PHYSICAL REVIEW B **66**, 035104 (2002)

Metal-insulator transition of donor-acceptor-type organic charge-transfer complex $(\mathrm{BETS})_2(\mathrm{Br}_2\mathrm{TCNQ})$: Site-selective NMR measurements

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(Received 16 October 2001; published 8 July 2002)

The roles of donor layers and acceptor stacks in the electronic properties of the charge transfer complex, $(\mathrm{BETS})_2(\mathrm{Br}_2\mathrm{TCNQ})$ were investigated by means of site-selective NMR measurements. Line broadening of ^{77}Se NMR indicating a magnetic ordering on the BETS site was observed at the metal-insulator transition temperature 12 K. This transition is caused by the spin-density-wave formation on the BETS layers. ^{13}C NMR on the cyano carbon in the $\mathrm{Br}_2\mathrm{TCNQ}$ molecule confirms that a spin singlet formation starts to develop on the one dimensional $\mathrm{Br}_2\mathrm{TCNQ}$ columns below 170 K and its three dimensional ordering appears below 80 K. From the analysis of the NMR line shape and shift, magnetic susceptibility was decomposed into the contributions of the BETS and $\mathrm{Br}_2\mathrm{TCNQ}$ sites.

DOI: 10.1103/PhysRevB.66.035104 PACS number(s): 71.30.+h, 75.30.Fv, 76.60.−k

I. INTRODUCTION

$(\mathrm{BETS})_2(X_2\mathrm{TCNQ})$ ($X=\mathrm{Cl}$ and Br [BETS and X_2TCNQ are abbreviations for bis(ethylendithio)tetraselenafuluvalene and 2,5-disubstituted-tetracyanoquinodimethane, respectively]), are all organic donor-acceptor-type charge transfer complexes, which consist of two-dimensional BETS layers and one-dimensional X_2TCNQ columns.[1] BETS and X_2TCNQ behave as donor and acceptor molecules, respectively. The valence of X_2TCNQ is considered to be -1 from an analysis of the C≡N stretching mode.[2] This suggests that there is one hole per two BETS molecules, i.e., that the conduction band is quarter-filled. One of the interesting properties of this system is that both the donor and acceptor contribute to the electromagnetic properties.[1] This is in contrast to the other conventional organic charge transfer complexes with closed shell anions, like $(\mathrm{TMTCF})_2X$ and $(\mathrm{BEDT\text{-}TTF})_2X$ families.[3]

Isostructural $(\mathrm{BETS})_2(\mathrm{Br}_2\mathrm{TCNQ})$ and $(\mathrm{BETS})_2(\mathrm{Cl}_2\mathrm{TCNQ})$ are metallic at high temperatures.[1] $(\mathrm{BETS})_2(\mathrm{Br}_2\mathrm{TCNQ})$ shows a resistivity minimum at about 15 K, followed by an insulating behavior at ambient pressure.[1] The metal-insulator (MI) transition temperature is slightly reduced by applying pressure. On the other hand, $(\mathrm{BETS})_2(\mathrm{Cl}_2\mathrm{TCNQ})$ remains metallic down to low temperatures.[1,4] Under a pressure of 3.5 kbar, a superconducting (SC) transition has been observed at 1.3 K.[1] At a higher pressure of about 6 kbar, the resistivity shows a minimum at about 13 K and increases at lower temperatures. A SC transition was still observed at about 1 K.[1] In $(\mathrm{BETS})_2(\mathrm{Cl}_2\mathrm{TCNQ})$, it is thus confirmed that an insulating phase is located in the neighborhood of the SC phase.[1,4]

From an analysis of the crystal structure, the cell volume of the $(\mathrm{BETS})_2(\mathrm{Br}_2\mathrm{TCNQ})$ is slightly larger than that of $(\mathrm{BETS})_2(\mathrm{Cl}_2\mathrm{TCNQ})$.[4] The substitution of the halogen atoms on the TCNQ molecules with larger size should be considered as "negative" chemical pressure, as far as the volume effect is concerned. This simple picture does not apply to this $(\mathrm{BETS})_2(X_2\mathrm{TCNQ})$ system, since the insulating state of $(\mathrm{BETS})_2(\mathrm{Cl}_2\mathrm{TCNQ})$ is stabilized under pressure. The relationship between the application of hydrostatic pressure and the chemical substitution was discussed in a separate paper.[4]

The first important question concerns the nature of these insulating states. To address this question, we have started the investigation of the MI transition of $(\mathrm{BETS})_2(\mathrm{Br}_2\mathrm{TCNQ})$.

