

An electron paramagnetic resonance study of a trigonally symmetric  $\text{Fe}^{3+}$  centre in  $\text{CsMgCl}_3$  single crystal

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2005 J. Phys.: Condens. Matter 17 1375

(<http://iopscience.iop.org/0953-8984/17/8/016>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 20:22

Please note that [terms and conditions apply](#).

# An electron paramagnetic resonance study of a trigonally symmetric $\text{Fe}^{3+}$ centre in $\text{CsMgCl}_3$ single crystal

H Takeuchi<sup>1</sup>, H Tanaka<sup>2</sup>, M Arakawa<sup>3</sup> and H Ebisu<sup>4</sup>

<sup>1</sup> Department of Advanced Science and Technology, Toyota Technological Institute, Nagoya, 468-8511, Japan

<sup>2</sup> Faculty of Science, Tokyo Institute of Technology, Tokyo 152-0033, Japan

<sup>3</sup> Department of Materials Science and Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan

<sup>4</sup> Department of Electrical and Computer Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan

Received 6 December 2004, in final form 25 January 2005

Published 11 February 2005

Online at [stacks.iop.org/JPhysCM/17/1375](http://stacks.iop.org/JPhysCM/17/1375)

## Abstract

EPR measurements have been made on single crystals of  $\text{CsMgCl}_3$  doped with iron. From x-ray irradiated samples, signals from a  $\text{Fe}^{3+}$  centre with trigonal symmetry are observed. Magnitudes of the spin-Hamiltonian parameters have been determined accurately by a direct matrix-diagonalization method. Negative signs of  $b_2^0$  and  $b_4^0$  parameters are determined from the observation of a depopulation effect at 4.2 K. The absolute sign of the  $b_4^3$  parameter is deduced to be negative by the use of spin-Hamiltonian separation analysis. The spectrum has been ascribed to a  $\text{Fe}^{3+}$  ion substituted for a  $\text{Mg}^{2+}$  ion without any charge compensators in its immediate neighbourhood. An empirical rule for the trigonally symmetric  $\text{Fe}^{3+}$  centre is presented; that is, negative and positive signs of  $b_2^0$  come respectively from trigonal elongation or compression of the ligand octahedron along the trigonal axis from the ordinary configuration. It is suggested that the magnitudes of  $|b_2^0|$  for the  $\text{Fe}^{3+}$  centre relative to those of  $|b_2^0|$  for the corresponding  $\text{Cr}^{3+}$  centre in the same matrix crystal are anomalously small in fluorides.

## 1. Introduction

The  $\text{CsNiCl}_3$ -type magnetic compounds have a crystal structure composed of linear chains of magnetic ions along the hexagonal  $c$  axis and triangular lattices in the  $c$  planes. The diamagnetic compound  $\text{CsMgCl}_3$  has this type of crystal structure. Its unit cell is shown in figure 1. The magnetic impurity centres formed in  $\text{CsMgCl}_3$  matrix crystals are considered to be the magnetically diluted systems for the  $\text{CsNiCl}_3$ -type magnetic compounds. Electron paramagnetic resonance (EPR) is useful for the investigation of interactions of magnetic

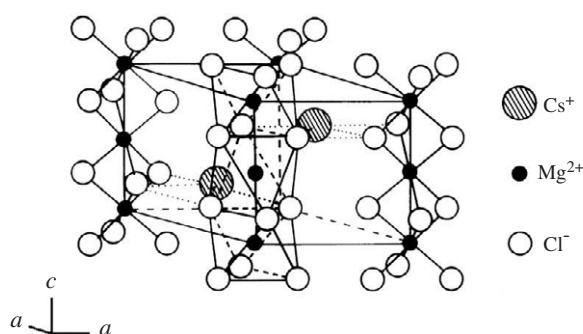


Figure 1. A unit cell of CsMgCl<sub>3</sub> crystal.

impurity ions with surroundings. So far, for transition-metal ions, the magnetic impurity centres of V<sup>2+</sup> [1, 2], Cr<sup>3+</sup> [3–5], Mn<sup>2+</sup> [2] and Ni<sup>2+</sup> [2] formed in CsMgCl<sub>3</sub> have been investigated by means of EPR.

In this paper, we will report results of EPR experiments for CsMgCl<sub>3</sub> crystals doped with iron. EPR signals with trigonal symmetry about the *c* axis were observed after x-ray irradiation for as-grown crystals. The spectrum was ascribed to a substitutional Fe<sup>3+</sup> ion at a Mg<sup>2+</sup> site without any charge compensators in its immediate neighbourhood. The angular variation of the spectrum observed can be described in terms of the spin Hamiltonian having trigonal symmetry with the electron Zeeman parameters  $g_{\parallel}$ ,  $g_{\perp}$  and the fine structure parameters  $b_2^0$ ,  $b_4^0$  and  $b_4^3$ . The magnitudes of the fine structure parameters and relative signs of  $b_2^0$  and  $b_4^0$  will be obtained from angular variation of the spectrum by fitting the spin Hamiltonian on a computer using a direct matrix-diagonalization method. The absolute sign of  $b_2^0$  can be determined by the use of the depopulation effect at low temperature. So, the absolute sign of  $b_4^0$  is also determined uniquely.

In the CsMgCl<sub>3</sub> crystal, two neighbouring MgCl<sub>6</sub> octahedra are connected along the *c* axis, sharing a common triangle face of chlorines. Due to the existence of the fourth-rank fine structure term  $(1/60)b_4^3O_4^3$ , EPR spectra split into two branches corresponding to the substitutional Fe<sup>3+</sup> ions at each Mg<sup>2+</sup> ion of the above two types of MgCl<sub>6</sub> octahedra except for some symmetry directions of the external magnetic field. However, we cannot determine which branch should be assigned to each octahedron. In such a case, the spin Hamiltonian can be fitted to the angular variation of the EPR spectrum, either with positive or negative  $b_4^3$  values having the same magnitudes. So, the relative sign of  $b_4^3$  and  $b_2^0$  cannot be determined. As a result the absolute sign of  $b_4^3$  cannot be obtained just by parameter fitting of the spin Hamiltonian to the spectra.

