

## Mössbauer Observation of the Quantum Levels of $\text{Fe}^{3+}$ Ions Doped in 1D Ising Ferromagnet $\text{Ca}_3\text{Co}_2\text{O}_6$

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We have measured the Mössbauer effect of  $^{57}\text{Fe}^{3+}$  ( $S = 5/2$ ) ions doped in a 1D Ising ferromagnet  $\text{Ca}_3\text{Co}_2\text{O}_6$ . The spectra with hyperfine fields corresponding to the exchange polarized Fe electron spins with  $m_z = \pm 5/2, \pm 3/2, \pm 1/2$  are first observed in the magnetically dense system for  $T \leq 20$  K, suggesting slow magnetic relaxation at the  $\text{Fe}^{3+}$  sites. The key lies in the large difference between magnetic characters of the host (Ising) and impurity (Heisenberg) spins, making the impurity spins extremely isolated in the host 1D Ising spin system. [S0031-9007(97)04334-2]

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Many compounds with the general formula  $A'_3\text{ABO}_6$  ( $A' = \text{Sr}, \text{Ca}, \dots, A = \text{Ni}, \text{Cu}, \text{Zn}, \dots, B = \text{Ir}, \text{Pt}, \dots$ ) have been synthesized, and the magnetic properties have been investigated from the viewpoint of one-dimensional (1D) magnetism [1].  $\text{Ca}_3\text{Co}_2\text{O}_6$  contains chains made of alternating face-sharing  $\text{CoO}_6$  octahedra (Co1) and  $\text{CoO}_6$  trigonal prisms (Co2) [2]. These chains are widely separated from each other by Ca ions. Another feature of the structure is that the chains form a triangular lattice, from which spin frustration effect might be expected if the interchain interaction is antiferromagnetic.

Magnetic properties of  $\text{Ca}_3\text{Co}_2\text{O}_6$  were investigated by Aasland *et al.* [3] and the present authors [4] independently. It was found that the intrachain interaction is ferromagnetic. The compound, moreover, exhibits a ferrimagnetic ordering of the ferromagnetic chains at low temperatures due to the antiferromagnetic interaction between ferromagnetic chains in a triangular net along the  $c$  axis. As is mentioned in Ref. [4], the ferrimagnetic state indicates that the Co ion has Ising spin character. According to neutron diffraction, the moments of the Co ions are suggested to be  $0.08\mu_B$  and  $3.00\mu_B$  for Co1 and Co2, respectively. Together with this fact, our magnetization measurements using an oriented sample [5] strongly indicate that Co1 is nonmagnetic while Co2 is magnetic with a magnetic moment of  $4\mu_B$ .

This study was carried out to elucidate the static and dynamic properties of the magnetically ordered states using Mössbauer spectroscopy for  $\text{Ca}_3(\text{Co}_{0.99}\text{Fe}_{0.01})_2\text{O}_6$ . We have succeeded in observing well-resolved nuclear hyperfine structures corresponding to the electronic levels ( $m_z = \pm 5/2, \pm 3/2, \pm 1/2$ ) of  $^6\text{S}$  ion,  $^{57}\text{Fe}^{3+}$  for  $T \leq 20$  K. This is quite an unusual case: In magnetically dense systems, an individual electron spin changes its  $z$  component at an approximate rate of  $J/\hbar$  ( $J$ : exchange interaction), which is fast enough to make a nuclear spin feel a time averaged effective field. In the present case, however, because the magnetic character of the host (Ising) and the impurity (Heisenberg) spins are considerably different, the

impurity spin is extremely isolated and thus can be treated as an "isolated paramagnetic moment." Another prominent result is that the spectra for  $T \geq 30$  K show an increasing relaxation rate of electronic spins as temperature increases, but it is still slow even at room temperature compared to the time window of the Mössbauer experiment.

