^{13}C NMR study of nesting instability in α-(BEDT-TTF)$_2$RbHg(SCN)$_4$

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The low-temperature nesting instability in the quasi-two-dimensional organic conductor, α-(BEDT-TTF)$_2$RbHg(SCN)$_4$, has been investigated by ^{13}C NMR. Below 12 K, drastic decreases in the Knight shift and $1/(T_1T)$ were observed with neither splitting nor broadening in the NMR spectra. The $1/(T_1T)$ shows no enhancement around the nesting instability, unlike the conventional spin-density-wave (SDW) transition. The present ^{13}C NMR data are suggestive of nonmagnetic transition but allow only an unusual case of mobile state in the SDW scenario. [S0163-1829(97)50238-4]

The molecular conductors based on the electron-donor molecule bis(ethylenedithio)tetrathiafulvalene (abbreviated to BEDT-TTF) have a variety of crystal structures and electronic phases including superconductors and magnetic insulators. Among these salts, α-(BEDT-TTF)$_2M$Hg(SCN)$_4$ (M = K and Rb) compounds are viewed with interest in the Fermi-surface instability of a pair of one-dimensional (1D) open Fermi surfaces in the presence of a two-dimensional (2D) closed Fermi surface[1] in contrast to the quasi-one-dimensional TMTSF systems with a pair of open Fermi surfaces alone, where TMTSF is tetramethyltetraselenafulvalene. While α-(BEDT-TTF)$_2M$Hg(SCN)$_4$ remains metallic at low temperatures, it exhibits several anomalous properties below 12 K for M = Rb and below 8 K for M = K: the anisotropy of susceptibility,[2] enhancement of magnetoresistance,[3] and increase of Hall coefficient.[4] These anomalies are believed to come from the nesting instability of the open part of the Fermi surfaces; the reconstruction of the Fermi surface in the low-temperature phase was demonstrated by transport measurements.[5] As for the nature of the low-temperature phase, a possibility of spin-density-wave (SDW) ground state was argued in terms of the susceptibility,[2] μSR (muon spin rotation),[6] torque,[7] and millimeter-wave magnetoabsorption[8] studies. Interestingly, the μSR experiment suggested an extraordinarily small magnetic moment ($0.003\mu_B$ for M = K). This curious observation and the anomalies in the transport properties imply that the condensation of the density wave due to nesting has some unusual features in the presence of the closed Fermi surface. A further investigation is required to illuminate the nature of the low-temperature density-wave state.

It is well known that NMR is a powerful probe to characterize SDW microscopically, as in the ^{77}Se NMR studies of TMTSF salts.[9] In the present work, we performed ^{13}C NMR experiments on the ^{13}C isotope labeled α-(BEDT-TTF)$_2$RbHg(SCN)$_4$. The results of spectra, Knight shift, and relaxation rate have elucidated peculiar magnetism of the low-temperature phase.

The ^{13}C NMR experiments were made for a single crystal, where the central double-bonded carbon sites in BEDT-TTF were enriched by ^{13}C isotopes, in a field of 80 kOe applied perpendicular to the conducting layers.

The ^{13}C NMR spectra are shown in Fig. 1(a). The shift is with respect to the line position of tetramethylsilane (TMS). Above 12 K, the spectra form a rather complicated line shape consisting of four lines. Below that, the two lines with smaller shifts start to merge and a small peak around 110–120 ppm diminishes with broadening, resulting in a simple doublet structure at the lowest temperature. Prior to analysis of the spectra, we examine the temperature dependence of the averaged shift, K, which is defined by the first moment of the whole spectrum. The origin of shift corresponding to a zero spin susceptibility in this field configuration is determined from the K-χ plot in a temperature range between 15 and 100 K. (Since the anisotropic part in the shift tensor of ^{13}C nuclei in question is comparable to the isotropic part, the sign of K can be positive or negative, depending on the orientation of field.) It is clear in Fig. 1(b) that $|K|$ decreases remarkably below 12 K and approaches a level of 60% of the high-temperature value.