^{1}H NMR measurements in this system were performed in our previous work.[4,5] However, ^{1}H nuclei are located on both molecules, and the hyperfine coupling between the ^{1}H nuclei and the conduction electrons is small, so that we obtained only a little information about the ground state. It was necessary to select nuclear sites which have larger hyperfine couplings. We thus decided to perform ^{77}Se NMR on Se sites in the BETS molecule and the ^{13}C NMR on the cyano carbon in the X_2TCNQ molecule. The hyperfine couplings on the ^{77}Se and the ^{13}C nuclear sites are much larger than that

0163-1829/2002/66(3)/035104(6)/$20.00

on the ^{1}H sites. ^{77}Se NMR detects the role of holes on the BETS layers, and the ^{13}C NMR detects the electrons on the Br_2TCNQ stacks.

II. EXPERIMENTS

The cyano carbons of the Br_2TCNQ and Cl_2TCNQ molecules were enriched by a ^{13}C isotope.[6] ^{77}Se NMR measurements were performed with ^{77}Se of natural abundance (7.5 %). NMR measurements were carried out on a polycrystalline samples of about 20 mg in weight. The NMR spectrum and relaxation rate were measured with a conventional pulsed NMR spectrometer in a temperature range between 5 and 70 K for ^{77}Se NMR and between 5 K and room temperature for ^{13}C NMR. The intensity of the ^{77}Se NMR signal was so small that we could not obtain a sufficient signal-to-noise ratio above 70 K with our present setup. The radio frequency (rf) used for the ^{13}C/^{77}Se NMR measurements was 88 MHz/73 MHz, which corresponds to resonance fields (H_0) of 8.2 T/9 T, respectively. The ^{13}C NMR spectra were obtained by a fast Fourier transformation of the spin echo signal following a $\pi/2$-π pulse sequence. The linewidth of the ^{77}Se NMR at low temperatures was much broader than the rf field strength (typically $\gamma H_1 \sim 140$ kHz as estimated from the width of the $\pi/2$ pulse ~ 7 μsec). Therefore the spectra were constructed by scanning frequency at a fixed magnetic field. The linewidth is defined as the square root of the second moment of the spectrum. The shift $^{13}K/^{77}K$, for ^{13}C/^{77}Se NMR, was determined by the center of gravity of the spectrum with respect to the zero shift position.[7] The spin lattice relaxation rates, $1/^{13}T_1$ for ^{13}C NMR and $1/^{77}T_1$ for ^{77}Se NMR, were determined by the measurement of the recovery of the nuclear magnetization after saturation comb pulses. The spin-spin relaxation rate or spin-echo decay rate, $1/^{13}T_2$ for ^{13}C NMR was measured by recording the spin echo intensity as a function of the time interval (τ') of the $\pi/2$-τ'-π pulse sequence.

III. RESULTS AND DISCUSSIONS

A. ^{77}Se NMR of BETS site: evidence of magnetic order in the BETS layer

^{77}Se NMR spectra for $(BETS)_2(Br_2TCNQ)$ are shown in Fig. 1. In the higher-temperature region above 20 K, an asymmetric spectrum was observed. This is a typical powder pattern for the case of uniaxial Knight shift. This is reasonable because the highest occupied molecular orbital of the BETS molecule consists of a p_z (π) orbital at each atomic site; the uniaxial symmetry comes from the π orbitals. The isotropic and anisotropic shifts are determined as $K_{\rm iso}=(K_\parallel+2K_\perp)/3=A\chi$ and $K_{\rm aniso}=(K_\parallel-K_\perp)/3=B\chi$, respectively, where $K_\parallel(K_\perp)$ is the shift for the field parallel (perpendicular) to the symmetry axis of the π orbital, χ is the electronic spin susceptibility, and A and B are the isotropic and anisotropic hyperfine coupling constants. $K_{\rm iso}$ gives the central shift and $K_{\rm aniso}$ contributes to the width of the spectrum. Since the NMR-active ^{77}Se sites are very dilute (the natural abundance is 7.5%), the nuclear dipolar interaction between ^{77}Se nuclei should be negligible (~ 0.8 kHz). In addition, ^{77}Se sites are rather far from the outer ^{1}H sites (the shortest ^{1}H-^{77}Se distance is ~ 0.49 nm). The nuclear dipolar width due to the nearest neighbor ^{1}H nuclei is calculated to be as small as ~ 0.2 kHz. Thus one can consider that the observed linewidth at high temperatures above 20 K comes only from $^{77}K_{\rm aniso}$. We measured the linewidth as the square of the second moment of the observed spectrum and determined $^{77}K_{\rm aniso}$ from the relation[9].

