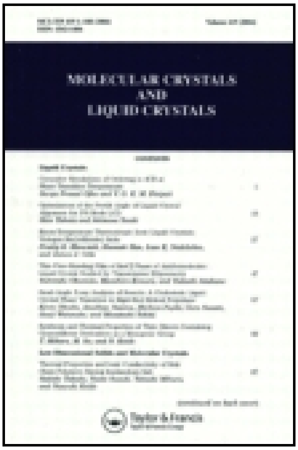

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: Seiichiro Iijima & Fumio Mizutani (1999): Mössbauer Study of the Direction of Spin Alignment in Oxalate-Bridged Metal Assemblies, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 335:1, 143-152

To link to this article: http://dx.doi.org/10.1080/10587259908028858

Mol. Cryst. and Liq. Cryst., 1999, Vol. 335, pp. 143-152
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Mössbauer Study of the Direction of Spin Alignment in Oxalate-Bridged Metal Assemblies

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The direction of spin alignment was investigated for three mixed crystal systems of molecule-based magnets, $NBu_4[Fe(II)_xMn(II)_{1-x}Cr(III)(ox)_3]$ ($x = 0.03–1$), $NBu_4[Mn(II)Fe(III)_xCr(III)_{1-x}(ox)_3]$ ($x = 0.04 – 1$) and $NBu_4[Fe(II)_xNi(II)_{1-x}Fe(III)(ox)_3]$ ($x = 0 – 1$), by using ^{57}Fe Mössbauer spectroscopy, where NBu_4^+ = tetra(*n*-butyl)ammonium ion and ox^{2-} = oxalate ion. With the decrease of x, the direction of the internal magnetic field ($\boldsymbol{H}_n$) at Fe(II) nucleus in $NBu_4[Fe(II)_xMn(II)_{1-x}Cr(III)(ox)_3]$ was changed gradually from parallel to perpendicular, to the honeycomb layers consisting of an alternate array of the bivalent and tervalent ions through ox^{2-} ligands; this indicates that the Mn(II) spin direction in $NBu_4[Mn(II)Cr(III)(ox)_3]$ ($x = 0$) is almost perpendicular to the honeycomb layers. An approximately perpendicular spin alignment was also indicated for the Cr(III) ions in the same compound, from the x-dependence of the Fe(III) spin direction in $NBu_4[Mn(II)Fe(III)_xCr(III)_{1-x}(ox)_3]$. A variation of *ca.* 50° in direction was observed for the $\boldsymbol{H}_n$ at Fe(III) in $NBu_4[Fe(II)_x Ni(II)_{1-x}Fe(III)(ox)_3]$.

Keywords: Mössbauer spectroscopy; oxalates; mixed-metal compounds; spontaneous magnetization; spin direction

INTRODUCTION

In the field of molecule-based magnetism, the oxalate-bridged mixed-metal assemblies $A[M(II)M'(III)(ox)_3]$ have attracted much attention in recent years[1-12], where A^+ = organic cations such as quarternary ammonium and phosphonium ions, and ox^{2-} = oxalate ion. The A[M(II)M'(III)$(ox)_3$] compounds have the same basic structure that is constructed by the honeycomb layers consisting of the alternate array of M(II) and M'(III) ions through ox^{2-} ligands, being separated by the templating counter ions A^+ [9-12], as schematically shown in Fig. 1. One of the most notable features of this class of compounds is that both of bulk ferromagnetic and ferrimagnetic interactions can be produced by choosing properly the M(II)-M'(III) combination[1-4]. For the investigation of the electronic and magnetic structures of iron containing members of A[M(II)M'(III)$(ox)_3$] family, ^{57}Fe Mössbauer spectroscopy has been employed as a powerful tool[13-17]. The angle (Θ) between the internal magnetic field ($\boldsymbol{H}_n$) and the principal axis of V_{zz} at the Mössbauer nucleus is a key parameter for determining the spectral pattern of a magnet[18-21], where V_{zz} is the principal component of the electric

