An EPR study of anisotropies of several Cr^{3+} centres in $CsMgCl_3$

An EPR study of anisotropies of several Cr^{3+} centres in $CsMgCl_3$

H Takeuchi†, H Tanaka† and M Arakawa‡

† Department of Physics, College of General Education, Nagoya University, Nagoya 464-01, Japan
‡ Department of Physics, Nagoya Institute of Technology, Nagoya 466, Japan

Abstract. EPR measurements at 300 K and 1.6 K have been made on $CsMgCl_3$ crystals doped with Cr^{3+} and Cr^{2+} and co-doped with Li^+ using X- and Q-band spectrometers. Together with signals from the pair centre, signals from three trigonal Cr^{3+} centres (I, III, IV) and a monoclinic centre (II) are observed from the as-grown crystal. Accurate spin-Hamiltonian parameters at 300 K and 1.6 K are obtained for all the centres using the matrix-diagonalization method. The signs of the b_2^0 parameters have been determined by the depopulation effect at 1.6 K. From a comparison of b_2^0 on the basis of the ligand-distortion model for the centres I, III and IV and intensity change by x-irradiation, the trigonal centre with $b_2^0 = 1049.4 \times 10^{-4} \, \text{cm}^{-1}$ is ascribed to the uncompensated Cr^{3+} ion and that with $b_2^0 = -2807 \times 10^{-4} \, \text{cm}^{-1}$ is ascribed to the Cr^{3+} ion associated with the nearest Mg^{2+} vacancy. From a spin-Hamiltonian separation analysis the monoclinic centre II is ascribed to a Cr^{3+} ion associated with the nearest Cs^+ vacancy.

1. Introduction

$CsNiCl_3$-like materials are interesting in their characteristic structure of linear chains of face-sharing octahedra along the c axis and of a triangular lattice in the c plane, as shown in figure 1. One of the ways to investigate single-ion anisotropy is to study electron paramagnetic resonances (EPR) in magnetically dilute systems. The EPR of chromium impurity ions in $CsMgCl_3$ has been studied by McPherson and Heung (1976) for three trigonal centres (A, B, C) of single Cr^{3+} ions with fine structure parameters $b_2^0 = \pm 2840, \pm 1270, \pm 860 \times 10^{-4} \, \text{cm}^{-1}$. McPherson and Devaney (1980) further investigated the trigonal centre B observed from Cr^{2+}-doped samples. From considerations of intensity change by x-irradiation they only ascribed the centre B to a Cr^{3+} ion associated with no charge compensators in its immediate neighbourhood (uncompensated centre). In the samples co-doped with Cr^{3+} and Li^+, they observed a trigonal centre with $b_2^0 = \pm 88 \times 10^{-4} \, \text{cm}^{-1}$ and ascribed it to a Cr^{3+} ion associated with a Li^+ at the nearest Mg^{2+} site. In their studies the signs of the fine structure parameters b_2^0 were not determined. Identifications of the centres A and C were left.

