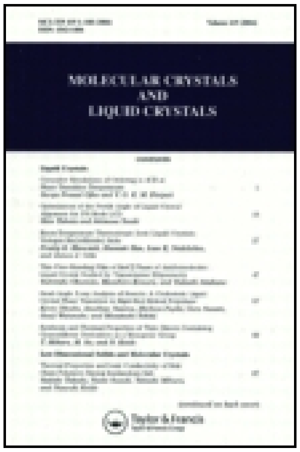

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Effect of Random Disorder on the Antiferromagnetism of Halogen-Doped $Al_{1-Y}Ga_YPcf$

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EFFECT OF RANDOM DISORDER ON THE ANTIFERROMAGNETISM OF HALOGEN-DOPED $Al_{1-y}Ga_yPcF$

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Abstract Crystal structure and magnetism of bromine-doped mixed crystals of fluoro-aluminum (AlPcF) and fluoro-gallium (GaPcF) phthalocyanines, i.e. $Al_{1-y}Ga_yPcF\text{-}Br_x$ with y=0, 0.2, 0.3, 0.5, 1 and $x\sim1$ are studied. A tetragonal phase is observed for y=0, 0.2 and 0.3 but not for y=0.5 and 1. In the tetragonal phase, the phthalocyanine(Pc) rings are cofacially stacked to form a one dimensional chain. With y=0, the mean inter-ring distance in the Pc chain is 3.56 Å. With y=0.2 and 0.3, on the other hand, the mean inter-ring distance is 3.59 Å and 3.60 Å, respectively, and no individual reflections of AlPcF-Br_x and GaPcF-Br_x are observed, which indicates that the GaPcF is randomly mixed into the AlPcF arrays. By the random incorporation of the GaPcF, a random disorder in the inter-ring distance along the Pc chain is induced. For y=0, 0.2 and 0.3, an antiferromagnetic transition occurs in the tetragonal phase at $T\sim100$ K, with no substantial y-dependence of the transition temperature. Thus, the random disorder induced by the GaPcF mixing does not affect the magnetic transition temperature.

INTRODUCTION

Halogen-doped AlPcF is known to exhibit an antiferromagnetic transition at 80 K in the case of powder[1,2] and 200 K in the case of thin film[3], the high T_c being the characteristic feature of this antiferromagnetism. The spins responsible for the magnetism reside on the phthalocyanine(Pc) chains and are localized. In its crystal structure, a large disorder (disorder I) exists along the chain direction c : The c coordinates of the Pc rings distribute around their average positions by ca. ±1 Å. Still unknown, however, are detailed features of the disorder and the relationship between the disorder and the magnetic ordering.

In the present study, another structural disorder (disorder II) is induced by mixing GaPcF into the AlPcF chain : The ring-to-ring distance along the chain is disturbed by the GaPcF mixing because the undoped GaPcF has a 0.15 Å-longer ring-to-ring distance than the undoped AlPcF.[4,5] It will be shown how the crystal structure and the magnetism of the halogen-doped AlPcF are affected by the GaPcF mixing, and discussed will be the relation between the disorder I and II.

EXPERIMENTAL

AlPcF and GaPcF were synthesized by literature procedures[6,7] and were purified by subliming twice at 490°C in a vacuum of 10^{-4} torr. The purified materials were weighed in the desired proportions, and the mixture of them was sublimed twice to obtain $Al_{1-y}Ga_yPcF$ powder.

Bromination of the $Al_{1-y}Ga_yPcF$ powder was done as described previously[2] : The $Al_{1-y}Ga_yPcF$ was reacted with Br_2 gas in a vacuum line, and then a portion of the reacted bromine was removed by pumping the $Al_{1-y}Ga_yPcF\text{-}Br_x$ powder. The cycle of the reaction and the removal processes was repeated 4 times. The temperature of the sample and the durations of the reaction and the removal processes were determined so as to get the doping level x close to unity. For example, in the case of y=0.2, the temperature was 35°C and the durations were 3 min for the reaction and 90 min for the removal, while, in the case of y=0.5, the temperature was 55°C and the durations were 3 min for the reaction and 45 min for the removal. Iodine doping of the $Al_{1-y}Ga_yPcF$ powder was done by the procedure reported previously.[1]

Powder x-ray diffraction measurement was done on a JEOL DX-GE-E apparatus using Ni-filtered Cu-K_α radiation. Electron Paramagnetic Resonance (EPR) measurement was done on a home-made K-band (24 GHz) apparatus with a TE_{111} cylindrical cavity employing a 100-kHz field modulation of 0.2 G. The static susceptibility measurement was done by the Faraday method using a Cahn 2000 Electro-Balance system. The details of the x-ray diffraction, the EPR and the static susceptibility measurements have been described elsewhere.[1] All the measurements at variable temperature were made by increasing the temperature from 4.2 K.