The spin-Hamiltonian separation method is useful for comparing fine structure parameters among magnetic centres in the same or different matrix crystals. This method was first proposed for identifying several Cr<sup>3+</sup> centres formed in layered perovskite fluorides [6], and was later applied to many Cr<sup>3+</sup> centres in other crystals. Also the method has been developed successfully for the low-symmetry Fe<sup>3+</sup> [7–9] and Gd<sup>3+</sup> centres. We will show in section 4 that the spin-Hamiltonian separation method can be used to deduce the absolute sign of the parameter  $b_4^3$  for the above type of trigonally symmetric Fe<sup>3+</sup> centres. It will be mentioned that the sign of the cubic parameter  $b_{4c}$  obtained from the sign of  $b_4^3$  for the present centre may hold for other Fe<sup>3+</sup> centres in chloride. Then, in contrast, the absolute signs of  $b_2^0$  parameter can be deduced by spin-Hamiltonian separation analysis without knowledge of the depopulation effect once the sign of  $b_{4c}$  is known for chloride.

For the trigonally symmetric Cr<sup>3+</sup> centres, McGarvey [10, 11] suggested on the basis of his theoretical calculation that the anisotropy of the <sup>53</sup>Cr hyperfine parameter ( $A - B$ ) and the sign of  $b_2^0$  parameter are related to the trigonal distortion of the ligand octahedron from the ordinary configuration. He considered that the d-electron distribution is concentrated more along the trigonal axis by compression of the ligand octahedron along the axis. Later, in this respect, Manoogian's group [12–15] examined by means of EPR and ENDOR experiments the relationship between the sign of  $b_2^0$  and the ligand distortion from the ordinary octahedral configuration for the Cr<sup>3+</sup> trigonal centres formed in single crystals of guanidinium aluminium sulfate hexahydrate (GASH), and the Ga alums RbGa(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O and CsGa(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O. Their results indicate that positive  $b_2^0$  corresponds to elongation of the octahedron and negative  $b_2^0$  to compression of the octahedron. This empirical rule holds for the trigonal Cr<sup>3+</sup>-V<sub>K</sub> centre in KZnF<sub>3</sub> as a compression case [16] and for the uncompensated Cr<sup>3+</sup> centre in CsMgCl<sub>3</sub> as an elongation case [3]. It is interesting to clarify whether similar empirical rule connecting the sign of  $b_2^0$  and the octahedral distortion of the ligand octahedron exists for trigonally symmetric Fe<sup>3+</sup> centres. On this basis, we will examine in section 5 the magnitudes of the second-rank axial parameters  $b_2^0$  for the Fe<sup>3+</sup> centres relative to those of  $b_2^0$  for the same type of Cr<sup>3+</sup> centres with trigonal symmetry in the same matrix crystals of fluoride, chloride and oxide.

## 2. Experimental procedures

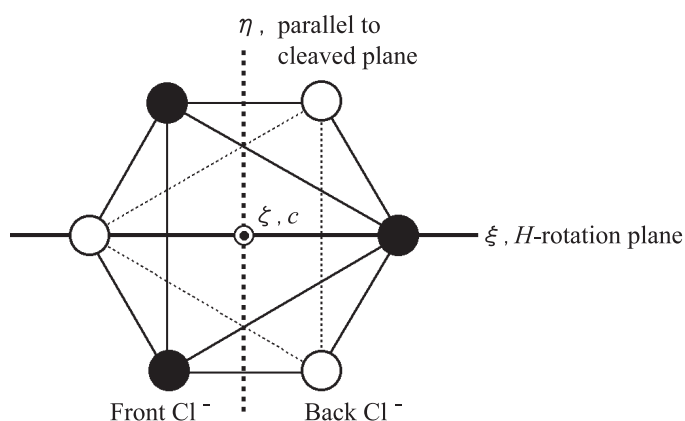
Single crystals of CsMgCl<sub>3</sub> doped with iron with a nominal concentration of 0.1 mol% were grown using the Bridgman technique. Starting mixtures of CsCl, MgCl<sub>2</sub> and FeCl<sub>3</sub> powders were sealed in a quartz tube after dehydration in a vacuum at 200 °C for about 70 h. The quartz crucible was heated to 700 °C to yield liquid mixtures. Then the crucible was pulled down to a temperature region of 500 °C at a rate of about 2.5 mm h<sup>-1</sup>. The crystals obtained were transparent and were cleaved easily.

From the spectra observed for the Cr<sup>3+</sup> centre with monoclinic symmetry in the previous work [3], the cleaved plane of CsMgCl<sub>3</sub> has been confirmed to be parallel to the plane including the  $c$  axis and bisecting some edges connecting chlorines in different layers. That is, the cleaved plane is parallel to the plane not including chlorine ions. The projection of this plane onto the  $c$  plane is shown in figure 2 by a vertical broken line.