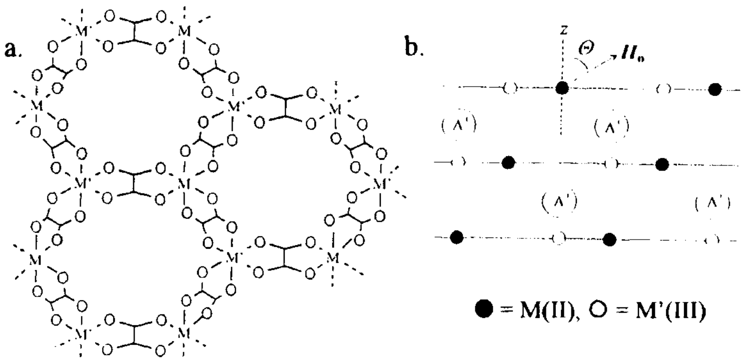

FIGURE 1 (a) Schematic [001] projection of the basal layer in A[M(II)M'(III)$(ox)_3$] and (b) schematic side view of the basal layers (a simplified [110] projection). The principal axis of V_{zz} and the angle Θ are shown for the M(II) site.

field gradient tensor. The principal axis of V_{zz} of iron in both the M(II) and M'(III) sites of A[M(II)M'(III)(ox)$_3$] is rationally thought to coincide with the D_3 axis which goes through the iron atoms and is perpendicular to the basal layers (see Fig. 1b). The previous paper[16] reported spectral pattern differences in Fe(III) absorption between the compounds NBu$_4$[M(II)Fe(III)(ox)$_3$] (M = Mn, Fe, Ni), and the differences suggested a wide variation of the Θ at Fe(III), where NBu$_4^+$ = tetra(*n*-butyl)ammonium ion. In the present study, we have measured ^{57}Fe Mössbauer spectra for NBu$_4$[Fe(II)$_x$Mn(II)$_{1-x}$Cr(III)(ox)$_3$] (x = 0.03 – 1), NBu$_4$[Mn(II)Fe(III)$_x$Cr(III)$_{1-x}$(ox)$_3$] (x = 0.04 – 1) and NBu$_4$[Fe(II)$_x$ Ni(II)$_{1-x}$Fe(III)(ox)$_3$] (x = 0 – 1) from the special interest in the Θ value, which reveals the direction of spin alignment in the crystal lattice of A[M(II)M'(III)(ox)$_3$] system.

EXPERIMENTAL

Compounds NBu$_4$[Fe(II)$_x$Mn(II)$_{1-x}$Cr(III)(ox)$_3$] (x = 0.03, 0.08, 0.15, 0.45) were prepared by adding an aqueous solution (2.5 ml) containing MnCl$_2$ and FeSO$_4$ (total amount of MnCl$_2$ and FeSO$_4$ = 0.5 mmol) to an aqueous solution (5 ml) of K$_3$Cr(ox)$_3$·3H$_2$O (0.5 mmol) containing tetra-*n*-butyl bromide (0.75 mmol). The microcrystals formed were collected by filter suction, washed with water, and dried over P$_4$O$_{10}$. The x values were calculated from the ratios of the content of Mn to that of Fe obtained by atomic absorption analyses. The microanalyses data for C, H and N, the atomic absorption analyses data for Mn and Fe, and the ICP emission anaysis data for Cr were in good agreement with the calculated data using these x values. Enrichments of ^{57}Fe were made for the cases x = 0.03, 0.08 and 0.15; the isotopic abundances of ^{57}Fe were calculated to be 95.1 % for the compounds with x = 0.03 and 0.08, and 17.7 % for that with 0.15.

Compounds $NBu_4[Mn(II)Fe(III)_xCr(III)_{1-x}(ox)_3]$ (x = 0.04, 0.26, 0.46, 0.71, 0.86 and 0.96) were prepared by adding an aqueous solution (3 ml) of $MnCl_2 \cdot 4H_2O$ (2 mmol) to an aqueous solution (10 ml) containing tetra-*n*-butyl bromide (3 mmol), $K_3Fe(ox)_3 \cdot 3H_2O$ and $K_3Cr(ox)_3 \cdot 3H_2O$ (total amount of $K_3Fe(ox)_3 \cdot 3H_2O$ and $K_3Cr(ox)_3 \cdot 3H_2O$ = 2 mmol). The chemical compositions of $NBu_4[Mn(II)Fe(III)_xCr(III)_{1-x}(ox)_3]$ were obtained from the atomic absorption data for Fe, the ICP emission data for Cr and the microanalyses data for C, H and N, similarly to the case of $NBu_4[Fe(II)_xMn(II)_{1-x}Cr(III)(ox)_3]$. Enrichments of ^{57}Fe were made for the cases x = 0.04 and 0.26; the isotopic abundances of ^{57}Fe were calculated to be 48.8 and 9.96 %, respectively.