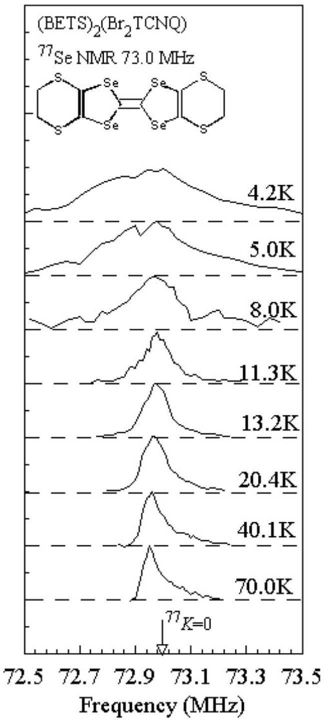

FIG. 1. ^{77}Se NMR spectra at various temperatures. The transverse axis is frequency as a unit of MHz. The $^{77}K=0$ was determined by the measurement of the standard sample.

$$\frac{\sqrt{\langle \Delta f^2 \rangle}}{^{77}\gamma H_0} = \frac{1}{2\pi}\sqrt{\frac{4}{5}}\,{}^{77}K_{\rm aniso},$$

where $\langle \Delta f^2 \rangle$ and $^{77}\gamma$ are the second moment of the spectrum and gyromagnetic ratio of the ^{77}Se nuclei. $^{77}K_{\rm iso}$ was determined from the central shift of the spectrum.

$^{77}K_{\rm iso}$ and $^{77}K_{\rm aniso}$ should be proportional to the local susceptibility at the ^{77}Se sites, $\chi_{\rm BETS}$. However, $^{77}K_{\rm iso}$ is very small; $^{77}K_{\rm iso}\sim 70$ ppm at temperatures above 20 K, which is too small to discuss the temperature dependence of $\chi_{\rm BETS}$ in detail.

There are no contributions to the on-site Fermi contact interaction because the π orbital has a node on the nuclear site. The Knight shift comes from the dipolar coupling between ^{77}Se nuclei and π orbitals. The small A value is natural for the case of π orbitals.[8] On the other hand, the observed linewidth above 20 K is about ~ 60 kHz, corresponding to $^{77}K_{\rm aniso}\sim 800$ ppm, much larger than $^{77}K_{\rm iso}$ in this system. Therefore, we can analyze the local susceptibility on the BETS sites through the linewidth, that

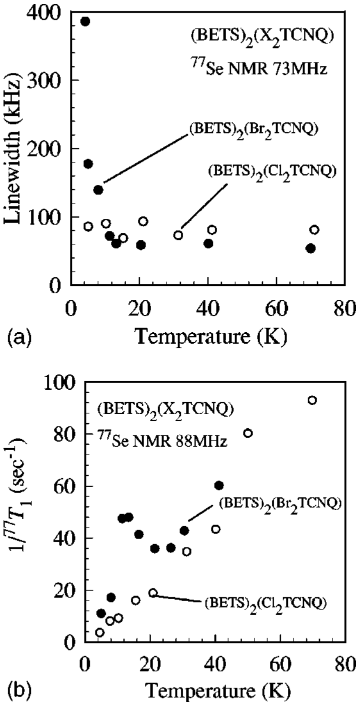

FIG. 2. (a) Temperature dependence of the linewidth of ^{77}Se NMR spectra of (BETS)$_2$(Br$_2$TCNQ) [closed circles] and (BETS)$_2$(Cl$_2$TCNQ) [open circles]. (b) Temperature dependence of the relaxation rate, $1/^{77}T_1$, of (BETS)$_2$(Br$_2$TCNQ) [closed circles] and (BETS)$_2$(Cl$_2$TCNQ) [open circles].

is, the anisotropic term of the hyperfine coupling, B. The linewidth is shown in Fig. 2(a) [closed circles for (BETS)$_2$(Br$_2$TCNQ)]. One can see that the observed linewidth is almost independent of temperature above 40 K. Therefore we conclude that $\chi_{\rm BETS}$ is independent of temperature in this temperature region. The linewidth of (BETS)$_2$(Cl$_2$TCNQ), which remains metallic at ambient pressure, is also constant in temperature. These indicate that holes on BETS molecules exhibit a Pauli paramagnetism in the metallic states. We note that the linewidth of (BETS)$_2$(Cl$_2$TCNQ) is slightly larger ($\sim$25%) than that of (BETS)$_2$(Br$_2$TCNQ), suggesting a larger spin susceptibility in (BETS)$_2$(Cl$_2$TCNQ) than in (BETS)$_2$(Br$_2$TCNQ). This is consistent with the magnetic susceptibility measurements.[10]