The identification of each Cr^{3+} centre may be carried out unambiguously by considering the relationships among the signs and magnitudes of the fine structure parameters of the several centres formed in the same or related samples. For this purpose a knowledge of the signs of the anisotropic parameters b_2^0 and $g_\parallel - g_\perp$ is indispensable. We therefore performed EPR experiments at room temperature and at 1.6 K for $CsMgCl_3$ single crystals doped with Cr^{3+} and Cr^{2+} ions, some of which were co-doped with Li^+. Three kinds of centres with effective spins $S = \frac{3}{2}$ (centres I, III, IV) and a centre with $S = \frac{5}{2}$ (centre V)
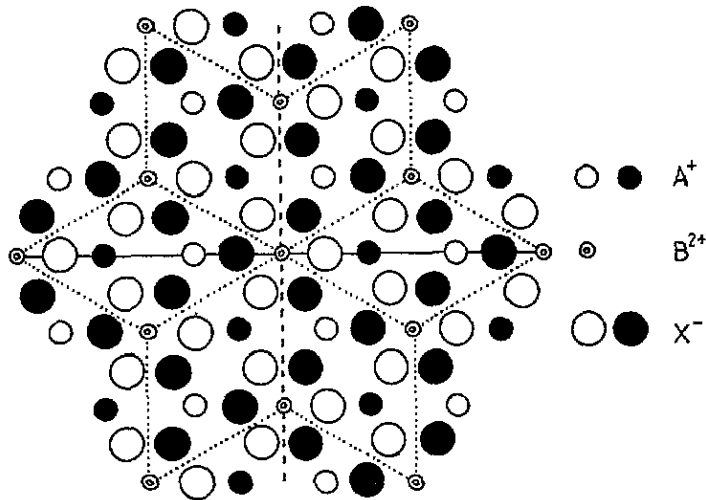
Figure 1. Projection of a CsNiCl$_3$-type crystal onto the c plane. B^{2+} ions are in the $z = 0$ plane; ions in the AX$_3$ layer with $z = \frac{1}{4}c$ are denoted by full circles and those with $z = -\frac{1}{4}c$ are denoted by open circles. The broken line denotes the projection of a cleaved plane which is parallel to the goniometer wall in the X-band measurements and parallel to the cavity bottom plane in the Q-band measurements. The full line denotes the projection of the plane within which the external field direction is rotated in the X-band measurements in figure 3 from $H \parallel c$ to $H \perp c$. In the Q-band measurements the external field is rotated in the broken plane.

were observed and can be described by spin Hamiltonians with trigonal symmetry about the crystalline c axis. Together with these trigonal centres, signals from a centre with $S = \frac{3}{2}$ having a finite b_2^2 parameter (centre II) were observed. This centre will be denoted as the 'monoclinic centre' due to the symmetry of the configuration of the surrounding ions, although the second-rank fine structure term has orthorhombic symmetry. In section 3, we report accurate values of the anisotropy of the g tensor and fine structure parameters b_n^m determined by matrix diagonalization of spin Hamiltonians for the trigonal and monoclinic Cr^{3+} centres. For all the centres absolute signs of the b_2^0 parameters are determined by the depopulation effect observed in the measurements at 1.6 K.

For the identification of the trigonal Cr^{3+} centres we use the empirical rule that a positive or negative b_2^0 value corresponds respectively to elongation or compression of the ligand octahedron along the trigonal axis (McGarvey 1964, Danilov *et al* 1972a, b, 1973, Manoogian *et al* 1974a, b, Takeuchi *et al* 1982). For the identification of the monoclinic centre we use the spin-Hamiltonian separation (SHS), which has been successfully applied to several Cr^{3+} and Fe^{3+} centres (Takeuchi *et al* 1982, 1991a, b, Arakawa *et al* 1988). Using these methods all the centres observed in our experiments will be ascribed clearly to each Cr^{3+} ion in section 4. It will be also shown that the ligand-distortion models for several Cr^{3+} centres are consistent with each other.

2. Experimental procedures

Single crystals doped with Cr^{3+} or Cr^{2+} ions with a nominal concentration of 1 mol% were grown using the Bridgman technique. Starting mixtures of CsCl, MgCl$_2$ and CrCl$_3$ (or CrCl$_2$) powders were sealed in a quartz tube after dehydration in a vacuum at 200 °C for

about 70 h. In some crystallizations LiCl powder was added to the starting mixture. The quartz crucible was heated to 700 °C to yield liquid mixtures. The crucible was pulled down to a temperature region of 500 °C at a rate of about 2.5 mm h^{-1}. The crystals obtained were transparent and had a purplish-red colour, and were cleaved easily. It is known that the cleaved plane of CsNiCl$_3$-type crystals is parallel to the symmetry plane including the c axis and divalent cations as shown by a broken line in figure 1.