RESULTS

X-ray Diffraction

The powder x-ray diffraction measurement for the ***non-doped*** $Al_{0.7}Ga_{0.3}PcF$ indicates that the Pc rings form cofacially stacked one dimensional chains similar to those of the AlPcF [4] and the GaPcF.[5] The inter-ring distance along the chain is 3.78 Å which is intermediate between the distances of 3.72 Å for the AlPcF [4] and 3.87 Å for the GaPcF.[5] Neither of the AlPcF- and the GaPcF-reflections are observed. These results indicate that the GaPcF is mixed randomly into the AlPcF chains when sublimed together, in agreement with other group's report.[8]

The powder x-ray diffraction patterns of the ***brominated*** $Al_{1-y}Ga_yPcF$ are shown in Fig.1 for several values of y. The pattern A in Fig.1 is for $AlPcF\text{-}Br_{0.89}$. It is found by the analysis of the pattern A that the crystal lattice is tetragonal with a=13.85 Å and c=7.13 Å and that the cofacially stacked Pc rings form one-dimensional chains laying parallel to the c axis.[2] The inter-ring distance along the Pc chain is 3.56 Å and the interchain distance is 13.85 Å. The bromine atoms also form one-dimensional chains laying parallel to the c axis. As reported previously,[2] it is this tetragonal phase (tetragonal I phase) that shows an antiferromagnetic transition at 80 K.

The patterns B and C in Fig.1 are for $Al_{0.8}Ga_{0.2}PcF\text{-}Br_{1.31}$ and $Al_{0.7}Ga_{0.3}PcF\text{-}Br_{1.13}$, respectively. Since these patterns resemble to the pattern A, these samples are isostructural with the $AlPcF\text{-}Br_{0.89}$. Thus the tetragonal I phase is formed as long

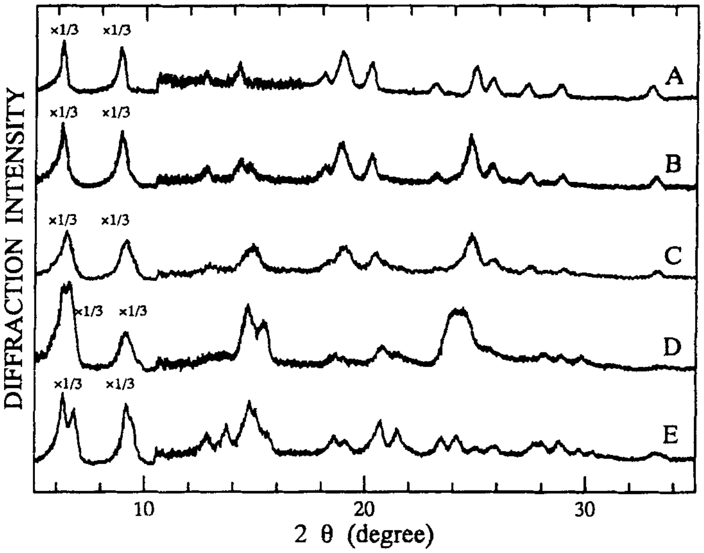

FIGURE 1 X-ray diffraction patterns of $Al_{1-y}Ga_yPcF\text{-}Br_x$ powder at room temperature. A : y=0, x=0.89 ; B : y=0.2, x=1.31 ; C : y=0.3, x=1.13 ; D : y=0.5, x=1.09 ; E : y=1, x=1.18.

as $y \lesssim 0.3$. The lattice parameters are a=13.85 Å and c=7.18 Å for B and a=13.82 Å and c=7.20 Å for C. This indicates that the mean inter-ring distance increases from 3.56 Å to 3.59 Å and 3.60 Å by the GaPcF mixing of y=0.2 and 0.3, respectively. No individual reflections from $AlPcF\text{-}Br_x$ or $GaPcF\text{-}Br_x$ are observed because of the formation of the copolymer of these two. The pattern C is significantly broader than the pattern A, which indicates that the crystallite size of the tetragonal I phase in C is smaller. The crystallite size for C is roughly estimated to be in the order of 300 Å using the Scherrer equation.[9]