Below about 12 K, which is the MI transition temperature of (BETS)$_2$(Br$_2$TCNQ), the spectrum becomes much broader than that in the metallic state. This drastic broadening is a clear indication of the appearance of an inhomogeneous local field, that is, evidence of a magnetic transition. The observed spectrum at 20 K seems to be slightly broadened as compared with the spectra at higher temperatures. We consider that this can be attributed to short range ordering of the spins, as a precursor of the transition. In (BETS)$_2$(Cl$_2$TCNQ), there is no such broadening observed.

Figure 2(b) shows the temperature dependence of $1/^{77}T_1$ of (BETS)$_2$(Br$_2$TCNQ), together with the results of $1/^{77}T_1$ of (BETS)$_2$(Cl$_2$TCNQ) for comparison. For (BETS)$_2$(Cl$_2$TCNQ), $1/^{77}T_1$ decreases monotonically with decreasing temperature, indicating a Korringa-like relaxation behavior as expected in a metallic state. This is consistent to the conducting behavior reported by Kondo *et al.*[2] Actually, $1/^{77}T_1$ is well proportional to temperature below about 30 K, but a slight deviation at higher temperatures is also notable.

$1/^{77}T_1$ of (BETS)$_2$(Br$_2$TCNQ) also follows a behavior above 20 K, similar to that of (BETS)$_2$(Cl$_2$TCNQ). Therefore we can regard that the electronic states of the (BETS)$_2$(Br$_2$TCNQ) at higher temperatures above 20 K is quite similar to that of (BETS)$_2$(Cl$_2$TCNQ).

In the case where the anisotropic term of the hyperfine coupling is dominant, as in the present case, the relation between the relaxation rate and the anisotropic Knight shift for the simplest case can be expressed as[11]

$$T_1TK^2_{\mathrm{aniso}}=\frac{1}{2}\left(\frac{\gamma_{\mathrm{e}}}{\gamma_{\mathrm{I}}}\right)^2\frac{\hbar}{4\pi_{\mathrm{B}}},$$

where $\hbar$, k_{B}, γ_{e} and γ_{I} are the Planck constant, the Boltzmann constant, the gyromagnetic ratio of the electron, and that of the nuclei, respectively. Here the $\vec{q}$ dependence of the hyperfine coupling and dynamic susceptibility have been neglected. The right-hand side contains only the universal values. Using the observed $^{77}K_{\mathrm{aniso}}$, the values of $(T_1T)^{-1}$ expected in the uncorrelated case is evaluated as $\sim$0.22 $\mathrm{s}^{-1}\,\mathrm{K}^{-1}$. The observed $(T_1T)^{-1}$ value in the higher-temperature region is about 1.5 $\mathrm{s}^{-1}\mathrm{K}^{-1}$, seven times as large as in the uncorrelated case. A large enhancement of the $(T_1T)^{-1}$ value may suggest the existence of antiferromagnetic correlations between the electronic spins.[12]

In (BETS)$_2$(Cl$_2$TCNQ), the observed $^{77}K_{\mathrm{aniso}}$ is 25% as large as that of (BETS)$_2$(Br$_2$TCNQ). On the other hand, the observed $(T_1T)^{-1}$ is about 1 $\mathrm{s}^{-1}\,\mathrm{K}^{-1}$ (evaluated below 40 K). The enhancement from the simplest Korringa relation in (BETS)$_2$(Cl$_2$TCNQ) is thus estimated as 3.3. The smaller enhancement seems reasonable in (BETS)$_2$(Cl$_2$TCNQ) without antiferromagnetic ordering. However, we do not claim this at the moment, since $(T_1T)^{-1}$ is not always constant but seems to increase at higher temperatures. We believe more careful measurements are required to address precise comparison.

$1/^{77}T_1$ of (BETS)$_2$(Br$_2$TCNQ) shows a clear peak at 12 K, the MI transition temperature. This is another evidence of the magnetic nature of the transition. The gradual enhancement of $1/^{77}T_1$ below 20 K down to 12 K is a manifestation of critical slowing down of spin fluctuations and the rapid decrease below 12 K reflects the temperature dependence of the thermal fluctuations of ordered magnetization.[13] These results clarify that the holes on the BETS layers are relevant to this magnetic ordering.