The room-temperature measurements were made using X-band and Q-band EPR spectrometers with 100 kHz-field modulation. In room-temperature measurements using the X-band spectrometer, the sample was mounted on a two-axes goniometer MGM-10 (Microdevice) to be rotated in a microwave cavity with a TE$_{011}$ mode. The cleaved plane shown by the broken line in figure 1 was pasted with silicon grease on the vertical goniometer wall, so that the external magnetic field was rotated in the plane shown by the full line in figure 1. The Q-band EPR spectrometer was used for the measurements at 1.6 K and 300 K. Details of the spectrometer are described in Takeuchi *et al* (1979). Liquid helium was pumped to retain the superfluid phase. In room-temperature and 1.6 K measurements using the Q-band spectrometer, the cleaved plane of the sample was pasted on the bottom wall of the microwave cavity with TE$_{012}$ mode, so that the external field was rotated in the cleaved plane shown by the broken line in figure 1. Therefore, the rotation plane of the external field includes Cs$^+$ ions in the X-band measurements and does not include them in the Q-band measurements.

Microwave frequencies were measured directly by a frequency counter R5373 (Advantest). An NMR probe EFM-2000 (Echo Electronics) was used for accurate measurements of the external magnetic field. The x-ray irradiations were performed using a Cu tube operating at 40 kV and 20 mA. Numerical computations were performed at the Computation Centre of Nagoya University.

3. Results

In room-temperature measurements using X- and Q-band spectrometers signals from three kinds of magnetic centres with $S = \frac{3}{2}$ (centres I, II, III) were observed for the Cr^{3+}-doped crystal, together with signals from the Cr^{3+}–V$_{Mg}$–Cr^{3+} pair centre reported by McPherson and Heung (1976). Accurate values of the pair-Hamiltonian parameters ($g_\parallel$, $g_\perp$, D_c, J, D_e) obtained by direct matrix diagonalization of the pair Hamiltonian have already been reported in Takeuchi *et al* (1993). Both angular variations of the X-band spectrum and Q-band spectrum of the centres I, II and III were described using the same spin-Hamiltonian parameters for each centre.

In low-temperature measurements at 1.6 K, using the Q-band spectrometer with the same setting as in the room-temperature measurements, an angular variation of the spectrum similar to the room-temperature results was observed, except for small changes of resonant fields and a remarkable depopulation effect in the signal intensities. We can therefore say that the fine structure parameter b_2^0 for each centre does not change drastically during the temperature change from 300 K to 1.6 K. These parameters can be considered to have the same signs at 300 K and 1.6 K. Recorder traces of EPR signals at 1.6 K with (*a*) H parallel to c and (*b*) H perpendicular to c are shown in figure 2 for an as-grown crystal doped with only Cr^{3+} ions. Signals from the centres I, II and III are marked with roman numerals respectively. Signals from the Cr^{3+}–V$_{Mg}$–Cr^{3+} pair centre are also observed even at the low temperature of 1.6 K due to its small exchange parameter J.

In an as-grown crystal doped with Cr^{2+} ions, the intensities of the centres I, II and III at room temperature were about three times weaker than those in the Cr^{3+}-doped crystal. On
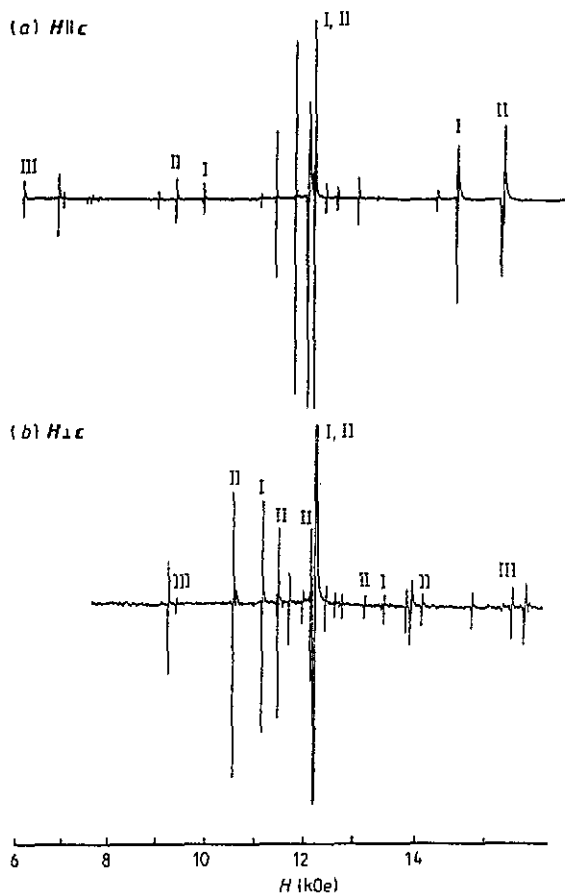
Figure 2. EPR signals observed at 1.6 K using the Q-band spectrometer from an as-grown sample of $CsMgCl_3$ doped with only Cr^{3+} ions when (a) $H \parallel c$ and (b) $H \perp c$.