Compounds $NBu_4[Fe(II)_xNi(II)_{1-x}Fe(III)(ox)_3]$ (x = 0.04, 0.10, 0.22 and 0.49) were prepared by adding an aqueous solution (2 ml) containing $Ni(NO_3)_2$ and $FeSO_4$ (total amount of $MnCl_2$ and $FeSO_4$ = 1.5 mmol) to an aqueous solution (10 ml) of $K_3Cr(ox)_3 \cdot 3H_2O$ (1.5 mmol) containing tetra-*n*-butyl bromide (2.25 mmol). Their chemical compositions were obtained from the atomic absorption data for Ni and Fe, and the microanalyses data for C, H and N.

Mössbauer spectra were measured with an instrument described previously[16]. The hyperfine parameters were obtained by lest-squares fitting to Lorentzian peaks. The isomer shifts are reported relative to metallic iron foil. The temperature accuracy was estimated to be ± 0.5 K.

RESULTS AND DISCUSSION

$NBu_4[Fe(II)Cr(III)(ox)_3]$ is known as a ferromagnet (the Curie temperature, T_c = 12 K)[2]. From the analysis of the Mössbauer line shape of this compound with the ordinary procedure for the cases where the magnetic hyperfine interaction and the quadrupole interaction are comparable[18-20], the

Θ value was estimated to be 90° with η (asymmetry parameter) = 0 and the negative sign of V_{zz}[13,14]. This Θ value means that the $\boldsymbol{H}_n$ at Fe(II) is parallel to the basal honeycomb-like layers.

The Mössbauer spectra of $\mathrm{NBu_4[Fe(II)}_x\mathrm{Mn(II)}_{1-x}\mathrm{Cr(III)(ox)_3]}$ (x = 0.03, 0.08, 0.15, 0.45) measured at 4.2 K were shown in Fig. 2. The compound with x = 0.45 showed virtually an identical spectrum to that of $\mathrm{NBu_4[Fe(II)Cr(III)(ox)_3]}$ (x = 1); the spectrum apparently consisted of a doublet at the lower energy side and a triplet at the higher energy side (Fig. 1a). When x was lowered below 0.45, the spectrum shape began to change gradually (Figs. 2b, c), and at x = 0.03, the spectrum apparently consisted of a doublet at lower energy side and a broad singlet at the higher energy side as shown in Fig. 2d. Although both the change of the sign of V_{zz} and

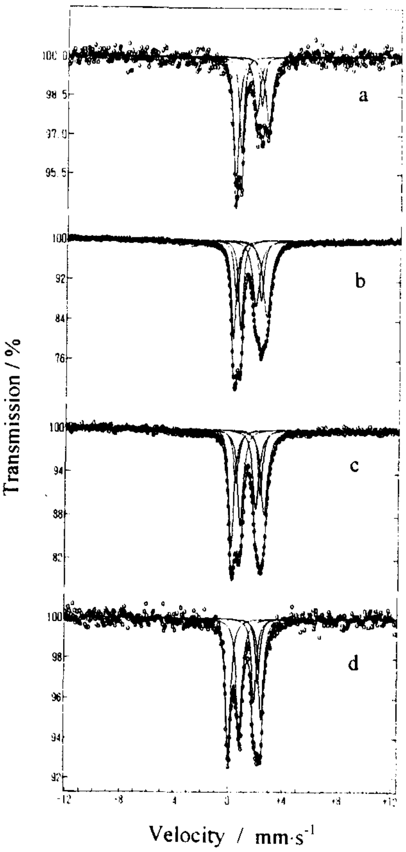

FIGURE 2 Mössbauer spectra at 4.2 K of $\mathrm{NBu_4[Fe(II)}_x\mathrm{Mn(II)}_{1-x}\mathrm{Cr(III)\ (ox)_3]}$ with x = (a) 0.45, (b) 0.15, (c) 0.08 and (d) 0.03.

the decrease of Θ, with decreasing x, can cause such a kind of spectral change, the former possibility was ruled out from the plot of the quadrupole splitting (ΔE_Q), determined just above T_c, against x. If the V_{zz}'s sign was changed from negative to positive with decreasing x, the ΔE_Q should be zero at a certain value of x. The ΔE_Q showed in practice only a slight and monotoniuos decrease by changing x from 1.0 to 0.03 (e.g., ΔE_Q = 1.81 mm/s (12 K) for x = 1 and ΔE_Q = 1.77 mm/s (8K) for x = 0.45 and 0.03). Therefore, the spectral change seen in Fig. 2 is ascribed to the decrease of Θ with decreasing x.