B. ^{13}C NMR of Br$_2$TCNQ site: observation of spin-Peierls-type fluctuation

Figure 3 shows the ^{13}C NMR spectrum at various temperatures. Not only does the resonance position have a large temperature dependence, but the line shape is markedly changed with temperature. The temperature dependence of

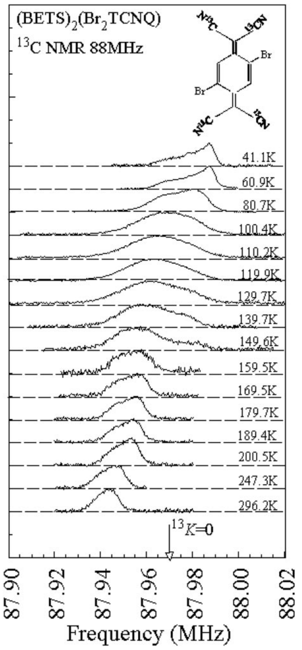

FIG. 3. Temperature dependence of ^{18}C NMR spectra at various temperatures. The intensities of the spectra were very small in a temperature range between 100 K and 160 K. The $^{18}K=0$ was determined by the measurement of the standard sample (tetramethylsilane).

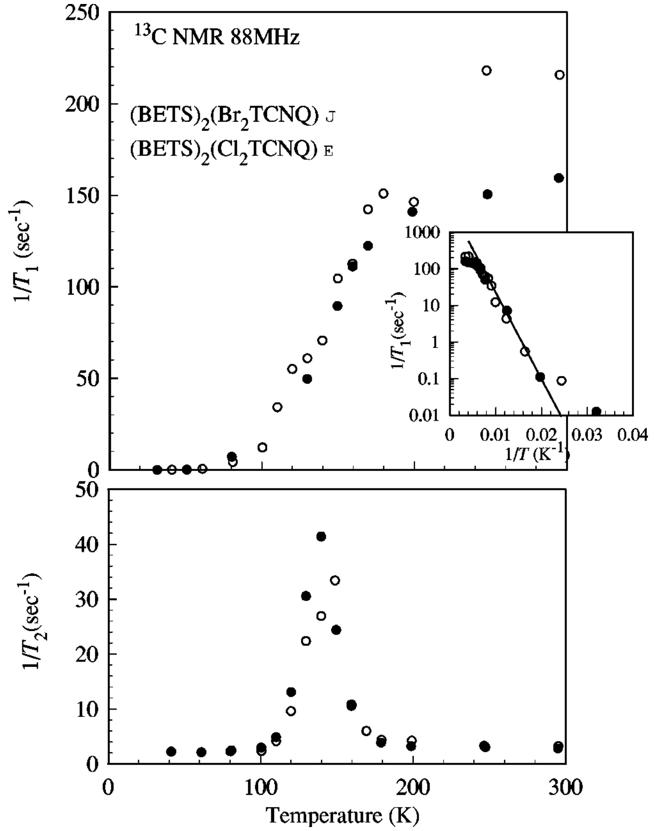

FIG. 4. Temperature dependence of $1/{}^{13}T_1$ and $1/{}^{13}T_2$ of (BETS)$_2$(Br$_2$TCNQ) [closed circles] and (BETS)$_2$(Cl$_2$TCNQ) [open circles]. An arrhenius plot of the $1/{}^{13}T_1$ is shown in the inset.

the spectrum seems to be divided into three temperature ranges: $T \geqslant 170$ K, $T \leqslant 80$ K, and the intermediate region $80\ \mathrm{K} \leqslant T \leqslant 170$ K.

At high temperatures above 170 K the line shape is asymmetric, and the central shift is negative. The shift decreases monotonically with decreasing temperature. The negative shift and the asymmetric line shape are characteristics of the ^{13}C NMR for cyano carbons. Since the carbon site of the cyano group is a node of the electronic density,[14,15] the main contribution to the ^{13}C Knight shift (^{13}K) comes from the core polarization due to the electron spin on the neighboring nitrogen site through the C≡N bond. The relation between ^{13}K and the spin susceptibility, χ_{total}, is discussed in Sec. III C.