the other hand, the intensity of the pair centre was almost same as that in the Cr^{3+}-doped crystal. After x-irradiation for about 3 h at room temperature, the signal intensity of the centre I became about four times stronger and a centre with $S = \frac{5}{2}$ and with comparable intensity to the centre I appeared.

In an as-grown crystal co-doped with Cr^{3+} and Li^+, we observed at room temperature a very strong EPR signal with $S = \frac{3}{2}$ and having small fine structure splitting (centre IV). We also observed signals from the centre I with an intensity about 40 times weaker than that of the as-grown crystal doped with only Cr^{3+} ions.

The angular variation of resonant fields for the centres I, III and IV have extremes only in the directions with H parallel to c and H perpendicular to c. This shows that the surroundings of the magnetic ions have trigonal symmetry about the c axis. These centres are therefore called the 'trigonal centres' hereinafter. In figure 3, signals observed for the centre II at 300 K using the X-band spectrometer with the two-axes goniometer are plotted against external field direction by open circles. Contrary to the trigonal centres, the angular variation shows extremes in the declined direction from the c axis with a tilt angle of about $4°$.

The spectra observed can be described by the following spin Hamiltonian with $S = \frac{3}{2}$:
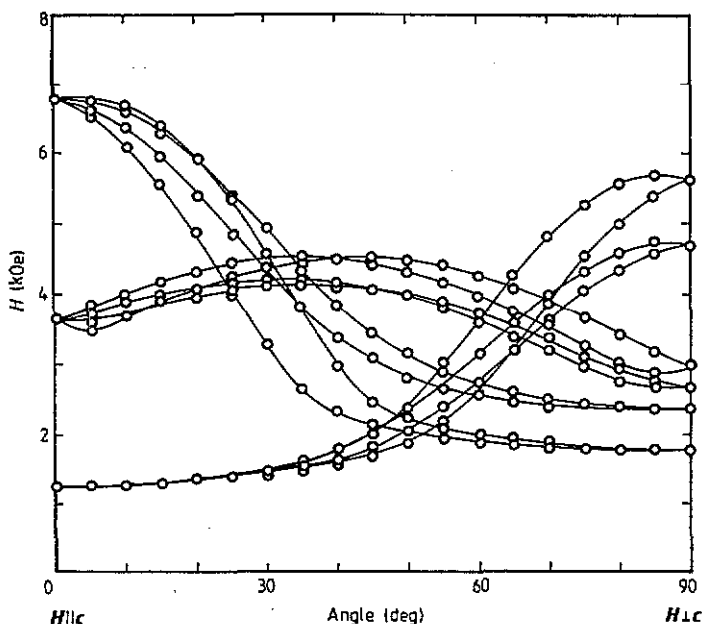
Figure 3. Angular variation of the EPR spectrum from the centre II at 300 K. Open circles show the signals observed. The full curves denote the calculated resonant fields using the parameters listed in table 1.

$$\mathcal{H} = g_x \beta S_x H_x + g_y \beta S_y H_y + g_z \beta S_z H_z + \tfrac{1}{3}(b_2^0 O_2^0 + b_2^2 O_2^2). \tag{1}$$