The Θ value of each $NBu_4[Fe(II)_xMn(II)_{1-x}Cr(III)(ox)_3]$ compound was estimated from the peak positions and the relative peak intensities of the Mössbauer absorptions [18-20] using the η value of 0, and was plotted against x in Fig. 3a. This figure shows that the Θ of $NBu_4[Fe(II)_xMn(II)_{1-x}Fe(III)(ox)_3]$ approaches 0° when the x is decreased extremely. This reveals that the direction of alignment of Mn(II) spins in $NBu_4[Mn(II)Cr(III)(ox)_3]$ is almost perpendicular to the basal layers, in accord with the results of a single crystal magnetization study suggesting an easy axis perpendicular to the basal layers for this compound[14].

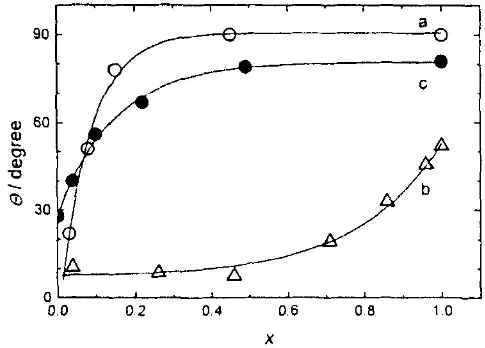

FIGURE 3 The variations Θ of with x for (a) $NBu_4[Fe(II)_xMn(II)_{1-x}Cr(III)(ox)_3]$, (b) $NBu_4[Mn(II)Fe(III)_xCr(III)_{1-x}(ox)_3]$ and (c) $NBu_4[Fe(II)_xNi(II)_{1-x}Fe(III)(ox)_3]$

Recently, it was shown that the neutron diffraction patterns observed for $[P(C_6D_5)_4][Mn(II)Cr(III)(ox)_3]$ ($P(C_6D_5)_4^+$ = tetra(d_5-phenyl)phosphonium ion) correspond to the perpendicular ferromagnetic alignment of Mn(II) and Cr(III) spins, although the calculated magnetic diffraction pattern still shows some deviations[11].

$NBu_4[Mn(II)Fe(III)(ox)_3]$ is known to act as an antiferromagnet with spin canting below the Néel temperature, T_N ~ 27 K[3,4,6]. Each Mössbauer spectrum at 4.2 K measured for the mixed crystals $NBu_4[Mn(II)Fe(III)_xCr(III)_{1-x}(ox)_3]$ consisted of a well-resolved magnetically-split sextet with a small absorption of ferric impurity; the spectra of the compounds with x = 0.04, 0.46 and 0.96 are shown in Fig. 4, as examples. The $S_1 - S_2$ value in the spectrum of $NBu_4[Mn(II)Fe(III)(ox)_3]$ (x = 1) is reported to be almost zero[16], where S_1 and S_2

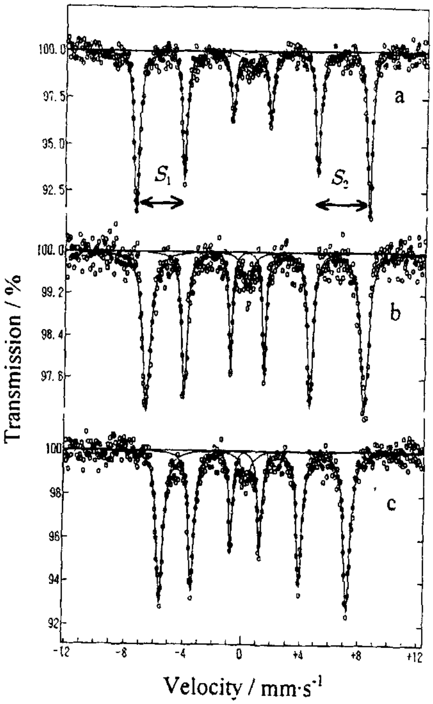

FIGURE 4 Mössbauer spectra at 4.2 K of $NBu_4[Mn(II)Fe(III)_xCr(III)_{1-x}(ox)_3]$ with x = (a) 0.96, (b) 0.46 and (c) 0.04.