The 1%  $^{57}\text{Fe}$ -doped  $\text{Ca}_3\text{Co}_2\text{O}_6$ , i.e.,  $\text{Ca}_3(\text{Co}_{0.99}\text{Fe}_{0.01})_2\text{O}_6$ , was prepared by a citrate sol-gel precursor technique. The detailed procedures have been described in Ref. [3]. Another sample with the same composition was prepared using a conventional solid state reaction [4]. Both samples gave almost the same magnetization curves and Mössbauer spectra, indicating the successful preparation of the samples. From the magnetization measurements on  $\text{Ca}_3(\text{Co}_{0.99}\text{Fe}_{0.01})_2\text{O}_6$  as a function of temperature and magnetic field, it has been concluded that the doping of  $^{57}\text{Fe}$  does not disturb the intrinsic properties of  $\text{Ca}_3\text{Co}_2\text{O}_6$  significantly. Mössbauer spectra were measured on powdered samples in a temperature range  $4.2 \leq T \leq 293$  K with a conventional spectrometer in transmission geometry. A room temperature  $\gamma$ -ray source of  $^{57}\text{Co}$  dissolved in Rh matrix was used. An  $\alpha$ -Fe absorber was used at room temperature to calibrate the Doppler velocity  $V$  and also as the standard for the isomer shift  $IS$ .

The spectra clearly showed that the magnetic relaxation time depends on temperature. The Mössbauer absorption spectra of  $\text{Ca}_3(\text{Co}_{0.99}\text{Fe}_{0.01})_2\text{O}_6$  for  $T \leq 20$  K are shown in Fig. 1. The spectrum at 4.2 K is resolved into two components (components 1 and 2) and the spectra at 8, 13, and 20 K are resolved into three components (components 1, 2, and 3) using a least square fitting program. Lorentzian line shapes with the line width of 0.30 mm/s are assumed. The fitted hyperfine parameters were summarized in Table I. It is noted that the hyperfine field  $H_{\text{hf}}$  points parallel to the  $c$  axis because the Co spins are directed strongly to the Ising spin axis, i.e., the  $c$  axis of the crystal. It appears that the electric field gradient is also directed in the  $z$  direction, which agrees with the principal axis of the crystal

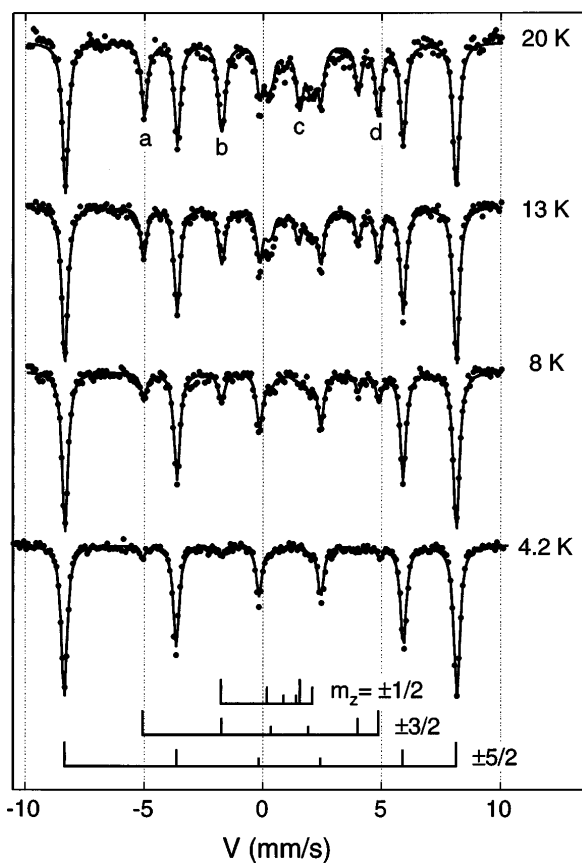


FIG. 1. Mössbauer spectra of  $^{57}\text{Fe}^{3+}$  in  $\text{Ca}_3\text{Co}_2\text{O}_6$  for  $T \leq 20$  K. The theoretical hyperfine structures for the three crystal-field states are shown at the bottom of the figure.

field gradient at a site with the trigonal symmetry. The  $IS$  of 0.52 mm/s and the quadrupole splitting  $QS$  ( $= e^2qQ/2$ ) of  $-1.23$  mm/s are almost identical for components 1–3, where  $eq$  and  $Q$  denote the electric field gradient and the nuclear quadrupole moment, respectively. We can conclude that the Fe ions are distributed at a crystallographically equivalent site, that is, either at the octahedral site (Co1) or the trigonal prism site (Co2). Since  $IS$  of high-spin  $\text{Fe}^{3+}$  compounds lies between 0.2–0.6 mm/s in general, it is reasonable to identify the present case as high-spin  $\text{Fe}^{3+}$ . Considering the large value of  $QS$ , the Fe ion is possibly doped in the trigonal prism site with lower local symmetry.