At low temperatures below 80 K, the spectral shape becomes more asymmetric, indicating a typical powder pattern of anisotropic shift with an uniaxial asymmetry. The line shape and the shift are almost independent of temperature in this temperature region. These behaviors of the ^{13}C NMR is quite similar to the cyano-carbon NMR spectrum often observed in a nonmagnetic state, such as the spin-Peierls state of (DMe-DCNQI)$_2$Li,[14] which exhibits a spin-Peierls transition at 60 K.

In a nonmagnetic insulating state, there is no contribution of the electron spins to the shift, so that the line-shape asymmetry comes from the anisotropy of the chemical shift. From the observed anisotropic spectrum, the principal values of the shift tensor for the cyano carbon of the Br$_2$TCNQ molecules are determined as 75, 75, and -150 ppm. These values agree quite well with 70, 70, and -140 ppm for the cyano carbon of (DMe-DCNQI)$_2$Li.[14] These results clearly indicate that the contribution of the electron spins ($^{13}K \propto \chi_{\mathrm{TCNQ}}$) vanishes on the Br$_2$TCNQ site below 80 K, just as in the spin-Peierls state of (DMe-DCNQI)$_2$Li. Thus we conclude that Br$_2$TCNQ molecules are in a nonmagnetic spin singlet state, at least below 80 K. This temperature, 80 K, is much higher than the MI transition temperature of this compound (~ 12 K). There is no intrinsic anomaly in ^{13}C NMR measurements below 80 K. Moreover, the ^{13}C NMR in (BETS)$_2$(Cl$_2$TCNQ) shows a behavior identical to that in (BETS)$_2$(Br$_2$TCNQ). All these facts indicate that electrons on the Br$_2$TCNQ sites are not related to the MI transition.

In the intermediate temperature range between 170 and 80 K, the ^{13}C NMR spectrum becomes unusually broadened. The central shift keeps decreasing with temperature, as in the higher-temperature region. Note that ^{13}K is still finite in this region.

This anomalous behavior should be related to the nonmagnetic transition at 80 K, below which χ_{TCNQ} vanishes. This feature, however, is in sharp contrast to the simple spin-Peierls transition in (DMe-DCNQI)$_2$Li, in which the detailed NMR study was performed.[14] To understand the reason for the line broadening, we carried out measurements of longitudinal (spin-lattice) and transverse (spin-spin) relaxation rates $1/{}^{13}T_1$ and $1/{}^{13}T_2$.

Figure 4 shows the temperature dependence of the spin-lattice relaxation ($1/{}^{13}T_1$). $1/{}^{13}T_1$ starts to decrease rapidly below 170 K; the temperature dependence is exponential over three decades, as shown in the inset. The effective activation energy is estimated as ~ 490 K. This behavior indicates that the spin gap is already opened at temperatures much higher than 80 K at which χ_{TCNQ} vanishes.

The temperature dependence of $1/{}^{13}T_2$ is also shown in the Fig. 4. $1/{}^{13}T_2$ exhibits an anomalous enhancement in this intermediate-temperature region, forming a huge peak at ~ 140 K. Now the observed line broadening is clearly related to the enhancement of the "homogeneous" width, $1/{}^{13}T_2$.

What happened in the $\mathrm{Br_2TCNQ}$ stacks at 170 and 80 K? The sudden decrease of $1/{}^{13}T_1$ indicates a clear gap opening in the ω_{N} (nuclear Larmor frequency) component of the spectrum density of spin fluctuations below 170 K. In the T_2 process, in addition to the ω_{N} component, much lower-frequency components are also effective (typically $\omega \sim \gamma \delta H$, where δH is the amplitude of the local field at the nuclear site, that is, $\omega/2\pi \sim 10$ kHz or so in the present case). The large enhancement of $1/{}^{13}T_2$ thus indicates the appearance of very slow dynamics of the local fields seen by the ${}^{13}\mathrm{C}$ nuclei and a rapid slowing down of the correlation rate of the dynamics, $1/\tau_{\mathrm{c}}(T)$, with decreasing temperature; a relaxation peak is expected at a temperature where $\gamma \delta H \tau_{\mathrm{c}}(T) \sim 1$ is satisfied.