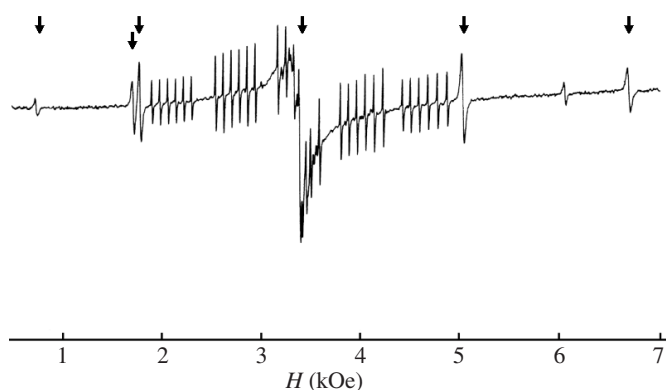
EPR measurements at room temperature were carried out using an X-band spectrometer with 100 kHz field modulation. In the measurements at room temperature, the sample was mounted on a two-axis goniometer MGM-10 (Microdevice) settled in the microwave cavity with a TE<sub>011</sub> mode. The cleaved plane of the sample was pasted on a vertical wall of a two-axis goniometer with the  $c$  axis in the horizontal plane. When the goniometer is rotated about the vertical axis, the direction of the external magnetic field can be changed from the  $c$  axis direction to the direction in the  $c$  plane. Microwave frequencies were measured directly by a frequency counter, R5373 (Advantest). Resonant fields were measured accurately by the proton NMR probe EFM-2000 (Echo Electronics). The magnetic fields measured at the sample position were corrected using the shielding factor determined with DPPH to remove the magnetic shielding effect of a trace of possible magnetic impurity included in the cavity material. The depopulation effect at 4.2 K was observed using an X-band microwave for determination of the sign of  $b_2^0$  at low temperature.

## 3. Results

EPR measurements were carried out first for as-grown crystals of CsMgCl<sub>3</sub> at room temperatures. EPR signals ascribable to any Fe<sup>3+</sup> ions were not observed. Instead some



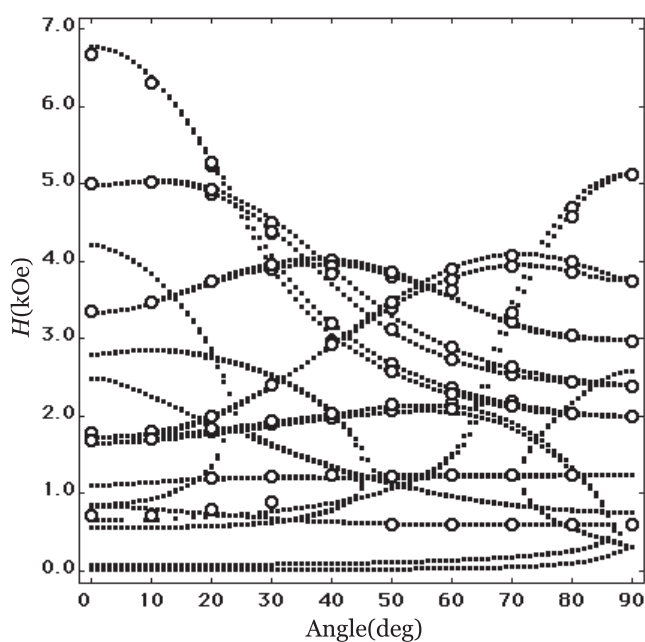
**Figure 2.** Projection of a  $\text{MgCl}_6$  octahedron with  $\text{Mg}^{2+}$  being at  $z = \frac{1}{2}c$  onto the crystalline  $c$  plane. Full circles show the front chlorines at  $z = \frac{3}{4}c$  and open circles show back chlorines at  $z = \frac{1}{4}c$ . If the  $\text{Mg}^{2+}$  ion exists at  $z = 0$  or  $z = c$ , then the open circles denote the front chlorines and full circles the back chlorines. The cleaved planes are parallel to the plane denoted by a vertical broken line. The projection of the  $H$  rotation plane is denoted by a solid line normal to the broken line. The principal  $\xi, \eta, \zeta$  axes system for the spin Hamiltonian is defined on the assumption that the central  $\text{Mg}^{2+}$  ion at  $z = \frac{1}{2}c$  is replaced by a  $\text{Fe}^{3+}$  ion.



**Figure 3.** An EPR spectrum of a  $\text{Fe}^{3+}$  centre in  $\text{CsMgCl}_3$  observed at 300 K with  $H \parallel c$  axis after x-ray irradiation. Signals from  $\text{Fe}^{3+}$  ions are indicated by arrows. The signal near 6 kOe is that from  $\text{Cr}^{3+}$  (centre I) [3]. The signals with hyperfine structure are those from  $\text{Mn}^{2+}$  ions.

EPR signals due to isolated  $\text{Mn}^{2+}$  ions were observed unexpectedly. Then the sample was x-ray irradiated at room temperature in a dark environment for 5 h using a Cu tube operating at 40 kV and 25 mA. Figure 3 shows a recorder trace observed at room temperature with  $H \parallel c$  axis. After x-ray irradiation a group of signals marked with arrows in the figure newly appeared. The signal from the centre I of  $\text{Cr}^{3+}$  [3] is also observed near 6 kOe after x-ray irradiation. The broad signal centred at about 3.4 kOe may be due to aggregation of some magnetic ions.

Figure 4 shows angular variation of resonant fields of this new spectrum measured with the external magnetic field  $H$  in the symmetry plane including the  $c$  axis ( $\zeta$  axis) and  $\xi$  axis shown in figure 2. Signals observed for the spectrum are shown by open circles. When the external field is declined from the  $c$  axis direction toward the  $\xi$  axis direction, each signal



**Figure 4.** Angular variation of the EPR spectrum from a  $\text{Fe}^{3+}$  centre formed in  $\text{CsMgCl}_3$  with  $H$  turned from the  $\zeta$  axis direction ( $0^\circ$ ) toward the direction parallel to the  $\xi$  axis ( $90^\circ$ ). Open circles are signals observed. The dotted curves denote the resonant fields calculated using the parameters listed in table 1.

splits into two branches. The splittings become large in the middle region of the angle. Then, two branches of each pair coincide again in the  $\xi$  axis direction. Moreover, all the resonant fields were constant and showed no splittings at all when the external field was rotated in the  $c$  plane. These facts show that the splittings of the signals do not originate from any canting of main principal axis of the second-rank fine structure terms from the crystalline  $c$  axis since such canting should cause splittings of the signals in the  $\xi$  axis direction and angular variation of resonant fields in the  $c$  plane due to the second-rank fine structure terms. The possibility of the association of any charge compensators lowering the trigonal symmetry about the  $c$  axis is excluded.