The most prominent features are that the hyperfine field for each component is independent of temperature and that the ratio of the effective magnetic fields  $H_{\text{hf}}$  is almost 5:3:1 (see Table I). From these facts, it is concluded that components 1–3 correspond to the electronic energy levels of the high-spin  $\text{Fe}^{3+}$  ( ${}^6S$ ), namely,  $m_z = \pm\frac{5}{2}$ ,  $\pm\frac{3}{2}$ , and  $\pm\frac{1}{2}$ , respectively. Such spectra have been observed only for magnetically dilute materials with slow magnetic relaxation, in which the electron spin-electron spin (S-S) interaction is exceedingly small [6–9]. This is the first observation of Mössbauer subspectra corresponding to the

TABLE I. Mössbauer parameters of the high-spin  $\text{Fe}^{3+}$  ions in  $\text{Ca}_3\text{Co}_2\text{O}_6$  for  $T \leq 20$  K.

$T$ (K)	Component	$m_z$	$IS$ (mm/s)	$QS$ (mm/s)	$H_{\text{hf}}$ (kOe)	$I$ (%)
4.2	1	$\pm\frac{5}{2}$	0.52	-1.23	512	92.8
	2	$\pm\frac{3}{2}$	0.52	-1.21	310	7.2
	3	$\pm\frac{1}{2}$	...	...	...	0
8	1	$\pm\frac{5}{2}$	0.52	-1.23	510	80.4
	2	$\pm\frac{3}{2}$	0.53	-1.23	306	14.2
	3	$\pm\frac{1}{2}$	0.45	-1.16	107	5.4
13	1	$\pm\frac{5}{2}$	0.52	-1.24	510	66.8
	2	$\pm\frac{3}{2}$	0.52	-1.25	306	22.1
	3	$\pm\frac{1}{2}$	0.50	-1.29	102	11.1
20	1	$\pm\frac{5}{2}$	0.52	-1.23	509	54.3
	2	$\pm\frac{3}{2}$	0.53	-1.24	305	26.9
	3	$\pm\frac{1}{2}$	0.51	-1.27	103	18.8

quantum levels of  $\text{Fe}^{3+}$  in a magnetic material having long range magnetic order.

In the presence of  $H_{\text{hf}}$  due to the electron spins, the hyperfine Hamiltonian  $\mathcal{H}_{\text{hf}}$  of a nuclear spin  $I$  is expressed

$$\mathcal{H}_{\text{hf}} = S_z A I_z = g_N \mu_N H_{\text{hf}} I_z, \quad (1)$$

where  $S_z$  is the  $z$  component of the electronic spin operator,  $A$  is the hyperfine interaction tensor, and  $I_z$  is the  $z$  component of the nuclear spin operator  $I$ ,  $g_N$  is the nuclear gyromagnetic ratio, and  $\mu_N$  is the nuclear magneton. By electron-nuclear double resonance of  $^{57}\text{Fe}^{3+}$  in MgO [10], the value of  $H_{\text{hf}}$  has been accurately determined,  $H_{\text{hf}} = 220S_z$  kOe. It is widely known that this relation is applicable to other dilute  $\text{Fe}^{3+}$  compounds [6–8]. In the present material, the similar value of  $H_{\text{hf}} = 204S_z$  kOe was obtained. This proportional relationship without any constant term indicates the absence of any transfer hyperfine field. In other words, the hyperfine field originates from the Fermi contact interaction, i.e., the polarization of the  $s$  electrons of Mössbauer atom due to the interaction with the unpaired  $d$  electrons at the same atom. Furthermore, a well-resolved hyperfine structure of  $m_z = \pm\frac{1}{2}$ , which in general corresponds to  $H_{\text{hf}} = 110$  kOe, has not been observed so far by the Mössbauer method, partly because the  $m_z = \pm\frac{1}{2}$  states greatly admix with other states [7,8]. It is remarkable that the spectrum corresponding to  $m_z = \pm\frac{1}{2}$  can be resolved well. See the spectrum at 20 K

in Fig. 1; the line  $c$  arises mainly from  $m_z = \pm\frac{1}{2}$ . One can also confirm the presence of this contribution by comparing the intensity of line  $b$  with that of line  $a$  or line  $d$ .