The patterns D and E are for $Al_{0.5}Ga_{0.5}PcF\text{-}Br_{1.09}$ and $GaPcF\text{-}Br_{1.18}$, respectively. It is seen that these are totally different from the patterns A - C so that the tetragonal I phase does not exist in these samples. The absence of the tetragonal I phase may be attributed to the too large inter-ring distance along the chain compared with the Br-Br interatomic distance in the neighboring bromine chain, because in the tetragonal I phase the mean inter-ring distance should nearly fit to the mean Br-Br distance.[2] It has been reported by Nohr et al.[10] that the doped state of the halogen is different between $AlPcF\text{-}I_x$ and $GaPcF\text{-}I_x$ for the doping level of $x \lesssim 1$, which may also be due to the difference in the inter-ring distance of the AlPcF and the GaPcF.

In the case of *iodine* doping of the $Al_{1-y}Ga_yPcF$, the tetragonal I phase is not formed for $y \geq 0.2$. Since our main interest is in the tetragonal I phase, the iodine-doped case was not studied in depth.

EPR

Figure 2 shows the room-temperature K-band EPR spectra of the $Al_{1-y}Ga_yPcF\text{-}Br_x$ powders. The spectra A and B are for the samples with y=0 and 0.2, respectively. As

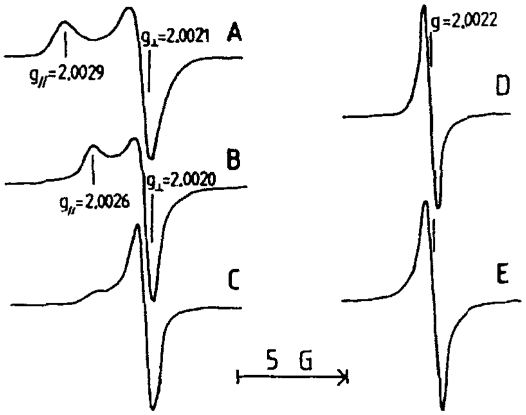

FIGURE 2 24GHz EPR spectra of $Al_{1-y}Ga_yPcF\text{-}Br_x$ powder at room temperature. A : y=0, x=0.89 ; B : y=0.2, x=1.00 ; C : y=0.3, x=1.03 ; D : y=0.5, x=1.09 ; E : y=1, x=1.18.

is seen in Fig.2, these two spectra have similar g-anisotropy of $g_{\parallel}$=2.0029±0.0002 and $g_{\perp}$=2.0021±0.0002 for A and $g_{\parallel}$=2.0026±0.0002 and $g_{\perp}$=2.0020±0.0002 for B. The spectrum C is for the sample with y=0.3. This spectrum has a shoulder at g=2.0026 region indicating that the spectrum C consists of the g-anisotropic component similar to A and B and of another component located at $g\sim$2.0022. The spectra D and E, on the other hand, are for the samples with y=0.5 and 1, respectively. These spectra have only a sharp line at g=2.0022±0.0002 and do not have the g-anisotropic component observed in A - C.

In our previous study,[1,2] the g-anisotropic signal for y=0 has been assigned to the tetragonal I phase whose x-ray diffraction pattern is shown in Fig.1A. The anisotropic signals observed for y=0.2 and 0.3 in Fig.2 are also ascribed to the tetragonal I phase because their g-values are close to those of the y=0 signal. In fact, the present x-ray diffraction study showed that the samples with y=0, 0.2 and 0.3 have the tetragonal I phase.