The angular variation of the EPR spectra can be explained only by introducing the fourth-rank fine structure term. When the external field is declined from the  $c$  axis toward the  $\xi$  axis direction in the symmetry plane including ligand directions, the fourth-rank fine structure term  $(1/60)b_4^3 O_4^3$  splits the spectra of the present centres having two different ligand directions corresponding to two neighbouring octahedra along the  $c$  axis. It should also be pointed out that the signals do not show any splitting when the external field is declined from the  $c$  axis toward the  $\eta$  axis direction in figure 2. We also confirmed that the spectra observed in the  $\zeta$ - $\eta$  plane show no splittings of the signals. For the trigonal magnetic impurity centre with  $S = \frac{5}{2}$ , the EPR spectrum should have a  $2\pi/3$  period and a  $\pi$  period simultaneously when the external field is rotated in the plane normal to the trigonal axis. As a result, the spectrum becomes constant in the normal plane. It is clear from above features of the spectra that the centre has trigonal symmetry about the crystalline  $c$  axis.

The characteristic angular variation of the spectrum shows that the signals come from a  $\text{Fe}^{3+}$  centre having trigonal symmetry about the crystalline  $c$  axis. All the signals in figure 4

**Table 1.** Spin-Hamiltonian parameters for the  $\text{Fe}^{3+}$  centre observed in  $\text{CsMgCl}_3$  at 300 K. The negative sign of  $b_4^3$  is determined in section 4. Units are in  $10^{-4} \text{ cm}^{-1}$  for  $b_2^0$ ,  $b_4^0$  and  $b_4^3$ .

	$g_{\parallel}$	$g_{\perp}$	$b_2^0$	$b_4^0$	$b_4^3$
$\text{CsMgCl}_3:\text{Fe}^{3+}$	2.0097(2)	2.0103(2)	-796.7(2)	-9.70(5)	-424(5)

are explained by just one kind of trigonal  $\text{Fe}^{3+}$  centre. The spectrum of the  $\text{Fe}^{3+}$  centre can be described by the following spin Hamiltonian with  $S = \frac{5}{2}$ :

$$\mathcal{H} = g_{\parallel}\beta S_{\zeta} H_{\zeta} + g_{\perp}\beta(S_{\xi} H_{\xi} + S_{\eta} H_{\eta}) + \frac{1}{3}b_2^0 O_2^0 + \frac{1}{60}(b_4^0 O_4^0 + b_4^3 O_4^3), \quad (1)$$

where  $g_{\parallel} \equiv g_{\zeta}$ ,  $g_{\perp} \equiv g_{\xi} = g_{\eta}$  and  $O_2^0$ ,  $O_4^0$ ,  $O_4^3$  are the Stevens operators given by Abragam and Bleaney [17]. The Zeeman tensor and the fine structure tensor are described in the common principal  $\xi$ ,  $\eta$ ,  $\zeta$  coordinate system defined in figure 2. The spin Hamiltonian was fitted to the spectra by a direct matrix-diagonalization method on a computer. The resonant fields measured accurately in the directions with  $\mathbf{H}$  parallel to the  $\zeta$  and  $\xi$  axes were used for this fitting. The magnitude of  $b_4^3$  was determined from the resonant fields in the high-field region for the directions with  $\mathbf{H}$  declined by  $80^\circ$  and  $100^\circ$  from the  $\zeta$  axis toward the  $\xi$  axis.

For the determination of the sign of  $b_2^0$ , we observed a depopulation effect using X-band microwaves at the low temperature of 4.2 K. The spectra observed at 4.2 K were similar to the corresponding spectra observed at 300 K. In the first-order approximation of the perturbation theory, the energy levels  $E_M$  for the states with the magnetic quantum number  $M$  are given by the following equations:

$$E_M = g_{\parallel}\beta H M + b_2^0 \left[ M^2 - \frac{35}{12} \right] \quad (\text{for } \mathbf{H} \parallel \zeta), \quad (6)$$

$$E_M = g_{\perp}\beta H M - \frac{1}{2}b_2^0 \left[ M^2 - \frac{35}{12} \right] \quad (\text{for } \mathbf{H} \parallel \xi). \quad (7)$$

For the transitions  $M = \pm\frac{5}{2} \leftrightarrow \pm\frac{3}{2}$  observed at 4.2 K with  $\mathbf{H} \parallel \zeta$  axis, the intensity of the low-field signal relative to that of the corresponding high-field signal increased from that observed at room temperature. On the other hand, for the transitions  $M = \pm\frac{5}{2} \leftrightarrow \pm\frac{3}{2}$  observed at 4.2 K with  $\mathbf{H} \parallel \xi$  axis, the intensity of the low-field signal relative to that of the corresponding high-field signal decreased from that observed at room temperature. These results suggest a negative sign of  $b_2^0$  at 4.2 K, considering the energy levels given in the above equations. It may be reasonable from this negative value of  $b_2^0$  at 4.2 K to suggest that  $b_2^0$  is also negative at room temperature. The sign of  $b_4^0$  relative to that of  $b_2^0$  was found to be positive by the fitting. Thus, both the absolute signs of  $b_2^0$  and  $b_4^0$  are determined to be negative.