For the centres I, III and IV, the parameters b_2^2 are unnecessary and the principal z axis is parallel to the c axis. For the centre II the parameters b_2^2 are needed and the principal z axis is declined by a small angle α from the c axis, and the x axis is in a symmetry plane in which the external field is rotated. The spin-Hamiltonian parameters obtained by the matrix-diagonalization method are listed in table 1 for both the room-temperature and 1.6 K measurements. The values in parentheses show the least-square errors for the last numerals determined by the fitting of the spin Hamiltonian to the resonant fields measured in the best setting. The signs of the fine structure parameters at 1.6 K were determined by the depopulation effect, and those at room temperature for the centres I, II and III are considered to be the same as at 1.6 K. As the sign of b_2^0 for the centre IV at 300 K has the possibility to be turned from that at 1.6 K due to the small magnitude of b_2^0, the determination of the sign is left. The full curves in figure 3 show the calculated angular variations using the parameters listed in table 1. For all the centres good agreement of the calculated values of the resonant field with experimental ones are obtained. For the trigonal centres we denote as $g_\parallel = g_z$ and $g_\perp = g_x = g_y$ hereinafter.

4. Discussion

4.1. Centre I

Signals from the centre I become very strong by x-irradiation for the as-grown crystal doped with Cr^{2+} ions. Davies and Horai (1971) reported that a Cr^{2+} ion in KMgF$_3$ converts to

Table 1. Experimental values of the spin-Hamiltonian parameters for the single Cr^{3+} centres in $CsMgCl_3$. The b_n^m are in units of $10^{-4}\,cm^{-1}$.

Centre	T (K)	g_x	g_y	g_z	b_2^0	b_2^2	α (deg)
Centre I	1.6	1.9841(2)	1.9841(2)	1.9838(2)	+1049.4(3)	—	—
	290	1.9868(2)	1.9868(2)	1.9868(2)	+1253.3(3)	—	—
Centre II	1.6	1.9893(5)	1.9896(5)	1.9832(5)	+1334.3(5)	−578(2)	+4.20(5)
	300	1.984(2)	1.985(2)	1.985(2)	+1546(6)	−552(6)	+4.0(3)
Centre III	1.6	1.995(5)	1.995(5)	1.990(5)	−2807(7)	—	—
	300	1.9831(3)	1.9831(3)	1.9861(3)	−2811.8(3)	—	—
Centre IV	1.6	1.9835(2)	1.9835(2)	1.9828(2)	−170.1(3)	—	—
	300	1.9864(2)	1.9864(2)	1.9858(2)	±86.6(2)	—	—
V^{2+} centre [a]	302	1.9747(2)	1.9747(2)	1.9729(1)	+965.0(1)	—	—

[a] Takeuchi and Tanaka (1992).

a Cr^{3+} ion by losing one electron due to x-irradiation and another Cr^{2+} ion converts to a Cr^+ ion by capturing the electron. A similar process is expected to happen in the present crystal, so the centre I is considered to be the same as the uncompensated centre (centre B) reported by McPherson and Heung (1976).

It is found by x-ray diffraction experiments that the chlorine octahedron in a matrix crystal is slightly elongated along the trigonal axis (McPherson et al 1970). From the positive b_2^0 value the ligand octahedron may be elongated along the trigonal axis considering the empirical rule that b_2^0 is positive or negative respectively for the trigonally elongated ligand octahedron or trigonally compressed one. The b_2^0 value for the V^{2+} centre is also positive and smaller than that for the Cr^{3+} centre. The ionic radius (Sanderson 1967) of a Cr^{3+} ion (0.63 Å) is almost the same as that of Mg^{2+} (0.66 Å). A V^{2+} ion has a larger ionic radius (0.88 Å), so that the chlorine octahedron surrounding V^{2+} may be expanded into a configuration closer to cubic symmetry. For the trigonal and tetragonal centres of $3d^3$ ions in perovskite fluorides we reported that b_2^0 and $g_{\parallel} - g_{\perp}$ have the same signs (Patel et al 1976, Takeuchi et al 1982). In the present hexagonal chloride $CsMgCl_3$ both the Cr^{3+} and V^{2+} centres show almost zero or negative $g_{\parallel} - g_{\perp}$ despite of very large positive b_2^0 values. This peculiar feature cannot be explained at present.