Figure 3 shows temperature dependence of the integrated EPR intensity of the $Al_{1-y}Ga_yPcF\text{-}Br_x$ powder. In the case of y=0, no EPR signal is detected between 4.2 K and 150 K and at around 150 K an EPR signal appears and its intensity increases as temperature increases to 220 K. As has been shown previously,[2] the quenching of the EPR intensity at $T < 150$ K occurs because of the antiferromagnetic transition at 80 K in the tetragonal I phase. In Fig.3, the effect of the antiferromagnetic transition can be seen up to 220 K indicating that the magnetic transition temperature distributes to a wide temperature region, which is ascribed to a large structural disorder (disorder I)[1,2] existing even with y=0. In the cases of y=0.2 and 0.3, a similar increase in the EPR intensity is seen in Fig.3 between 160 and 220 K, which indicates that the antiferromagnetic transition occurs also in these cases. Furthermore the transition temperature of these two cases is in the same temperature region as for the y=0 case, so that the T_N should be at around 100 K. In the cases of y=0.5 and 1, on the other hand, no anomaly is seen in the temperature dependence of the

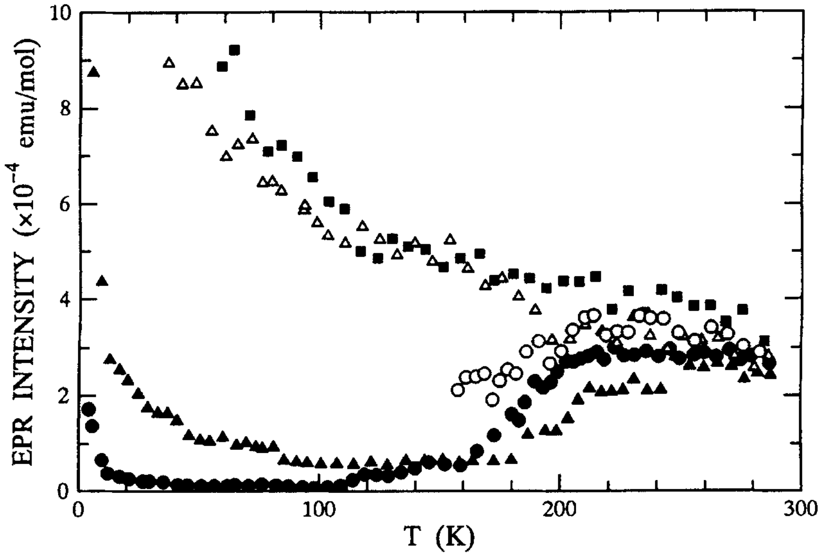

FIGURE 3 Temperature dependence of the integrated EPR intensity of $Al_{1-y}Ga_yPcF\text{-}Br_x$ powder. ○ : $y=0$, $x=0.89$; ● : $y=0.2$, $x=1.00$; ▲ : $y=0.3$, $x=1.03$; △ : $y=0.5$, $x=1.09$; ■ : $y=1$, $x=1.18$. The EPR intensity is shown in the unit of the magnetic susceptibility, emu/mol.

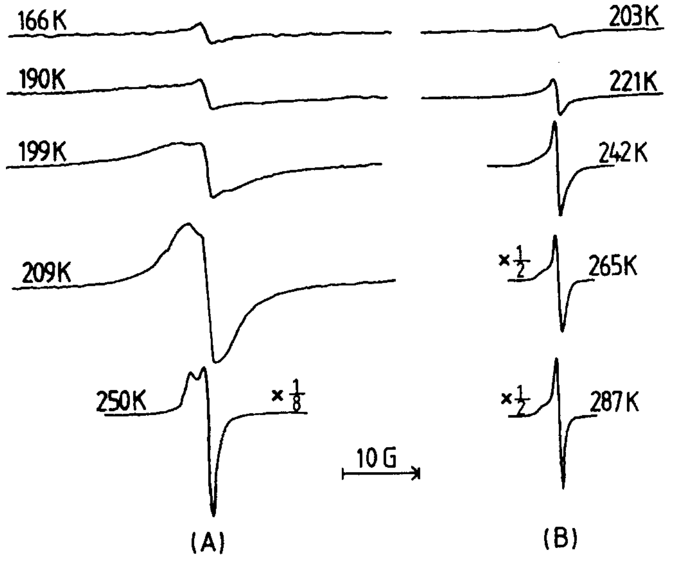

FIGURE 4 Temperature dependence of the EPR lineshape of $Al_{1-y}Ga_yPcF\text{-}Br_x$ powder. (A) $y=0.2$, $x=1.00$; (B) $y=0.3$, $x=1.03$.