represent the interval between the lowest-energy and second lowest-energy peaks, and that between the highest-energy and second highest-energy peaks, respectively (cf. Fig. 4a). The $S_1 - S_2$ became negative (Fig. 4a) on lowering the x, and exhibited a large negative value (~ 1.2 mm/s) at x values below *ca.* 0.5 (Figs. 4b,c). The Θ for the Fe(III) in $\mathrm{NBu_4[Mn(II)Fe(III)}_x\mathrm{Cr(III)}_{1-x}\mathrm{(ox)_3]}$ was obtained by the approximate equation for axial symmetry, $S_1 - S_2 = -(1/2)eV_{zz}Q(3\cos^2\Theta - 1)$, which can be applied to the cases where the magnetic hyperfine interaction is much larger than the quadrupole interaction[21]. ΔE_Q just above the magnetic transition temperature was employed as the value of $|(1/2)eV_{zz}Q|$ for the calculation[5], and the positive sign of V_{zz} was found for the Fe(III) nuclei in all $\mathrm{NBu_4[Mn(II)Fe(III)(ox)_3]}$ compounds[22]. The estimated Θ values were plotted against x in Figs. 3b. On lowering the x from 1, the Θ decresed rapidly first, and then it approached a constant value close to zero. This figure indicates that the Cr(III) spins in $\mathrm{NBu_4[Mn(II)Fe(III)(ox)_3]}$, as well as the Mn(II) spins in the same compound, are aligned along an axis almost perpedicular to the basal planes, as expected. An interesting difference was, however, observed in the the Θ - x profile between the Fe(II) in $\mathrm{NBu_4[Fe(II)}_x\mathrm{Mn(II)}_{1-x}\mathrm{Cr(III)(ox)_3]}$ and the Fe(III) in $\mathrm{NBu_4[Mn(II)Fe(III)}_x\mathrm{Cr(III)}_{1-x}\mathrm{(ox)_3]}$. It seems that the single ion magnetic anisotropy of high-spin Fe(II)[6,17] governs the Θ - x profile of the former Fe(II).

It is known that $\mathrm{NBu_4[Ni(II)Fe(III)(ox)_3]}$ and $\mathrm{NBu_4[Fe(II)Fe(III)(ox)_3]}$ act as ferrimagnets (T_N = 28 and 43 K, respectively) [3,4]. The Mössbauer spectra measured at 4.2 K for the mixed crystals $\mathrm{NBu_4[Fe(II)}_x\mathrm{Ni(II)}_{1-x}\mathrm{Fe(III)(ox)_3]}$ consisted of a superposition of magnetically-split Fe(II) and Fe(III) absorptions (data not shown). The Fe(III) component was a well-resolved sextet similar to the spectra of $\mathrm{NBu_4[Mn(II)Fe(III)}_x\mathrm{Cr(III)}_{1-x}\mathrm{(ox)_3]}$, and the Θ value of Fe(III) in each $NBu_4[Fe(II)_xNi(II)_{1-x}Fe(III)(ox)_3]$ compound was estimated from the $S_1 - S_2$ value[21]. The positive sign of V_{zz} at Fe(III) was determined for all $NBu_4[Fe(II)_xNi(II)_{1-x}Fe(III)(ox)_3]$ compounds from the investigation of their ΔE_Q values at temperatures just above T_N[16,22]. A variation of *ca.* 50° was observed for Θ in these mixed crystals, as shown in Fig. 3c. The Θ of Fe(III) in $NBu_4[Fe(II)_xNi(II)_{1-x}Fe(III)(ox)_3]$ begins to decrease rapidly when the x comes to fairly small values; the single ion magnetic anisotropy of high-spin Fe(II) is ascribable to the Θ - x profile (Fig. 3c), similarly to the case of the Fe(II) in $NBu_4[Fe(II)_xMn(II)_{1-x}Cr(III)(ox)_3]$. Only slight decreases in the magnitude of $\boldsymbol{H}_n$ (H_n) on lowering x were observed for the Fe(II) in $NBu_4[Fe(II)_xMn(II)_{1-x}Cr(III)(ox)_3]$ (H_n = 38 kOe for x = 1 and 27 kOe for x = 0.03) and for the Fe(III) in $NBu_4[Fe(II)_xNi(II)_{1-x}Fe(III)(ox)_3]$ (H_n = 537 kOe for x = 1 and H_n = 509 kOe for x = 0), while the H_n at Fe(III) in $NBu_4[Mn(II)Fe(III)_xCr(III)_{1-x}(ox)_3]$ exhibited a relatively large change with x (H_n = 502 kOe for x = 1 and H_n = 400 kOe for x = 0.04).