4.2. Centre IV

The Cr^{3+} ions in a K_2ZnF_4 crystal are charge compensated by a Li^+ ion on the nearest Zn^{2+} site rather than the nearest Zn^{2+} vacancy (Takeuchi and Arakawa 1983). Similarly, the excess monovalent positive charge on the Cr^{3+} ion can just be compensated by a monovalent deficient charge of the Li^+ ion substituting for the nearest Mg^{2+} ion. From the trigonal symmetry, the adaptable ionic radius of Li^+ (0.68 Å) for Mg^{2+} and just-compensation, the strong centre IV observed in Li^+-co-doped crystal may be ascribed to a Cr^{3+} ion associated with a Li^+ at the nearest Mg^{2+} site on the c axis. Experimental results show that the centre IV dominates the other Cr^{3+} centres due to just-compensation. This centre is considered to be the same as the Li^+-associated Cr^{3+} centre with $b_2^0 = \pm 88 \times 10^{-4}\,cm^{-1}$ reported by McPherson and Devaney (1980).

Contrary to the uncompensated centre, b_2^0 for the Cr^{3+}–Li^+ centre has a small negative value, i.e. $-170.1 \times 10^{-4}\,cm^{-1}$ at 1.6 K. It may be suggested that a change from elongation to compression of the octahedral ligand coordination occurs by the association of a Li^+ ion to the uncompensated Cr^{3+} centre. For the trigonal Cr^{3+}–V_K centre in $KZnF_3$, negative $g_{\parallel} - g_{\perp}$ can be explained by considering the front fluorine deviations toward the opposite direction to the K^+ vacancy (Takeuchi 1993). The change of b_2^0 from the uncompensated

centre to the Li^+-associated centre at 1.6 K is $-1220 \times 10^{-4}\,cm^{-1}$, which is comparable with $b_2^0 = -1613 \times 10^{-4}\,cm^{-1}$ for the Cr^{3+}–V_K centre in $KZnF_3$ (Patel *et al* 1976). It may be said that the effective monovalent negative charge on the Li^+ ion relative to the matrix crystal may deviate the three front chlorines toward the opposite direction to the Li^+ ion, resulting in the compression effect almost cancelling the elongated configuration in the uncompensated centre.

4.3. Centre III

From the magnitude of b_2^0 at room temperature the centre III may be the same as the centre A reported by McPherson and Heung (1976). The Cr^{3+} ions in the centre III may be associated with some charge compensator. It was clarified from knowledge of the signs of b_2^0 for the centres I and III that the change of b_2^0 from the uncompensated centre to the centre III is $-3856 \times 10^{-4}\,cm^{-1}$ at 1.6 K, which is about three times larger than the corresponding change of the centre IV. The most probable charge compensator may be the nearest Mg^{2+} vacancy on the trigonal axis, as shown in figure 4. In fact, the centre III has the same sign of b_2^0 as that of the single-ion anisotropy parameter $D_c = -2214 \times 10^{-4}\,cm^{-1}$ for the Cr^{3+}–V_{Mg}–Cr^{3+} pair centre (Takeuchi *et al* 1993, McPherson and Heung 1976), and the magnitude is close to that of D_c. We may therefore identify the centre III as the Cr^{3+} centre associated with a nearest Mg^{2+} vacancy. The Mg^{2+} vacancy has a divalent effective negative charge relative to the matrix crystal, so that a stronger compression effect of front chlorines than that in the Li^+-associated centre is expected.
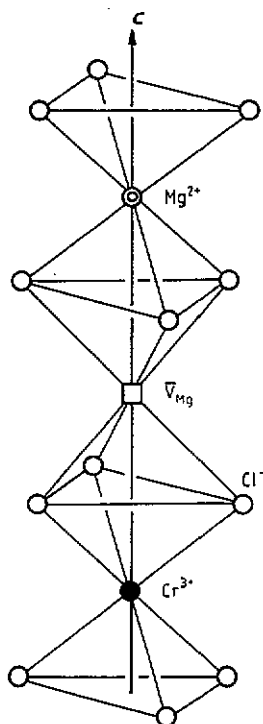

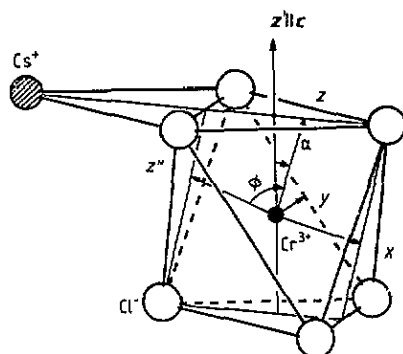**Figure 4.** Schematic structure for the centre III.