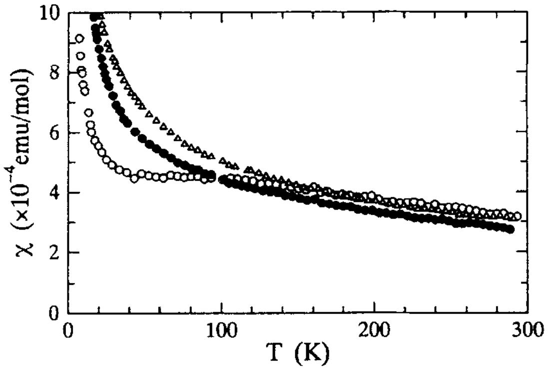

FIGURE 5 Temperature dependence of the static susceptibility χ of $Al_{1-y}Ga_yPcF\text{-}Br_x$ powder measured by the Faraday method. ○ : y=0, x=0.89 ; ● : y=0.2, x=1.00 ; △ : y=0.5, x=1.09.

EPR intensity, so that no magnetic transition occurs in these cases. This result is consistent with the present x-ray diffraction results since the y=0.5 and 1 samples do not contain the tetragonal I phase which is responsible for the antiferromagnetic transition.

The temperature dependence of the EPR line shape is shown in Fig.4 in the cases of y=0.2 and 0.3. For y=0.2, a weak single line is observed at 166 K which originates from an impurity spins rather than the g-anisotropic spins in the tetragonal I phase. At 190 K, a weak broad signal appears, and this signal becomes sharper and stronger as temperature increases, and finally at 250 K, the g-anisotropic signal similar to Fig.2B is observed. A similar anomaly, although less clear because of an overlap of the large impurity signal at g=2.0022, is also seen in the case of y=0.3 : At 203 K, no shoulder corresponding to the $g_{\parallel}$ component of the tetragonal I phase is seen. At T = 242 K, the shoulder appears and, as temperature increases, the intensity of the shoulder increases. Thus, both in the cases of y = 0.2 and 0.3, the anomalous temperature dependence of the line width and the intensity is observed for the g-anisotropic component. This anomalous behavior is characteristic[1,2] of the antiferromagnetic transition in the tetragonal I phase.

Static Susceptibility

Figure 5 shows the temperature dependence of the static susceptibility χ measured by the Faraday method for y=0, 0.2 and 0.5. The χ for y=0 shows a broad maximum at around 100 K corresponding to the antiferromagnetic transition,[2] and at $T < 20$ K, the χ increases because of the impurity spins. In the case of y=0.2, however, no anomaly due to the antiferromagnetic transition is seen in Fig.5, which is interpreted as due to the overlap of the large Curie-Weiss susceptibility of the impurity spins. Most of the impurity spins detected by the static susceptibility measurement for y=0 and 0.2 are not detected by EPR at least at $T \leq T_N$, which can be seen by the comparison of Figs.3 and 5. This may be due to the large local field fluctuation at the sites of the impurity spins caused by the magnetic ordering in the tetragonal I phase. At y=0.5, the temperature dependence of χ agrees with that of the EPR

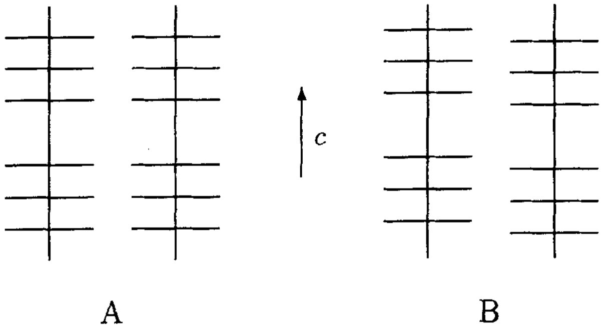

FIGURE 6 Two models for the structural disorder I. A: Short range correlation between the c-coordinates of the Pc rings is maintained along the direction perpendicular to the c axis. B: The correlation is destroyed.

intensity shown in Fig.3, which is as expected since no magnetic transition occurs in this case.