Hereafter, we consider two extremes: magnetically dilute and dense systems. For the magnetic materials having a high density of magnetic ions, for example metallic iron or  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, where S-S interaction is very large [11],  $S_z$  in Eq. (1) is replaced by  $\langle S_z \rangle$  (the  $z$  component of the *effective* electronic spin) and the value of  $\langle S_z \rangle$  decreases with temperature: In the case of the itinerant electron systems, the magnitude of the moment of spin itself varies with temperature. Even in the case of the localized electron system, owing to the fast S-S relaxation rate compared with the nuclear precession time of a nuclear spin,  $\langle S_z \rangle$  is the thermal average of the  $m_z$  states obeying the mean-field theory.

On the other hand, for the dilute magnetic materials such as a solid solution of 0.08% Fe in corundum [7–9], resolved paramagnetic hyperfine structures of the quantum levels of Fe<sup>3+</sup> ion are observable. The hyperfine field originating from each  $m_z$  state is independent of temperature. The requirement of the observation is that the S-S and electron spin-lattice (phonon) relaxation time of the Mössbauer ion is sufficiently long compared with the precession time of the nuclear spin.

The observation of the hyperfine structures of high-spin Fe<sup>3+</sup> must be attributed to the large difference of magnetic character between the host (Ising) and the impurity (Heisenberg) spins. Theoretical treatment of the localized impurity spin state in antiferromagnets and ferromagnets are given in Ref. [12], and the references therein, in which the localized spin wave mode around the impurity was calculated. Experimentally, Date *et al.* observed the impurity spin resonance for the Ising spin systems such as CoCl<sub>2</sub> · 2H<sub>2</sub>O and FeCl<sub>2</sub> [13]. According to their discussion, the Fe spin with a small anisotropy energy interacts with the neighboring Co spins through relatively weak exchange interactions. On the other hand, since the strongly coupled Co spins are Ising-like, the spin reversal energy or the spin-cluster excitation energy of the host spin system lies much higher than the Fe spin energy so that the impurity spin state can be regarded as an extremely isolated, low-lying localized state for the sake of obeying the energy conservation rule. Thus, one can treat the impurity Fe spin as an “isolated paramagnetic moment” in the ordered host spin system. In this case, the electronic spin levels of Fe<sup>3+</sup> are, to a good approximation, described as the six levels split by the molecular field produced by surrounding Co ions, as discussed later. Consequently, the situation of Ca<sub>3</sub>(Co<sub>0.99</sub>Fe<sub>0.01</sub>)<sub>2</sub>O<sub>6</sub> is similar to the case of the magnetically dilute materials in the sense that energy exchange hardly occurs not only between the Fe spins but also between the Fe and the host spins.

Next, we turn our attention to the relative populations of  $m_z = \pm\frac{5}{2}$ ,  $\pm\frac{3}{2}$ , and  $\pm\frac{1}{2}$  states. The temperature variations of the relative area intensities  $I$  shown in Fig. 2 sug-

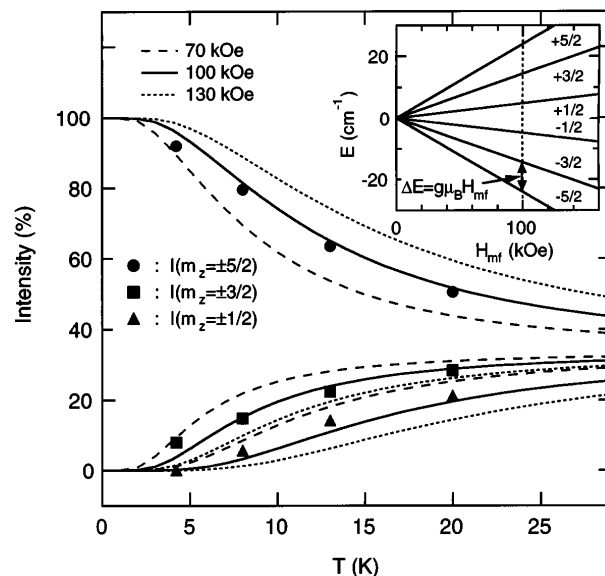


FIG. 2. Temperature dependence of the relative intensities of three components corresponding to  $|m_z| = \frac{5}{2}$ ,  $\frac{3}{2}$ , and  $\frac{1}{2}$ . Calculated intensity ratios are shown for a given  $H_{mf}$ : broken lines,  $H_{mf} = 70$  kOe; solid lines, 100 kOe; dotted lines, 130 kOe. Inset: Electronic levels for high-spin Fe<sup>3+</sup> ( $^6S, L = 0$ ) vs  $H_{mf}$ .