The spectral shape is analyzed below. The present compound has four BEDT-TTF molecules in a unit cell. These molecules are not equivalent in crystallography and are specified by two A molecules, one B, and one C molecule, which form two types of columns: one is a stacking of A molecules (A column) and the other is an alternate stacking of B and C molecules (BC column). Each BEDT-TTF molecule has two neighboring ^{13}C sites which are coupled by nuclear dipole. When the neighboring ^{13}C sites are equivalent, the Pake doublet will be observed in the spectrum. The angles between the field direction and the ^{13}C=^{13}C vector (21.6°, 21.3°, and 20.5° for A, B, and C molecules, respectively[10]) yield a 88 ppm splitting in the Pake doublet
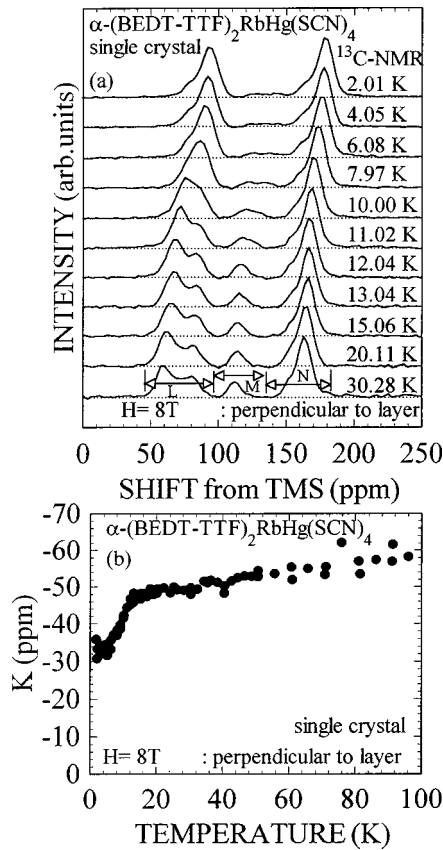
FIG. 1. (a) ^{13}C NMR spectra and (b) averaged Knight shift under a perpendicular field of 8 T.

for all the molecules from $d = \frac{3}{2}(\gamma\hbar/H_0 r^3)(1 - 3\cos^2\theta)$ with the field value of $H_0 = 80$ kOe and the ^{13}C$=^{13}$C distance of $r = 1.36$ Å. This is what we ought to observe in the B and C molecules, which have an inversion center in each molecule so that the two neighboring ^{13}C sites are equivalent. On the other hand, the two ^{13}C sites within the A molecule are nonequivalent since the A molecule is off the inversion center. In this case, the Pake doublet is modified into a quartet such as in the case of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, where the nonequivalence of the two ^{13}C sites is caused by the intramolecular symmetry breaking due to the tilted dimerization.[11,12] The position and relative intensity of each line in the quartet depends on the shift difference between the neighboring ^{13}C sites, ΔK, as follows:[13]

$$K_{\pm}^{\text{outer}} = K \pm \left\{ \tfrac{4}{3}d + \sqrt{(\tfrac{2}{3}d)^2 + 4(\Delta K)^2} \right\}/4$$

$$\left[I^{\text{outer}} = 1 + \frac{1}{\sqrt{1 + 9(\Delta K/d)^2}} \right],$$

$$K_{\pm}^{\text{inner}} = K \pm \left\{ \tfrac{4}{3}d - \sqrt{(\tfrac{2}{3}d)^2 + 4(\Delta K)^2} \right\}/4$$

$$\left[I^{\text{inner}} = 1 - \frac{1}{\sqrt{1 + 9(\Delta K/d)^2}} \right], \quad (1)$$
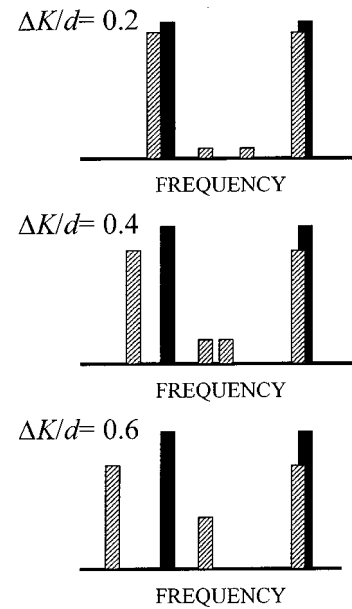