DISCUSSION

Our main interest is in the relation between the structural disorder (disorder I and II) and the magnetism of the tetragonal I phase in the $Al_{1-y}Ga_yPcF\text{-}Br_x$, so that the discussion is limited to the y=0, 0.2 and 0.3 cases. The disorder I exists even without the GaPcF mixing, i.e. y=0. This disorder is induced by the misfitting of the Br-atom array to the neighboring Pc-ring array[1,2] : The mean inter-ring spacing in the Pc-ring array is 3.56 Å, while the typical interatomic distance in Br_3^-, which is assumed to be the reduced state of the bromine in the tetragonal I phase[2], is 2.53 Å.[11] As a result, the c-coordinates of the Pc rings as well as those of the Br atoms distribute around their average positions by ca. ±1 Å. The detailed features of the disorder I, however, has been unknown. It is expected that the Br_3 chain induces a distortion in the Pc-ring array with the wavelength of three times the mean-inter-ring distance.[1,2,12] What is focused in the present discussion is whether or not the disorder I maintains a short range phase coherence of the distortion between the neighboring chains as is illustrated in Fig.6. Comparing the two cases of Figs.6A and 6B, the interchain magnetic interaction should be weaker for Fig.6B, so that the antiferromagnetic transition temperature T_N should be lower in this case.

In the present study, a random disorder (disorder II) has been induced by the GaPcF mixing into the AlPcF chains. In the disorder II, the inter-ring distance along the chain should be randomly disordered, because the inter-ring distance of the GaPcF is larger than that of the AlPcF and the GaPcF is mixed randomly into the AlPcF chains. If the disorder I maintains the phase coherence of the distortion as shown in Fig.6A, it is expected that the T_N becomes lower by the introduction of the disorder II, since the correlation between the c-coordinates of the Pc rings in the neighboring chains is destroyed by the disorder II. On the other hand, if the disorder I does not maintain the phase coherence as shown in Fig.6B, the T_N should not be affected by the disorder II, since the correlation between the c-coordinates of the Pc rings has already been destroyed in Fig.6B. The present experimental result is that the T_N is not affected by the disorder II even with the GaPcF content of $y = 0.3$, which supports the disorder model in Fig.6B. The content of $y = 0.3$ should be large enough to disturb the magnetic interaction of all the spins since the wavefunction of an unpaired spin extends over three Pc rings along the chain[2]. It is concluded that the phase coherence of the distortion is not maintained along the direction perpendicular to the chains in the disorder I.

CONCLUSIONS

In the $Al_{1-y}Ga_yPcF\text{-}Br_x$ powder with $x{\sim}1$, the tetragonal I phase exists for $y \lesssim 0.3$, and the GaPcF distributes randomly in the AlPcF chains. In the tetragonal I phase for $y = 0$, 0.2 and 0.3, the antiferromagnetic transition occurs in the same temperature region of ca. 100 K. This means that the random disorder (disorder II) induced by the GaPcF mixing does not affect the strength of the magnetic interaction. This indicates that, in the disorder I, the correlation between the c-coordinates of the Pc rings in the neighboring chains is not maintained.

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REFERENCES

1. I.Hiromitsu, H.Yamamoto and T.Ito, Phys.Rev., B52, 7252 (1995).
2. I.Hiromitsu, N.Ikeda, H.Yamamoto and T.Ito, J.Phys.Soc.Jpn, 64, 12 (1995).
3. I.Hiromitsu, S.Ohkubo, J.Takeuchi and T.Ito, J.Phys.Soc.Jpn, 63, 2716 (1994).
4. I.Hiromitsu, S.Ohkubo, J.Takeuchi and T.Ito, Solid State Commun., 89, 605 (1994).
5. K.J.Wynne, Inorg.Chem., 24, 1339 (1985).
6. J.P.Linsky, T.R.Paul, R.S.Nohr and M.E.Kenney, Inorg.Chem., 19, 3131 (1980).
7. J.E.Owen and M.E.Kenney, Inorg.Chem., 1, 334 (1962).
8. R.E-Martin, N.Hussein and M.Willis, Mol.Cryst.Liq.Cryst., 229, 229 (1993).
9. C.W.Dirk, T.Inabe, K.F.Schoch and T.J.Marks, J.Am.Chem.Soc., 105, 1539 (1983).
10. R.S.Nohr, P.M.Kuznesof, K.J.Wynne, M.E.Kenney and P.G.Siebenman, J.Am.Chem.Soc., 103, 4371 (1981).
11. T.J.Marks and D.W.Kalina, in Extended Linear Chain Compounds, edited by J.S.Miller (Plenum, New York, 1982), Vol.1, Chap.6, pp.197-332.
12. C.J.Schramm, R.P.Scaringe, D.R.Stojakovic, B.M.Hoffman, J.A.Ibers and T.J. Marks, J.Am.Chem.Soc., 102, 6702 (1980).