The spin-Hamiltonian parameters obtained are listed in table 1. Dotted curves in figure 4 show the theoretical curves calculated using the spin-Hamiltonian parameters listed in table 1. Good agreement of the calculated values with experimental resonant fields is obtained.

It should be emphasized that the sign of  $b_4^3$  relative to that of  $b_2^0$  cannot be determined uniquely by parameter fitting for the present type of trigonally symmetric centre. That is, the spin Hamiltonian can be fitted to the angular variation of the spectrum using either a positive or negative  $b_4^3$  value with the same magnitude independently of the sign of  $b_2^0$ . So, the absolute sign of  $b_4^3$  cannot be determined by parameter fitting. The determination of the absolute sign of  $b_4^3$  is to be settled in the following section, where the  $b_2^0$ ,  $b_4^0$  and  $b_4^3$  parameters will be considered using the spin-Hamiltonian separation method.

**Table 2.** Values of  $b_{2a}$ ,  $b_{4a}$ ,  $b_{4c}$  and  $b_{4a}/b_{2a}$  derived for several Fe<sup>3+</sup> centres. The units are 10<sup>-4</sup> cm<sup>-1</sup> for the separated fine structure parameters. The values for CsMgCl<sub>3</sub>:Fe<sup>3+</sup> are determined by the analysis in section 4.

Matrix	$b_{2a}$	$b_{4a}$	$b_{4c}$	$b_{4a}/b_{2a}$	Symmetry	Distortion
CsMgCl <sub>3</sub>	-796.7	+5.29	+22.49	-0.007	Trigonal	Elongation
KZnF <sub>3</sub>	+103.4	-1.30	+22.80	-0.013	Trigonal [19]	Compression
Rb <sub>2</sub> ZnF <sub>4</sub>	-403.3	+5.4	+24.30	-0.014	Tetragonal [7]	Compression
Rb <sub>2</sub> CdF <sub>4</sub>	-369.3	+7.0	+20.2	-0.019	Tetragonal [9]	Compression
RbCdF <sub>3</sub>	-421.7	+6.0	+19.1	-0.014	Tetragonal [8]	Compression
RbCdF <sub>3</sub>	—	—	+22.3	—	Cubic [20]	Regular
CsCdF <sub>3</sub>	-547.7	+6.5	+18.5	-0.012	Tetragonal [8]	Compression
Al <sub>2</sub> O <sub>3</sub>	+1679	-33.6	+115	-0.020	Trigonal [21]	Compression

#### 4. Analysis

The spin-Hamiltonian separation method is useful for comparing fine structure parameters among magnetic centres in the same or different matrix crystals. Here we show that the spin-Hamiltonian separation can be used to determine the absolute sign of the fine structure parameter  $b_4^3$  for the Fe<sup>3+</sup> centre in CsMgCl<sub>3</sub>.

The fine structure terms in the spin Hamiltonian (1) can be separated into uniaxial components of the second-rank and the fourth-rank tensor operators and the cubic component of the fourth-rank tensor operator as follows [18];

$$\frac{1}{3}b_2^0O_2^0 + \frac{1}{60}(b_4^0O_4^0 + b_4^3O_4^3) = \frac{1}{3}b_{2a}O_2^0 + \frac{1}{60}\left[b_{4a}O_4^0 + b_{4c}\left(-\frac{2}{3}O_4^0 - \frac{40\sqrt{2}}{3}O_4^3\right)\right], \quad (2)$$

where the separated axial parameters  $b_{2a}$ ,  $b_{4a}$  and cubic parameter  $b_{4c}$  are related to the raw parameters  $b_2^0$ ,  $b_4^0$ ,  $b_4^3$  by the equations

$$b_{2a} = b_2^0, \quad b_{4a} = b_4^0 - \frac{1}{20\sqrt{2}}b_4^3, \quad b_{4c} = -\frac{3}{40\sqrt{2}}b_4^3. \quad (3)$$

It may be noted that the cubic parameter  $b_{4c}$  has opposite sign to  $b_4^3$ . The separated fine structure parameters obtained for the Fe<sup>3+</sup> centres formed in cubic and layered perovskite fluorides KZnF<sub>3</sub>, Rb<sub>2</sub>ZnF<sub>4</sub>, Rb<sub>2</sub>CdF<sub>4</sub>, RbCdF<sub>3</sub>, CsCdF<sub>3</sub> and oxide Al<sub>2</sub>O<sub>3</sub> are tabulated in table 2. In the fifth column in table 2, the ratios  $b_{4a}/b_{2a}$  for fluorides and oxide are given. As seen from the table, there is an empirical rule for trigonal and tetragonal Fe<sup>3+</sup> centres in perovskite fluorides that the axial parameters  $b_{2a}$  and  $b_{4a}$  have opposite signs and the ratios  $b_{4a}/b_{2a}$  are almost in the range from -0.01 to -0.02.

As mentioned in the preceding section, the relative sign of  $b_2^0$  and  $b_4^3$  for the present type of trigonal Fe<sup>3+</sup> centre cannot be determined by the parameter fitting of the spin Hamiltonian for the spectrum. We try to determine the absolute sign of the  $b_4^3$  parameter using the above relations by separating the fine structure terms into axial and cubic terms for both the cases of positive and negative  $b_4^3$ . Using the relations in equation (3), we obtain the following results in units of 10<sup>-4</sup> cm<sup>-1</sup>:

$$\text{Case (i) } b_4^3 > 0: b_{2a} = -796.7(5), \quad b_{4a} = -24.69, \quad b_{4c} = -22.49 \quad (4)$$

$$\text{Case (ii) } b_4^3 < 0: b_{2a} = -796.7(5), \quad b_{4a} = +5.29, \quad b_{4c} = +22.49. \quad (5)$$