FIG. 2. Model calculation of the ^{13}C NMR spectra. It consists of a quartet (shaded bars) and a doublet (closed bars). For details see text.

where K is the averaged shift, d is the splitting of the Pake doublet (88 ppm in the present case), and the relative intensity is given in parentheses. Assuming that the ^{13}C sites in the BC column have nearly the same Knight shift, we expect spectra with a total of six lines as depicted in Fig. 2, where the hatched and closed lines coming from A and B (C) molecules, respectively, are positioned so that the lines with the highest shift nearly merge like the observation. One can see variation of the line profile and relative intensity with the value of $\Delta K/d$. In case of $\Delta K/d = 0.4$–0.6, for example, the central two lines nearly merge into a single line, giving an apparent four-line profile, which corresponds to the spectra observed above 12 K. As ΔK decreases, associated with a decrease in K below 12 K, the central line becomes split with diminished intensity, reproducing the observation below 12 K.

Examination of each line intensity of the spectra as shown in Fig. 3(a) gives further consequences as follows. The first is that the total NMR intensity keeps nearly constant in the
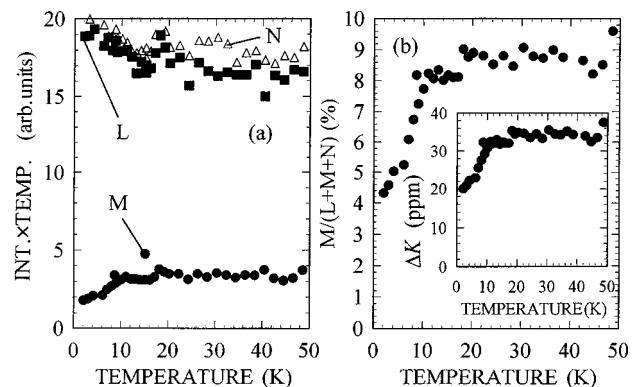

FIG. 3. (a) Line intensities of the spectra in Fig. 1 and (b) fraction of the central line (line M). The inset shows the shift difference, ΔK, deduced from Eq. (2).
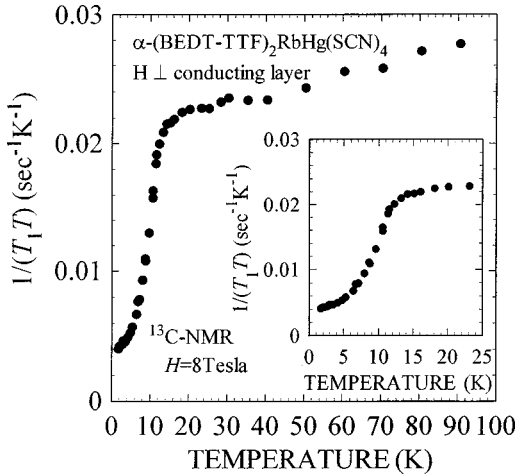
FIG. 4. ^{13}C nuclear spin-lattice relaxation rate. The low-temperature region is expanded in the inset.

whole temperature range measured. This guarantees that we do not miss any part of NMR signal and rules out partial escape of signal out of the frequency window due to magnetic ordering. The second is that the intensity L is nearly the same as the intensity N, which is consistent with the Pake doublet plus quartet picture. The third is the transfer of the spectral weight from the central part (M) to the outer part (L and N) below 12 K. The relative intensity of M shown in Fig. 3(b) is related to ΔK in the form of

$$M/(L+M+N) = \frac{1}{4}\left(1 - \frac{1}{\sqrt{1+9(\Delta K/d)^2}}\right) \qquad (2)$$

through Eq. (1) The temperature profile of the resultant ΔK shown in the inset of Fig. 3(b) is characterized by a sudden decrease below 12 K, followed by saturation to the 60% value at the lowest temperature, and is scaled to the behavior of the averaged shift in Fig. 1(b). This fact further corroborates a decrease of the Knight shift, K, below 12 K. As seen above, all of the observed aspects of the spectra are successfully explained by the doublet plus quartet model. There is no sign of appearance of static local field.