gest that the molecular field  $H_{mf}$  splits the six electronic levels of Fe<sup>3+</sup>, and each  $m_z$  level is populated according to the probability  $p(m_z) = N \exp(-g\mu_B H_{mf} m_z / k_B T)$ , where  $N$  is a normalization constant and  $k_B$  is the Boltzmann constant.  $H_{mf}$  comes from the intra- and interchain exchange interaction and the dipolar interactions between the Fe and the surrounding Co spins. The inset of Fig. 2 shows the Zeeman splitting of the  $m_z$  levels as a function of  $H_{mf}$ . Here, the crystalline field effect is neglected because it is much smaller than the magnetic effect in the present case [8]. For a particular value of  $H_{mf}$ , we calculated the population distribution for each  $m_z$  level, where the  $g$  value is assumed to be 2. As shown in Fig. 2, the best fit is obtained when  $H_{mf} = 100 \pm 10$  kOe, giving the Zeeman splitting of  $g\mu_B H_{mf} = 9.4$  cm<sup>-1</sup>.

The temperature variation of the Mössbauer spectrum measured in the temperature range  $30 \leq T \leq 293$  K is shown in Fig. 3. Resolved hyperfine structures of Fe<sup>3+</sup> were still observed at 30 and 34 K in a paramagnetic region, but these spectra are broadened due to the relaxation of the electronic spins. As the temperature increases, the observed spectrum becomes broader, indicating that the relaxation rate becomes faster. An asymmetry in the spectrum is observed at room temperature, which shows that the relaxation time is still slow within the time window of the Mössbauer method. We emphasize here that such slow relaxation phenomena have not been studied by electron spin resonance.

In order to estimate the characteristic time  $\tau$  of fluctuation of  $H_{hf}$  in the presence of quadrupole interaction, we use the Blume and Tjon Hamiltonian [14]

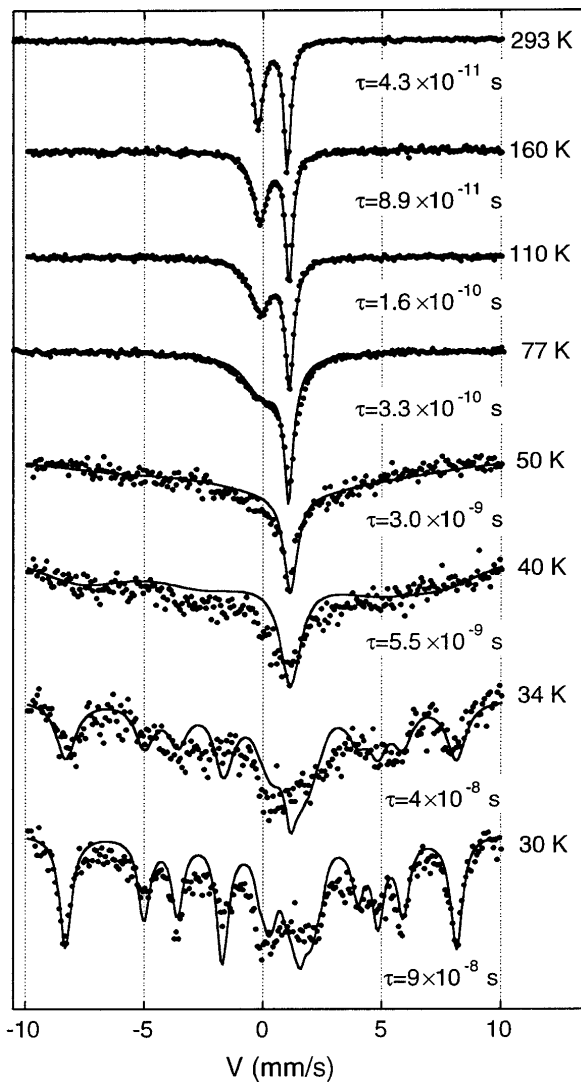


FIG. 3. Mössbauer spectra for  $30 \leq T \leq 293$  K. The solid lines are the computed spectra using Blume's theory [14].