Figure 5. Definitions of the coordinate system for the spin Hamiltonian of the centre II and of the z'- and z''-axes of the uniaxial terms used in the spin-Hamiltonian separation analysis.

4.4. Centre II

The centre II is considered to be a Cr^{3+} centre associated with some charge compensator. It can be said from the four branches near the $H \parallel c$ direction seen in figure 3 that one of the equivalent charge compensators in the centre II exists in the symmetry plane in which the external field is rotated. As $b_2^2/b_2^0 \simeq 0.36$ is considerably smaller than one and b_2^0 is close to that for the uncompensated centre, we can regard the centre II as a result of a weak perturbation for the centre I. We can therefore analyse the centre II by SHS for the second-rank fine structure terms as performed for the $Fe^{3+}-V_{Rb}$ centre in Rb_2ZnF_4 (Takeuchi et al 1991a).

We separate the fine structure terms into two uniaxial terms as follows:

$$b_2^0[3S_z^2 - S(S+1)] + b_2^2(S_x^2 - S_y^2) = b_{2(1)}^0[3S_z'^2 - S(S+1)] + b_{2(2)}^0[3S_z''^2 - S(S+1)] \quad (2)$$

where the z' axis is parallel to the c axis and the z'' axis is declined by an angle ϕ from the z axis toward the c axis apart from the x axis in the symmetry plane, as shown in figure 5. Equation (2) is valid when the following conditions are satisfied:

$$b_{2(1)}^0 \sin 2\alpha + b_{2(2)}^0 \sin 2\phi = 0 \quad (3)$$

$$b_{2(1)}^0 + b_{2(2)}^0 = b_2^0 + b_2^2 \quad (4)$$

$$\tan \phi = -\frac{2b_2^2}{(3b_2^0 + b_2^2)\tan \alpha}. \quad (5)$$

From the experimental values of b_2^0, b_2^2 and α we can calculate $b_{2(1)}^0$, $b_{2(2)}^0$ and ϕ. The results are listed in table 2. The ratios of $b_{2(1)}^0$ to the axial parameters $b_2^0(I)$ for the uncompensated centre are almost the same values 1.11 for 300 K and 1.6 K although $|b_2^0|$ decreases and $|b_2^2|$ increases from 300 K to 1.6 K. The comparable values of $b_{2(1)}^0$ with $b_2^0(I)$ and small values of $b_{2(2)}^0$, which may be the measure of the perturbation, are consistent with the view that this centre is weakly perturbed. The perturbation angles from the c axis, i.e. $\phi - \alpha$, are in the range 71–74°. The values are very close to the angle 69.77° (McPherson et al 1970), which is the direction of a nearest Cs^+ ion from the c axis in the matrix crystal. The distance to a Cs^+ ion from a Mg^{2+} ion is 4.473 Å, which is much larger than the distance

3.094 Å to a nearest Mg^{2+} ion (McPherson *et al* 1970). From the above analysis we can ascribe the centre II to a Cr^{3+} ion associated with a nearest Cs^+ vacancy. Although the second-rank fine structure term for the centre II is the same as that for the orthorhombic centre with $S = \frac{3}{2}$, it may be proper to call this centre the 'monoclinic centre' since the site symmetry of this centre is monoclinic C_{1h}. The ligand chlorines may be slightly distorted to yield the weak perturbation field component by the presence of the nearest Cs^+ vacancy.

Table 2. Calculated values of $b_{2(1)}^0$, $b_{2(2)}^0$ and ϕ from the experimental values of b_2^0, b_2^2 and α for the centre II and the ratios of $b_{2(1)}^0$ to the b_2^0 parameters for the centre I.