Figure 4 shows the temperature dependence of $1/(T_1T)$, which is similar to that of the square of the Knight shift or spin susceptibility above 12 K. It is well established that antiferromagnetic spin fluctuations give a peaklike enhancement of $1/(T_1T)$ around the transition due to the critical slowing down in the spin-ordered systems, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl (Refs. 13 and 14) and (TMTSF)$_2$PF$_6$ (Ref. 9). For the present system, however, no enhancement of $1/(T_1T)$ is observed around the transition temperature, 12 K. Instead, $1/(T_1T)$ shows a decrease, which starts gradually below ~ 20 K and is accelerated below 12 K. This behavior is in sharp contrast to that of the conventional SDW or antiferromagnetic systems mentioned above. The decrease of $1/(T_1T)$ is reasonably considered to reflect reconstruction of the Fermi surfaces by nesting. The value of $1/(T_1T) = 0.00425$ s^{-1} K^{-1} at 2 K is 18% of the value, 0.023 s^{-1} K^{-1}, at 15 K, which corresponds to the reduction of the electronic density of states to 43%.

The electronic coefficient of specific heat, γ, is suppressed down to $\sim 35\%$ of that above 12 K (Ref. 15). The low-

temperature behavior of the NMR shift, relaxation rate, and specific heat are qualitatively explained by reduction of the density of states due to disappearance of part of the Fermi surfaces. It is noted that the reduction rates are different from each other; 60% in the shift, 43% in $1/(T_1T)$, and 35% in γ. If the relaxation enhancement factor in Korringa's relation and the Wilson ratio are different between the closed Fermi surface and the open ones, which is to disappear below 12 K, the reduction ratio may well depend on K, $1/(T_1T)$, or γ. However, the difference between the K and γ reductions seems too large to be explained in terms of the Wilson ratio.

Except for this quantitative discrepancy in detail, the whole NMR results seen above are in favor of the picture of a nonmagnetic transition such as charge density wave (CDW). However, we have no idea which kind of CDW reconciles the susceptibility anisotropy observed below 12 K (Ref. 2) and other magnetic properties[6–8] at present. Even if it is a SDW, on the other hand, the present NMR results give unconventional restriction to the possible SDW picture, if any, which is investigated below.