The above results clearly demonstrate that the direction of spin alignment or the easy axis of magnetization in $A[M(II)M'(III)(ox)_3]$ system can be controlled freely by the method of mixed crystallization. In addition to the reported control of the mode of magnetic interactions (ferromagnetism, ferrimagnetism, etc.) in the same system[1-4], this observation of the "fine tuning" of magnetic structure would stimulate the researches of molecule-based magnetic materials for practical applications such as electronic devices.

References

[1] Z.J. Zhong, N. Matsumoto, H. Okawa and S. Kida, *Chem. Lett.*, **87**,(1990).

[2] H. Tamaki, Z.J. Zhong, N. Matsumoto, S. Kida, M. Koikawa, N. Achiwa, Y. Hashimoto and H. Okawa, *J. Am. Chem. Soc.*, **114,** 6974 (1992).

[3] H. Tamaki, M. Mitsumi, K. Nakamura, N. Matsumoto, S. Kida, H. Okawa and S. Iijima. *Chem. Lett.*, 1975 (1992).

[4] H. Okawa, N. Matsumoto, H. Tamaki and M. Ohba, *Mol. Cryst. Liq. Cryst.*, **233,** 257 (1993).

[5] C. Mathonière, S.G. Carling, D. Yusheng and P. Day, *J. Chem. Soc., Chem. Commun.*, 1551 (1994).

[6] C. Mathonière, C.J. Nuttall, S.G. Carling and P. Day, *Inorg. Chem.*, **35,** 1201 (1996).

[7] A. Bhattacharjee, S. Iijima, F. Mizutani, H. Hayakawa, M. Hagiwara and K. Katsumata, *Mol. Cryst. Liq. Cryst.*, **286,**141 (1996).

[8] E.I. Zhilyaeva, O.A. Bogdanova, R.N. Lyubovskaya, N.S. Ovanesyan, S.I. Pirumova and O.S. Roshchupkina, *Synth. Metals,* **85,**1663 (1997).

[9] L.O. Atovmyan, G.V. Shilov, R.N. Lyubovskaya, E.I. Zhilyaeva, N. S. Ovanesyan, S.I. Pirumova, I.G. Gusakovskaya and Yu.G. Morozov, *JETP Lett.*, **58,**766 (1993).

[10] S. Decurtins, H.W. Schmalle, H.R. Oswald, A. Linden, J. Ensling, P. Gütlich and A. Hauser, *Inorg. Chim. Acta,* **216,** 65 (1994).

[11] R. Pellaux, H.W. Schmalle, R. Huber, P. Fisher, T. Hauss, B. Ouladdiaf and S. Decurtins, *Inorg. Chem.*, **36,** 2301 (1997).

[12] M. Clemente-León, E. Coronado, J.-R. Galán-Mascarós and C.J. Gómez-García, *Chem. Commun.*,1727 (1998).

[13] S. Iijima, T. Katsura, H. Tamaki, M. Mitsumi, N. Matsumoto and H. Okawa, *Mol. Cryst. Liq. Cryst.*, **233,** 263 (1993).

[14] N.S. Ovanesyan, G.V. Shilov, L.O. Atovmyan, R.N. Lyubovskaya, A.A. Pyalling and Yu.G. Morozov, *Mol. Cryst. Liq. Cryst.*, **273,**175 (1995).

[15] W.M. Reiff, J. Kreisz, L. Meda and R.U. Kirss, *Mol. Cryst. Liq. Cryst.*, **273,** 181 (1995).

[16] S. Iijima, F. Mizutani, M. Mitsumi, N. Matsumoto and H. Okawa, *Inorg. Chim. Acta,* **253,** 47 (1996).

[17] S. Iijima and F. Mizutani, *Mol. Cryst. Liq. Cryst.*, **306,** 227 (1997).

[18] R.L. Collins, *J. Chem. Phys.*, **42,** 1072 (1965).

[19] S.V. Karyagin, *Sov. Phys. Solid State,* **8,** 391 (1966).

[20] W. Kündig, *Nucl. Instrum. Methods,* **48,** 219 (1967).

[21] W.M. Reiff, *Coord. Chem. Rev.*, **10,** 37 (1973).

[22] S. Iijima and F. Mizutani, unpublished results.