A possible mechanism is as follows: A spin singlet formation with a magnetic gap of about 490 K starts to develop in the one-dimensional TCNQ columns below 170 K with strong spin fluctuations. Since the intercolumn interactions are very weak in the present system, each TCNQ chain behaves independently, and fluctuations of the spin-singlet coupling in the one-dimensional (1D) columns remain in the intermediate-temperature region. The characteristic frequency of the fluctuations of ~ 10 kHz is determined by the dynamics of a short-range spin-Peierls ordering containing lattice degrees of freedom, and is much lower than any kind of dynamics of electronic origins and ω_{N}.[16] These slow fluctuations in the columns can be detected by the $1/{}^{13}T_2$ and linewidth measurements. This kind of line broadening is essentially homogeneous. A 3D ordering of the spin-Peierls state takes place at a much lower temperature, 80 K in the present system, demonstrating the existence of the fluctuated spin-Peierls state over a wide temperature range.

As seen in the crystal structure, the $\mathrm{Br_2TCNQ}$ columns are well separated from the BETS molecules, suggesting a strong one dimensionality. According to the x-ray measurements by Kondo *et al.*, 1D $2k_{\mathrm{F}}$ diffuse streaks were observed below 200 K, and 3D diffuse spots appeared only below liquid nitrogen temperature. The existence of the 1D regime prior to the 3D ordering is often observed in the Peierls system but not usual in the case of the spin-Peierls transition, since the 3D couplings have been well developed at the transition temperature in typical spin-Peierls systems.[14,17] The 1D nature of the spin-Peierls formation is very consistent with the above-mentioned picture to explain the ${}^{13}\mathrm{C}$ NMR anomalies. The diffuse x-ray streaks have evidenced the interchain incoherence, but tell little about the dynamics. The ${}^{13}\mathrm{C}$ NMR anomalies should be considered as the first direct observations of 1D dynamics of the spin-Peierls fluctuations.

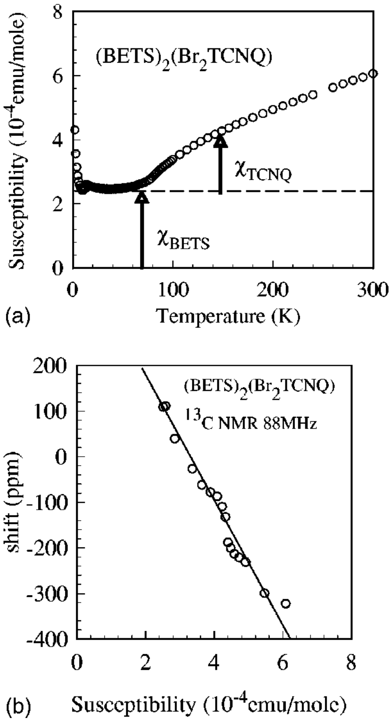

FIG. 5. (a) Temperature dependence of the static susceptibility. The diamagnetic core contributions were subtracted (BETS: -2.4×10^{-4} emu/mole, $\mathrm{Br_2TCNQ}$: -1.3×10^{-4} emu/mole).

In $(\mathrm{BETS})_2(\mathrm{Cl_2TCNQ})$ similar behaviors of ${}^{13}\mathrm{C}$ NMR relaxation have been observed, as shown in Fig. 4. It is noteworthy that there is no appreciable anomaly in the static susceptibility nor in resistivity around 200 and 80 K. The present study gives clear evidence that the conducting BETS holes and the localized TCNQ spins behave independently of each other.

C. Decomposition of the local susceptibility, χ_{BETS} and χ_{TCNQ}

The total static susceptibility χ_{total} was measured by using a superconducting quantum interference device magnetometer for the same sample used in the present NMR measurements. As shown in Fig. 5(a), χ_{total} gradually decreases with decreasing temperature from room temperature, and becomes constant below about 80 K. The anomaly around 80 K is attributed to the stabilization of 3D spin Peierls state on the $\mathrm{Br_2TCNQ}$ columns. The temperature dependence of ${}^{13}K$ scales to χ_{total}, as shown in Fig. 5(b). The hyperfine coupling constant of ${}^{13}\mathrm{C}$ NMR, ${}^{13}A$, is estimated from the slope of the ${}^{13}K$-χ plot as -7.4 kOe/μ_{B}. This is a reasonable value. This strongly suggests that the temperature dependence of the susceptibility is dominated by that of the $\mathrm{Br_2TCNQ}$ site and the local susceptibility on the BETS site (χ_{BETS}) is almost temperature independent in the whole temperature range. The latter has actually been confirmed by the ${}^{77}\mathrm{Se}$ NMR at least below 80 K. Since the ${}^{13}\mathrm{C}$ NMR shift below 80 K (~ 120 ppm) is well explained as the chemical shift,[14] we can take the local susceptibility on the $\mathrm{Br_2TCNQ}$ site, χ_{TCNQ}, to be zero in this temperature range. Consequently, χ_{BETS} is estimated as 2.2×10^{-4} emu/mole (the value of the total susceptibility below 80 K). From the above discussion, we propose that the total susceptibility should be divided into χ_{BETS} and χ_{TCNQ}, as shown in Fig. 5(a).

