^0 [S_x^2 - \frac{1}{3} S(S+1)] \quad (2)$$

in the xyz -coordinate system with $H \parallel z$ and $c \parallel x$. The four levels for $S = \frac{3}{2}$ can be expressed as follows:

$$\begin{aligned} |\psi_1\rangle &= c_1 |\frac{3}{2}\rangle + s_1 |-\frac{1}{2}\rangle & |\psi_4\rangle &= c_2 |-\frac{3}{2}\rangle + s_2 |+\frac{1}{2}\rangle \\ |\psi_3\rangle &= -s_1 |\frac{3}{2}\rangle + c_1 |-\frac{1}{2}\rangle & |\psi_2\rangle &= -s_2 |-\frac{3}{2}\rangle + c_2 |+\frac{1}{2}\rangle \end{aligned} \quad (3)$$

where $c_1 = \cos \alpha$, $s_1 = \sin \alpha$, $c_2 = \cos \gamma$, $s_2 = \sin \gamma$ and

$$\begin{aligned} \cos 2\alpha &= (2 - \epsilon)/2\sqrt{1 - \epsilon + \epsilon^2} & \sin 2\alpha &= \sqrt{3}\epsilon/2\sqrt{1 - \epsilon + \epsilon^2} \\ \cos 2\gamma &= (2 + \epsilon)/2\sqrt{1 + \epsilon + \epsilon^2} & \sin 2\gamma &= -\sqrt{3}\epsilon/2\sqrt{1 + \epsilon + \epsilon^2} \end{aligned} \quad (4)$$

with $\epsilon = b_2^0/g_{\perp}\beta H$. The high-, mid-, and low-field groups correspond to the $\psi_1 \leftrightarrow \psi_2$, $\psi_2 \leftrightarrow \psi_3$, and $\psi_3 \leftrightarrow \psi_4$ transitions, respectively, for the case of positive b_2^0 .

Then, we obtain for $T_{mn} = (2/g_{\perp})^2 |\langle \psi_m | \mathbf{h} \cdot \mathbf{g} \cdot S | \psi_n \rangle|^2$ as follows:

$$\begin{aligned} T_{12} &= 3c_3^2 + 4s_1^2 c_2^2 + 4\sqrt{3}s_1 c_2 c_3 \cos 2\phi \\ T_{23} &= 3s_3^2 + 4c_1^2 c_2^2 - 4\sqrt{3}c_1 c_2 s_3 \cos 2\phi \\ T_{34} &= 3c_3^2 + 4c_1^2 s_2^2 + 4\sqrt{3}c_1 s_2 c_3 \cos 2\phi \end{aligned} \quad (5)$$

where $c_3 = \cos(\alpha + \gamma)$ and $s_3 = \sin(\alpha + \gamma)$. Calculated curves using the values determined for g_{\perp} and b_2^0 in table 1 are shown in figure 5, and are in good agreement with observed ones. In the assumed case of negative b_2^0 , the feature of the resonant fields and intensity variations does not change except for the exchange of the $\psi_1 \leftrightarrow \psi_2$ and the $\psi_3 \leftrightarrow \psi_4$ transitions.

4. Discussion

For the present V^{2+} centre in CsMgCl_3 , contrary what we might expect from the electrostatic model (Patel *et al* 1976), $g_{\parallel} - g_{\perp} < 0$ in spite of $b_2^0 > 0$. There may be other contributions that are not considered in the simple electrostatic model. Since the hyperfine-interaction parameters of V^{2+} for CsMgCl_3 are closer to those for oxide rather than those for fluoride, as seen from table 1, the covalency effect in CsMgCl_3 may be considerably large (Owen and Thornley 1966). In contrast to perovskite-like crystals, the surrounding ions (except for ligands), especially the two nearest Mg^{2+} ions on the c -axis and the second-nearest Cl^- shell, may produce a strong axial field. For adequate understanding, the spin-Hamiltonian parameters should be analysed by considering the contributions from covalency, excited multiplets, outward relaxation of the octahedron, the crystalline field from distant ions, and so on.