$\mathcal{H}_{\text{hf}} = g_N \mu_N h I_z f(t)$ , which describes the line shape in the presence of a fluctuating magnetic field which jumps at random between the value  $+h$  and  $-h$ , where  $f(t)$  is a random function of time and it takes a value of either  $+1$  or  $-1$ . For 30 and 34 K, the population of the six levels was calculated by assuming the exchange field is the same as that at lower temperatures.  $IS = 0.52$  mm/s and  $QS = -1.23$  mm/s were used as fixed parameters. For the purpose of simplifying the analysis and obtaining an approximate relaxation rate from the line broadening, we assumed that the three components corresponding to  $h_1 = 510$  kOe,  $h_2 = 307$  kOe, and  $h_3 = 103$  kOe relax independently with the same relaxation time  $\tau$ . Note that this model is not ideal because in reality faster relaxation would be expected between the states with  $|\Delta m_z| = \pm 1$  such as  $m_z = \pm \frac{5}{2} \leftrightarrow \pm \frac{3}{2}$  rather than the relaxation with  $|\Delta m_z| > 1$ . For  $T \geq 40$  K, we assumed one component with  $h = 510$  kOe and the temperature independent  $QS$

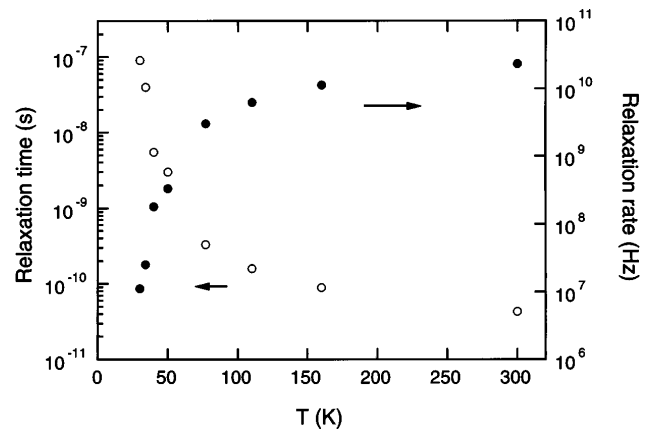


FIG. 4. Temperature dependence of relaxation time and rate of  $\text{Fe}^{3+}$  in  $\text{Ca}_3\text{Co}_2\text{O}_6$ .

of  $-1.23$  mm/s. The best fit spectra are shown by the solid lines in Fig. 3.  $IS = 0.45$  mm/s at 293 K is smaller than 0.50–0.51 mm/s at lower temperatures, which is due to the second order Doppler shift. As shown in Fig. 4, the relaxation time increases exponentially with decreasing temperature. The electron spin-lattice relaxation, in which  $\tau$  increases with temperature, is considered as one of the relaxation mechanisms. It is noted, however, that in the case of 0.08%  $^{57}\text{Fe}$  in corundum, well-resolved hyperfine structures were still observed at 78 K [7]. Thus in the case of  $\text{Ca}_3(\text{Co}_{0.99}\text{Fe}_{0.01})_2\text{O}_6$ , the dynamics of the 1D Ising spin ferromagnetic chain would also cause the present relaxation effect.

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- [1] T.N. Nguyen and H.-C. zur Loye, *J. Solid State Chem.* **117**, 300 (1995).
- [2] H. Fjellvåg *et al.*, *J. Solid State Chem.* **124**, 190 (1996).
- [3] S. Aasland, H. Fjellvåg, and B. Hauback, *Solid State Commun.* **101**, 187 (1997).
- [4] H. Kageyama *et al.*, *J. Phys. Soc. Jpn.* **66**, 1607 (1997).
- [5] H. Kageyama *et al.*, *J. Phys. Soc. Jpn.* (to be published).
- [6] F.E. Obenshain *et al.*, *Phys. Rev. Lett.* **14**, 365 (1965).
- [7] G.K. Wertheim and J.P. Remeika, *Phys. Lett.* **10**, 14 (1964).
- [8] H.H. Wickman and G.K. Wertheim, *Phys. Rev.* **148**, 211 (1966).
- [9] J.W.G. Wignall, *J. Chem. Phys.* **44**, 2462 (1966).
- [10] P.R. Locher and S. Geschwind, *Phys. Rev.* **139**, A991 (1965).
- [11] R.S. Preston, S.S. Hanna, and J. Heberle, *Phys. Rev.* **128**, 2207 (1962).
- [12] H. Ishii, J. Kanamori, and T. Nakamura, *Progr. Theor. Phys.* **33**, 795 (1965).
- [13] M. Date and M. Motokawa, *Phys. Rev. Lett.* **15**, 854 (1965); N. Fujii, M. Motokawa, and M. Date, *J. Phys. Soc. Jpn.* **25**, 700 (1968).
- [14] M. Blume and J.A. Tjon, *Phys. Rev.* **165**, 446 (1968).