In the positive  $b_4^3$  case (i), the ratio  $b_{4a}/b_{2a}$  becomes about +0.031, which has opposite sign to those obtained for perovskite fluorides. So, the positive  $b_4^3$  case is not feasible. On the other hand, the value of  $b_{4a}$  ( $=+5.29 \times 10^{-4}$  cm<sup>-1</sup>) for the negative  $b_4^3$  case (ii) is comparable to the



values for perovskite fluorides, and the ratio  $b_{4a}/b_{2a}$  ( $=-0.007$ ) has the same sign as those for perovskite fluorides. From the above analysis, it appears reasonable to consider  $b_4^3 < 0$  for the trigonally symmetric  $\text{Fe}^{3+}$  centre in  $\text{CsMgCl}_3$ . This results in the cubic parameter  $b_{4c}$  being determined to be positive for  $\text{CsMgCl}_3$  as seen in table 2. The  $\text{Mg}^{2+}$  site in  $\text{CsMgCl}_3$  has similar coordination to perovskite fluoride crystals, where the magnetic ion is surrounded octahedrally by six negative monovalent anions. In fact, the  $b_{4c}$  parameter determined for the  $\text{Fe}^{3+}$  centre in  $\text{CsMgCl}_3$  is very close to that for the trigonally symmetric  $\text{Fe}^{3+}-\text{V}_K$  centre in  $\text{KZnF}_3$ .

The  $b_{4c}$  parameters for the fluoride host crystals have values near  $+20 \times 10^{-4} \text{ cm}^{-1}$  in each case with trigonal, tetragonal and cubic symmetry. As the  $b_{4c}$  parameters in the perturbed  $\text{Fe}^{3+}$  centres are considered to deviate only a little from the  $b_{4c}$  value in the cubic  $\text{Fe}^{3+}$  centre, the sign of  $b_{4c}$  may be common among different types of low-symmetry  $\text{Fe}^{3+}$  centres in fluorides. As regards the sign of the  $b_{4c}$  parameter, there exists an empirical rule among the fluoride, chloride and oxide host crystals with sixfold and fourfold coordinations that the signs of the  $b_{4c}$  parameters for  $\text{Gd}^{3+}$  centres are common throughout the kinds of ligand ions and the coordination numbers [22]. It is reported that the covalent spin transfer increases in the series of ligands  $\text{F}^- \rightarrow \text{Cl}^- \rightarrow \text{Br}^- \rightarrow \text{I}^-$  in the same type of crystals [23]. The covalency in  $\text{CsMgCl}_3$  is considered to be close to that in  $\text{Al}_2\text{O}_3$  since the covalent orbital reductions in the isotropic parameter  $A_s$  of the central hyperfine interaction of  $\text{Mn}^{2+}$  centres are almost the same for  $\text{CsMgCl}_3$  and  $\text{Al}_2\text{O}_3$  [2, 24]. As the  $\text{Fe}^{3+}$  centre in the oxide crystal  $\text{Al}_2\text{O}_3$  also has a positive  $b_{4c}$  value, the cubic parameters  $b_{4c}$  of  $\text{Fe}^{3+}$  centres may have a common sign for fluoride, chloride and oxide host crystals. The above result suggests the possibility that the spin-Hamiltonian separation can be used to deduce the absolute sign of  $b_2^0$  without knowledge of the depopulation effect at low temperature if the value of  $b_{4c}$  is known.

## 5. Discussion

In the host crystal of  $\text{CsMgCl}_3$ , the bond angle  $\text{Cl}^- - \text{Mg}^{2+} - \text{Cl}^-$  is reported to be  $85.64^\circ$  with  $\text{Cl}^-$  ions in the same layer [2]. That is, the chlorine octahedron surrounding the central  $\text{Mg}^{2+}$  ion is elongated along the crystalline  $c$  axis from the ordinary octahedral configuration. With respect to the deformation of the anion octahedron, there is an empirical rule for EPR spectra of  $\text{Cr}^{3+}$  trigonal centres that positive and negative  $b_2^0$  values correspond respectively to elongation and compression of the ligand octahedron along the trigonal axis. In the previous work [3], we reported EPR results for the trigonally symmetric  $\text{Cr}^{3+}$  centres (centres I, III, IV) formed in  $\text{CsMgCl}_3$ . The intensity of centre I was enhanced considerably after x-ray irradiation. This indicates that some chromium exists in the  $\text{Cr}^{2+}$  state substituting for  $\text{Mg}^{2+}$  ions and some  $\text{Cr}^{2+}$  ions are changed into  $\text{Cr}^{3+}$  ions by x-ray irradiation. So, centre I is ascribed to a  $\text{Cr}^{3+}$  ion without any charge compensator in its immediate neighbourhood. In view of the positive sign of  $b_2^0$  for this charge-uncompensated centre, the ligand octahedron is considered to be elongated along the  $c$  axis similarly to that of the host crystal. For the as-grown crystal, the spectrum from a  $\text{Cr}^{3+}$  ion associated with a nearest  $\text{Mg}^{2+}$  vacancy on the  $c$  axis (centre III) is also observed. In view of the negative  $b_2^0$  value for the centre III, the ligand octahedron in the centre is considered to be compressed trigonally along the  $c$  axis due to the lack of a nearest  $\text{Mg}^{2+}$  ion.