T (K)	$b_{2(1)}^0$ (10^{-4} cm^{-1})	$b_{2(2)}^0$ (10^{-4}cm^{-1})	ϕ (deg)	$b_{2(1)}^0/b_2^0$(I)
1.6	1166	−410	78	1.111
300	1397	−401	75	1.115

It is also confirmed from the analysis of the centre II using the X-band spectrometer that the cleaved plane of the CsNiCl₃-type crystal is parallel to the symmetry plane represented by the broken line in figure 1.

5. Conclusions

The spin-Hamiltonian parameters for the Cr^{3+} centres (centres I, II, III, IV) in CsMgCl₃ observed at 1.6 K and 300 K have been determined. The signs of b_2^0 for the trigonal centre I and the monoclinic centre II are determined to be positive and those for the trigonal centres III and IV are negative from the depopulation effect observed at 1.6 K. The ligand octahedron of the uncompensated Cr^{3+} centre (centre I) is considered to be elongated along the c axis because of the positive b_2^0 parameter. The monoclinic centre (centre II) is ascribed to the Cr^{3+} ion associated with the nearest Cs^+ vacancy by the spin-Hamiltonian separation analysis. The trigonal centre III is ascribed to the Cr^{3+} ion associated with the nearest Mg^{2+} vacancy by a comparison of the b_2^0 parameters for three trigonal centres I, III, IV and D_c for the Cr^{3+}–V_{Mg}–Cr^{3+} pair centre. Among the three just-compensated Cr^{3+} centres observed in as-grown crystals, the Cr^{3+}–Li^+ centre (centre IV) is dominant over the Cr^{3+}–V_{Cs} centre (centre II) and Cr^{3+}–V_{Mg}–Cr^{3+} pair centre. The b_2^0 parameters for the trigonal centres I, III and IV are qualitatively understood by the trigonal distortion of the ligand octahedron.

References

Arakawa M, Ebisu H and Takeuchi H 1988 *J. Phys. Soc. Japan* **57** 3573–9
Danilov A G and Manoogian A 1972a *Phys. Rev.* B **6** 4097–103
—— 1972b *Phys. Rev.* B **6** 4103–11
Danilov A G, Vial J C and Manoogian A 1973 *Phys. Rev.* B **8** 3124–33
Davies J J and Horai K 1971 *J. Phys. C: Solid State Phys.* **4** 671–81
Manoogian A and Auger B 1974a *Can. J. Phys.* **52** 1731–8
Manoogian A and Leclerc A 1974b *Phys. Rev.* B **10** 1052–8
McGarvey B R 1964 *J. Chem. Phys.* **40** 809–12
McPherson G L and Devaney K 1980 *J. Phys. C: Solid State Phys.* **13** 1735–43
McPherson G L and Heung W M 1976 *Solid State Commun.* **19** 53–6
McPherson G L, Kistenmacher T J and Stucky G D 1970 *J. Chem. Phys.* **52** 815–24
Patel J L, Davies J J, Cavenett C, Takeuchi H and Horai K 1976 *J. Phys. C: Solid State Phys.* **9** 129–38
Sanderson R T 1967 *Inorganic Chemistry* (New York: Reinhold)
Takeuchi H 1993 *Research Bulletin, College General Education Nagoya University* B **37** 11–24
Takeuchi H and Arakawa M 1983 *J. Phys. Soc. Japan* **52** 279–83
Takeuchi H, Arakawa M, Aoki H, Yosida T and Horai K 1982 *J. Phys. Soc. Japan* **51** 3166–72
Takeuchi H, Arakawa M and Ebisu H 1991a *J. Phys.: Condens. Matter* **3** 4405–20
Takeuchi H, Ebisu H and Arakawa M 1991b *J. Phys. Soc. Japan* **60** 304–12
Takeuchi H, Horai K and Arakawa M 1979 *J. Phys. Soc. Japan* **46** 18–25
Takeuchi H and Tanaka H 1992 *J. Phys.: Condens. Matter* **4** 10 071–8
Takeuchi H, Tanaka H and Arakawa M 1993 *J. Phys. Soc. Japan* **62** 2518–9