In the preceding section, the characteristic variation of the signal intensity observed in the $c \perp H$ sample rotation is explained by the variation in the transition probability of each fine-structure line with the angle of declination ϕ of the c -axis

from the direction of microwave magnetic field H_1 . The ϕ -dependence of normal-type signals may be observed in any EPR spectra from axial centres with effective spins $S \geq 1$, if the fine-structure lines of an axial centre are not superposed by those from other equivalent centres that are only different in the principal ζ -axis directions. The intensity measurement with the CsMgCl_3 matrix is unambiguous, since neither the intensity anomaly by site-preference as reported by Geschwind and Remeika (1961) nor the line overlapping observed in charge-compensated axial centres occur in the present crystal. As seen from equation (5), the intensities are expected to vary remarkably for large ϵ . So, it would be advantageous, for the observation of intensity variation, to experiment with an X-band spectrometer rather than K- or Q-band ones. The feature of the intensity variation in figure 5 observed for three lines is not changed by reversing the sign of b_2^0 . So, this measurement is useful in finding the c -axis direction in a microwave cavity irrespective of the sign of b_2^0 .

In an isolated magnetic ion, as shown in section 3, the EPR signal intensity depends on $\cos 2\phi$ in the $c \perp H$ sample rotation where the high-field line is strong near $\phi = 0^\circ$ and the low-field one near $\phi = 90^\circ$. Natsume *et al* (1980) extended the general theory of lineshape by Kubo and Tomita (1954) to low-dimensional cases to explain the shift of the central point of the broad resonant line observed for the $c \perp H$ orientation in their EPR study of the quasi-one-dimensional magnetic compound TMMC. They found that the magnitude of the shift is dominated by dimensionality and enhanced in a quasi-one-dimensional system by the long-time tail of the spin-correlation function. In their results, the shift δH is positive at $\phi = 0^\circ$ and varies with $\cos 2\phi$ in the $c \perp H$ orientation. It may safely be said from the following consideration that the ϕ -dependent shift in the concentrated system is ascribed to the elementary ϕ -dependent intensity variation of the individual ions, although the main anisotropy comes from the electric field in the former and from the electric field and magnetic-dipolar one in the latter. In a concentrated material, the resonance position of each magnetic ion may be perturbed mainly by magnetic dipolar fields from neighbouring ions and be distributed with an asymmetrically broadened EPR profile where the high-field side is emphasized near $\phi = 0^\circ$ and the low-field side near $\phi = 90^\circ$ when $\theta \simeq 90^\circ$. Furthermore, in the presence of a strong exchange interaction the asymmetrically broadened profile is narrowed into an almost symmetric Lorentzian shape. Since the main contribution to the dipolar field comes from the intrachain ions in quasi-one-dimensional magnetic materials, the combined effect of the dipolar and exchange interactions among the spins may result in a shift of the central point of the exchange-narrowed resonance profile with $\delta H > 0$ near $\phi = 0^\circ$ and $\delta H < 0$ near $\phi = 90^\circ$.

5. Conclusions

It is confirmed by direct matrix-diagonalization analysis of the spin Hamiltonian that the spectrum observed from room-temperature EPR measurements can be ascribed to only one kind of V^{2+} ions at the Mg^{2+} site. Accurate values of the spin-Hamiltonian parameters are determined, including their signs and anisotropies. The intensity variation of normal-type signals is found and the ϕ -dependence can be explained unambiguously by the variation of the transition probability from strict theoretical calculations. It is shown that the ϕ -dependence of the normal-type signal intensity in the present isolated ion is the elementary process for the ϕ -dependent shift observed in quasi-one-dimensional magnetically-concentrated materials. The

hyperfine parameters show that the covalency of the VX_6 octahedron in $CsMgCl_3$ is between the fluoride and oxide of the magnesium compounds and considerably close to that of oxide. It was found for the $3d^3$ ion in the present hexagonal matrix that the relation of the anisotropy $g_{\parallel} - g_{\perp}$ and b_2^0 cannot be explained by simple electrostatic theory where the electrostatic field only from ligands and the second-order perturbation contribution within the 4F term are considered. It is suggested that other contributions to the parameters must be considered for quantitative explanation of the parameters.

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