Similarly to the  $\text{Cr}^{2+}$  ions, iron ions in the as-grown crystal of  $\text{CsMgCl}_3$  may exist in the  $\text{Fe}^{2+}$  state, substituting for  $\text{Mg}^{2+}$  ions, and be changed into  $\text{Fe}^{3+}$  ions by x-ray irradiation. So, the  $\text{Fe}^{3+}$  centre observed may be considered not to be associated with any charge compensators in its immediate neighbourhood. The ionic radii in inorganic crystals are  $0.72 \text{ \AA}$  for  $\text{Mg}^{2+}$ ,  $0.65 \text{ \AA}$  for  $\text{Fe}^{3+}$  and  $0.62 \text{ \AA}$  for  $\text{Cr}^{3+}$  [25]. Since a  $\text{Fe}^{3+}$  ion has an ionic radius very close to that

**Table 3.** Values of  $b_2^0$  parameters for the trigonally symmetric Fe<sup>3+</sup> and Cr<sup>3+</sup> centres in fluoride, chloride and oxide single crystals. The units are in 10<sup>-4</sup> cm<sup>-1</sup> for  $b_2^0$ .

Matrix	$b_2^0(\text{Fe}^{3+})$	$b_2^0(\text{Cr}^{3+})$	$b_2^0(\text{Fe}^{3+})/b_2^0(\text{Cr}^{3+})$	Distortion
KZnF <sub>3</sub> :M <sup>3+</sup> -V <sub>K</sub>	+103.4 [19]	-1613 [16]	-0.06	Compression
CsMgCl <sub>3</sub>	-796.7	+1253.3 [3]	-0.64	Elongation
Al <sub>2</sub> O <sub>3</sub>	+1679 [21]	-1920 [26]	-0.87	Compression

of the Cr<sup>3+</sup> ion, the octahedral configuration surrounding the central Fe<sup>3+</sup> ion is considered to be elongated along the *c* axis.

Here, we compare the  $b_2^0$  values for the same types of Cr<sup>3+</sup> and Fe<sup>3+</sup> centres in the same crystals. The (111)-K<sup>+</sup> vacancies associated with Cr<sup>3+</sup> and Fe<sup>3+</sup> centres formed in KZnF<sub>3</sub> crystals are considered to have trigonally compressed ligand octahedra [16, 19]. The trigonal distortion of the ligand octahedron is confirmed by <sup>19</sup>F ENDOR experiments for six ligands in the Fe<sup>3+</sup> centre, where three ligand F<sup>-</sup> ions forming a regular triangle deviate away from a nearest K<sup>+</sup> vacancy because of the vacancy's effective negative charge relative to the host lattice. Similar ligand distortion by the nearest K<sup>+</sup> vacancy is also confirmed in the previous <sup>19</sup>F ENDOR investigation for the monoclinic Cr<sup>3+</sup> centre formed in the layered perovskite fluoride K<sub>2</sub>MgF<sub>4</sub> crystal [6], which has a lattice constant *a* close to that of KZnF<sub>3</sub>. The K<sup>+</sup> vacancy associated centre in KZnF<sub>3</sub> has an advantage in its formation compared to other types of charge-compensated centres, since the centre is just charge compensated and the vacancy is very close to the central ion. Values of  $b_2^0$  for these centres are listed in table 3. In contrast with  $b_2^0$  having a negative value for the Cr<sup>3+</sup> centre,  $b_2^0$  is positive for the Fe<sup>3+</sup> centre. Another example of a trigonally compressed ligand octahedron is the substitutional centre in Al<sub>2</sub>O<sub>3</sub>. In this host crystal,  $b_2^0 < 0$  for the Cr<sup>3+</sup> centre and  $b_2^0 > 0$  for the Fe<sup>3+</sup> centre. These signs are consistent with those for the (111)-K<sup>+</sup> vacancy associated centres in KZnF<sub>3</sub>. Thus, we notice a rule that Cr<sup>3+</sup> and Fe<sup>3+</sup> ions in the same type of trigonally compressed centres formed in the same crystal may have opposite signs of  $b_2^0$  parameters. In this connection, we expect that Cr<sup>3+</sup> and Fe<sup>3+</sup> ions may have opposite signs of  $b_2^0$  parameters in the cases of trigonally elongated centres. As discussed, ligand octahedra of the uncompensated Cr<sup>3+</sup> and Fe<sup>3+</sup> centres in CsMgCl<sub>3</sub> are considered to be trigonally elongated. The  $b_2^0$  value for the uncompensated Cr<sup>3+</sup> centre in CsMgCl<sub>3</sub> is positive. Thus, the negative value of  $b_2^0$  determined in section 3 for the Fe<sup>3+</sup> centre in CsMgCl<sub>3</sub> by the use of the depopulation effect at low temperature is consistent with the above expectation for the trigonally elongated centre.

Ratios of  $b_2^0$  for the Fe<sup>3+</sup> centre to that for the Cr<sup>3+</sup> centre in the same matrices KZnF<sub>3</sub>, CsMgCl<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> are listed in table 3. It may be seen from this table that there is an empirical rule for the Fe<sup>3+</sup> and Cr<sup>3+</sup> trigonal centres. That is, the  $b_2^0$  parameters for the same type of Fe<sup>3+</sup> and Cr<sup>3+</sup> centres in the same matrix crystal have opposite signs. From the negative value of the  $b_2^0$  parameter for the uncompensated Fe<sup>3+</sup> centre in CsMgCl<sub>3</sub>, the empirical rule is confirmed to hold for the case of the elongated ligand octahedron. The magnitude of the ratio  $b_2^0(\text{Fe}^{3+})/b_2^0(\text{Cr}^{3+})$  for CsMgCl<sub>3</sub> is about 10 times larger than that for KZnF<sub>3</sub>, and rather close to that for Al<sub>2</sub>O<sub>3</sub>. This suggests that the magnitude of  $|b_2^0|$  for the Fe<sup>3+</sup> centre relative to that of  $|b_2^0|$  for the same type of Cr<sup>3+</sup> centre in the same matrix is anomalously small also in other fluorides. This point should be examined for other matrix crystals in the future.