The same situation is realized in $(\mathrm{BETS})_2(\mathrm{Cl_2TCNQ})$. The estimated χ_{BETS} value in $(\mathrm{BETS})_2(\mathrm{Cl_2TCNQ})$ is 2.8×10^{-4} emu/mole.

From the value of $^{77}K_{aniso}\sim800$ ppm and χ_{BETS}, the anisotropic term of the hyperfine coupling constant at ^{77}Se site, ^{77}B, was estimated to be 21 kOe/μ_{B}. This value is much larger than the isotropic hyperfine coupling $^{77}A\sim0.9$kOe/μ_{B} from the relation $^{77}K_{\mathrm{iso}}={}^{77}A\chi_{\mathrm{BETS}}$. If one Bohr magneton is localized in a unit cell at low temperatures, the width of the ^{77}Se NMR spectrum should be about 8 MHz, considering the estimate of the hyperfine field ~21 kOe and the fact that a unit cell contains two BETS molecules. The observed linewidth at 5 K in Fig. 2(a) is at most 600 kHz. This means that the amplitude of the ordered moment is as small as about 8% μ_{B} per unit cell.

What is the nature of the magnetic ordered state below 12 K? Comparing with similar organic systems, there are two possibilities. One is a Mott insulating state expected in a half-filled system. The present compound is quarter-filled as mentioned before, but it might be considered as half-filled when the spin-singlet formation on the $\mathrm{Br_2TCNQ}$ stack results in a doubling of the unit cell and a reconstruction of the Brillouin zone. However, this does not seem to be the case, since the MI transition temperature is much lower than the temperature at which the spin singlet formation takes place. In addition, the localized moment seems to be small (less than 10% μ_B/unit cell). Such a small value is expected only when the Hubbard gap is very small. The other possibility is a spin-density-wave (SDW) transition due to the nesting of the Fermi surface. The metallic behavior just above the transition is confirmed by the measurement of $1/^{77}T_1$ as shown in Fig. 2(b), which favors this possibility. Moreover, the band calculation has suggested the nesting character of the Fermi surface.[2] From these reasons, we conclude that the MI transition in the BETS layers should be an SDW transition.

IV. SUMMARY

In summary, site-selective ^{77}Se/^{13}C NMR measurements on the organic charge-transfer complex, $(\mathrm{BETS})_2(\mathrm{Br_2TCNQ})$, were carried out. (1) It was confirmed that the formation of a magnetic ordering on the BETS site takes place at the same temperature as the MI transition. This magnetic state is concluded to be a SDW. (2) Spin singlet formation occurred only in the one-dimensional columns on the $\mathrm{Br_2TCNQ}$ site at 170 K, and three-dimensional ordering appears below 80 K. (3) The susceptibility was decomposed into the contributions of a donor (χ_{BETS}) and an acceptor (χ_{TCNQ}) from the analysis of the NMR shift and the linewidth. The amplitude of the magnetic modulation on the BETS sites is estimated to be as small as about 8% μ_B per unit cell.

Electronic properties on the donor and the acceptor stacks seem to be well-separated and their coupling or interference seems to be small. The present results suggest a situation similar to the $(\mathrm{TMTSF})_2X$ and $(\mathrm{DMET})_2X$ salts.[18] The SC transition and the interplay between the SC and insulating state of the isostructural $(\mathrm{BETS})_2(\mathrm{Cl_2TCNQ})$ are interesting.

ACKNOWLEDGMENTS

The authors thank H. Abe for technical support. This work was partially supported by ''Future Project'' No. JSPS-REFTF97P00105 from the Japan Society for Promotion of Science, and Grant-in-Aid for Scientific Research No. 11740211, from the Ministry of Education, Science, Sports and Culture, Japan.

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[10] χ_{BETS} is $\sim2.5\times10^{-4}$ emu/mole for $(\mathrm{BETS})_2(\mathrm{Br_2TCNQ})$ as obtained in Sec. III C. For $(\mathrm{BETS})_2(\mathrm{Cl_2TCNQ})$, the χ_{BETS} value was evaluated as $\sim2.8\times10^{-4}$ emu/mole by the same analysis.

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