The hyperfine field at the nuclear site is expressed as $h_i = \Sigma A_{ij}m_j$ ($i,j=x,y,z$), where A_{ij} is the hyperfine coupling tensor and m_j is the magnetization defined per BEDT-TTF molecule. Here, x and y axes are set in the conducting a-c plane and the z axis is perpendicular to it; the applied field is parallel to the z axis. The NMR spectrum sees the h_z component. In the case of the SDW state, $h_z(\vec{r}) = A_{zx}\Delta m_x(\vec{r}) + A_{zy}\Delta m_y(\vec{r}) + A_{zz}\{m_z^r + \Delta m_z(\vec{r})\}$, where $\Delta m_i(\vec{r})$ is the SDW moment with spatial variation and m_z^r is a paramagnetic component coming from the residual Fermi surfaces. From the susceptibility measurements, the SDW moment, if any, is suggested to be parallel to the conducting layer.[2] Therefore, spectral broadening, namely, the spatial variation in $h_z(\vec{r})$, originates from the first two off-diagonal terms; $\Delta h_z = 2|A_{zx}\Delta m_x(\vec{r}) + A_{zy}\Delta m_y(\vec{r})| \equiv 2|(\vec{A}_{z,(xy)} \cdot \Delta \vec{m}_{(xy)})|$. As seen in Fig. 1(a), there is no appreciable broadening in the spectra well below 12 K within the experimental uncertainty of less than 10 ppm (8×10^{-5} T at the present field), which gives a severe constraint to the upper limit of the static SDW moment as follows. Since the moment direction in the xy plane is unknown, we calculated the in-plane θ dependence of $\Delta h_z / \Delta m_{(xy)} = 2|(\vec{A}_{z,(xy)} \cdot \vec{u})|$ for A, B, and C molecules, where $\vec{u}$ is the unit vector in the x-y plane, and A_{zx} and A_{zy} were evaluated for the three BEDT-TTF species by the geometrical transformation of the ^{13}C hyperfine tensor values (0.0, -0.2, 1.4) (Ref. 16) in units of Tesla/($\mu_B \cdot$ BEDT-TTF). From Fig. 5, one expects that the envelope of $2|(\vec{A}_{z,(xy)} \cdot \vec{u})|$, which is represented by the bold curve, is in a range of 0.8 ± 0.2 Tesla/($\mu_B \cdot$ BEDT-TTF). This tensor value and the above local-field uncertainty, 8×10^{-5} T, set an upper limit of the static moment, if any, to as small as $1 \times 10^{-4} \mu_B$/molecule, which is much smaller than the moment ($3 \times 10^{-3} \mu_B$) suggested by μSR for the K salt.[6] This should be taken as the absence of static ordering. In order for SDW to be compatible with this observation, one has to invoke a mechanism of the motional narrowing. In other words, SDW is possible only in a mobile state such as a sliding or interlayer-incoherent state. If the motional characteristic frequency of SDW is higher than the NMR fre-
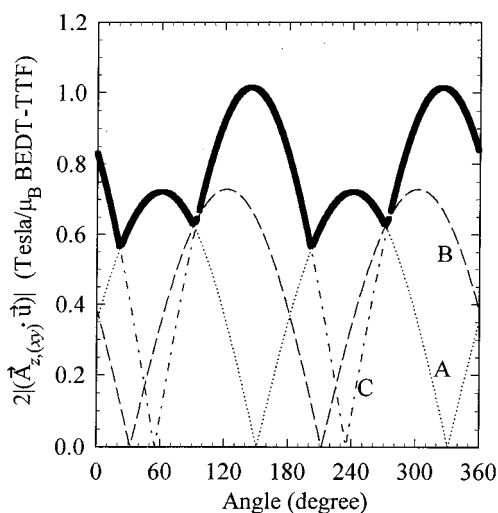
FIG. 5. Off-diagonal hyperfine splitting field along the z direction with the electron spin aligned in θ direction within the x-y (conducting) plane for A (dotted curve), B (dashed curve), and C (dash-dotted curve) molecules.

quency, the peak in T_1^{-1} coming from the critical slowing down around the transition is reasonably expected to be suppressed. It is noted that the incommensurate nature of the nesting vector, possibly small SDW gap which helps depinning, and extreme two-dimensionality of the electronic state seem favorable for the mobile SDW picture.

The comparison between the temperature profiles of the NMR shift and the spin susceptibility leads to an additional consequence in the SDW scenario. The averaged shift, K, in Fig. 1(b) is expressed by the form of $K = \langle h_z(\vec{r})/H_0 \rangle = A_{zz}\langle m_z(\vec{r})/H_0 \rangle$ because the first two off-diagonal terms

present in the ordered state in the above expression are averaged out. The $\langle m_z(\vec{r})/H_0 \rangle$ is just the spin susceptibility, which is not varied across 12 K in the present field direction.[2] Therefore, the 40% reduction in K below 12 K should be attributed to the decrease in A_{zz}, which is determined by two factors; one is the highest occupied molecular orbital (HOMO) profile around the ^{13}C sites and the other is the molecular configuration with respect to the field. Since such a large modification in the HOMO charge density at low temperature is unrealistic, the latter, namely, displacement of the BEDT-TTF molecule, is responsible for the A_{zz} variation. This is consistent with the small absolute value of K (50 ppm even above 12 K), which means that the molecular configuration is near that giving a zero shift and thus the relative variation of K is sensitive to the molecular displacement around this configuration.

In conclusion, the ^{13}C NMR spectra, Knight shift, and relaxation rate have no sign of local field generation or antiferromagnetic spin fluctuations typical of conventional SDW. The present NMR results suggest that the low-temperature phase is nonmagnetic, or give unconventional restrictions to the possible SDW picture which reconciles the susceptibility behavior; the static SDW moment should be extremely small, less than $10^{-4}\mu_B$, or vanish, implying a sliding or fluctuating state, and should be accompanied by molecular displacement.

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