## 6. Conclusion

In iron doped CsMgCl<sub>3</sub> crystal, Fe<sup>2+</sup> ions replace host Mg<sup>2+</sup> ions and are changed to Fe<sup>3+</sup> ions by x-ray irradiation. The EPR spectrum from the Fe<sup>3+</sup> centre has trigonal symmetry

about the crystalline  $c$  axis. From the symmetry the  $\text{Fe}^{3+}$  centre is identified to be the charge-uncompensated centre where a  $\text{Fe}^{3+}$  ion replaces a  $\text{Mg}^{2+}$  ion without any charge compensators in its immediate neighbourhood. The spin-Hamiltonian parameters have been obtained by fitting on a computer except for the absolute signs of the fine structure parameters  $b_2^0$ ,  $b_4^0$  and  $b_4^3$ . The negative sign of  $b_2^0$  is determined by the observation of a depopulation effect at 4.2 K. The sign of the fourth-rank parameter  $b_4^3$  relative to the sign of  $b_2^0$  cannot be determined by parameter fitting in principle for the present type of trigonally symmetric centre. The spin-Hamiltonian separation analysis can be used to deduce the absolute sign of the  $b_4^3$  parameter when the absolute sign of  $b_2^0$  is given. All of the absolute signs of  $b_2^0$ ,  $b_4^0$  and  $b_4^3$  are determined to be negative by the analysis. It is found that the cubic parameter  $b_{4c}$  for the  $\text{Fe}^{3+}$  centres has positive sign in fluorides, chloride and oxide. The spin-Hamiltonian separation may be used to deduce the absolute sign of  $b_2^0$  from the given value of  $b_{4c}$  without knowledge of the depopulation effect at low temperature.

As for the relationship between the axial parameter  $b_2^0$  and the trigonal distortion of ligand octahedron, the empirical rule for EPR spectra of the  $\text{Cr}^{3+}$  centre is extended to the  $\text{Fe}^{3+}$  centre. That is,  $b_2^0$  is positive for  $\text{Fe}^{3+}$  and negative for  $\text{Cr}^{3+}$  in the trigonally compressed ligand configuration and  $b_2^0$  is negative for  $\text{Fe}^{3+}$  and positive for  $\text{Cr}^{3+}$  in the trigonally elongated ligand configuration. It is suggested that the  $|b_2^0|$  values for the  $\text{Fe}^{3+}$  centre relative to those of  $|b_2^0|$  for the corresponding  $\text{Cr}^{3+}$  centre in the same matrix are anomalously small in fluorides.

### Acknowledgments

The authors give appreciative thanks to Dr M Mori for his help with the x-ray irradiation and Mr R Tanizawa for his help and useful discussions on the EPR experiments and analysis.

### References

- [1] Takeuchi H and Tanaka H 1992 *J. Phys.: Condens. Matter* **4** 10071–8
- [2] McPherson G L, Kistenmacher T J and Stucky G D 1970 *J. Chem. Phys.* **52** 815–24
- [3] Takeuchi H, Tanaka H and Arakawa M 1993 *J. Phys.: Condens. Matter* **5** 9205–14
- [4] McPherson G L and Heung W-M 1976 *Solid State Commun.* **19** 53–6
- [5] McPherson G L and Devaney K 1980 *J. Phys. C: Solid State Phys.* **13** 1735–43
- [6] Takeuchi H, Arakawa M, Aoki H, Yosida T and Horai K 1982 *J. Phys. Soc. Japan* **51** 3166–72
- [7] Takeuchi H, Arakawa M and Ebisu H 1991 *J. Phys.: Condens. Matter* **3** 4405–20
- [8] Takeuchi H, Arakawa M and Ebisu H 1987 *J. Phys. Soc. Japan* **56** 3677–82
- [9] Takeuchi H, Ebisu H and Arakawa M 1991 *J. Phys. Soc. Japan* **60** 304–12
- [10] McGarvey B R 1964 *J. Chem. Phys.* **40** 809–12
- [11] McGarvey B R 1964 *J. Chem. Phys.* **41** 3743–58
- [12] Danilov A G and Manoogian A 1972 *Phys. Rev. B* **6** 4097–111
- [13] Danilov A G, Vial J C and Manoogian A 1973 *Phys. Rev. B* **8** 3124–33
- [14] Manoogian A and Leclerc A 1974 *Phys. Rev. B* **10** 1052–8
- [15] Manoogian A and Auger B 1974 *Can. J. Phys.* **52** 1731–8
- [16] Patel J L, Davies J J, Cavenett B C, Takeuchi H and Horai K 1976 *J. Phys. C: Solid State Phys.* **9** 129–38
- [17] Abragam A and Bleaney B 1970 *Electron Paramagnetic Resonance of Transition Ions* (Oxford: Clarendon)
- [18] Takeuchi H, Ebisu H and Arakawa M 1995 *J. Phys.: Condens. Matter* **7** 1417–26
- [19] Krebs J J and Jeck R K 1972 *Phys. Rev. B* **5** 3499–505
- [20] Rousseau J J, Rousseau M and Fayet J C 1976 *Phys. Status Solidi b* **73** 625–31
- [21] Symmons H F and Bogle G S 1962 *Proc. Phys. Soc.* **79** 468–72
- [22] Arakawa M, Aoki H, Takeuchi H, Yosida T and Horai K 1982 *J. Phys. Soc. Japan* **51** 2459–63
- [23] Owen J and Thornley J H M 1966 *Rep. Prog. Phys.* **29** 675–728
- [24] Al'tshuler S A and Kozyrev B M 1974 *Electron Paramagnetic Resonance in Compounds of Transition Elements* (New York: Wiley) p 332
- [25] Shannon R D 1976 *Acta Crystallogr. A* **32** 751–67
- [26] Wenzel R F and Kim Y W 1965 *Phys. Rev. A* **140** 1592–8