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Antiferromagnetic Fluctuations in the Organic Superconductor κ -(BEDT-TTF)₂Cu(NCS)₂ under Pressure

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We measured the ¹³C-NMR spectrum and T_1 of the quasi-two-dimensional organic superconductor κ -(BEDT-TTF)₂Cu(NCS)₂ under pressure. This material was thought to show a relationship between T_c and the effective cyclotron mass m_c^* , obtained from the Shubnikov–de Haas (SdH) effect. We found that κ -(BEDT-TTF)₂Cu(NCS)₂ behaved as a Fermi liquid at low temperature under all pressures, and antiferromagnetic fluctuations were expected. The pressure dependence of the Korringa factor is similar to that of the effective cyclotron mass m_c^* , suggesting that antiferromagnetic fluctuations contribute to the superconductivity of this material. We also found that, under pressure, T^* was shifted to 150 K, the temperature characteristic of the shift from bad metal to good metal.

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Organic conductors make important contributions to strongly correlated systems and their superconductivity. Antiferromagnetic fluctuations are thought to be as important in the emergence of superconductivity as they are in the heavy-fermion system and high- T_c cuprates [1]. However antiferromagnetic fluctuations in κ -type organic superconductors are shown to be suppressed at the characteristic temperature, T^* [2], and these salts act as good metals at low temperature, as shown by the T^2 dependence of their resistivity [3]. Hence their magnetic fluctuations and electron correlations at low temperature are still unclear. Organic superconductors have an anisotropic electron structure and are sensitive to physical or chemical pressure. κ -(BEDT-TTF)₂Cu(NCS)₂ is a well-known organic superconductor with $T_c = 10.4$ K [4]. As shown in Fig. 1(b), this material consists of alternating layers of conduction sheets of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) molecules and insulator sheets of the counter anion. In κ -(BEDT-TTF)₂X, two BEDT-TTF molecules [shown in Fig. 1(a)] form a dimer in the conduction sheet [4]. Examination of its band structure shows that the highest occupied molecular orbital (HOMO) splits into two bands [Fig. 1(c)] [5]. The upper, antibonding band is half-filled, whereas the lower, bonding band is fully filled. Thus, there is one carrier per dimer, and this salt is expected to show strong electron correlation. Indeed, the electron states of κ -(BEDT-TTF)₂X have been shown to depend on anions or pressure [6–16], suggesting a relationship between antiferromagnetism and superconductivity and leading to many experimental and theoretical studies on the κ phase [16–22]. The dependence of physical properties on pressure is a characteristic feature of organic conductors, enabling the performance of system-

atic studies on the phase diagrams of strongly correlated systems [13–15]. Two types of pressure are known: chemical pressure, in which the system is controlled by anions or molecular size, and physical pressure. Compared with chemical pressure, physical pressure has the advantage of being quantifiable. The application of pressure in this material has been shown to steeply decrease T_c , with superconductivity suppressed above 0.6 GPa [16]. Systematic analysis of the Shubnikov–de Haas (SdH) effect was also performed under pressure [23]. In this material, the Fermi level lies in the antibonding band, and there is a cylindrical Fermi surface [Fig. 1(d)]. One of the more important parameters in the investigation of electron correlation is the effective cyclotron mass, m_c^* . As this mate-

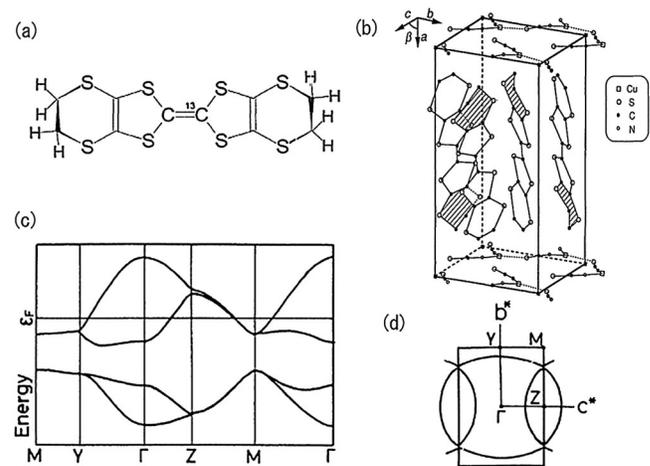


FIG. 1. (a) Isotope labeled BEDT-TTF molecule. (b) The crystal structure of κ -(BEDT-TTF)₂Cu(NCS)₂ [4]. (c) Band structure and (d) Fermi surface of κ -(BEDT-TTF)₂Cu(NCS)₂ [5].

rial has a closed Fermi surface, the SdH effect can be observed at low temperature and m_c^* can be estimated by analyzing the amplitude. The m_c^* in the SdH effect is different from the thermodynamic effective mass m^* , in that the latter depends on the density of states at the Fermi level. When pressure was applied, m_c^* decreased dramatically from ambient pressure to 0.5 GPa, and then slowly decreased. The electron-phonon interaction, λ_{e-ph} and the electron-electron interaction, λ_{e-e} , should contribute to m_c^* , as shown by the equation $m_c^* = (1 + \lambda_{e-ph}) \times (1 + \lambda_{e-e})m_c = (1 + \lambda^*)m_c$, where m_c is the bare cyclotron mass. The pressure dependence of m_c^* is similar to that of T_c and the λ^* dependence of T_c is expressed as $T_c \propto \exp(-1/c\lambda^*)$ [24]. As the electron-phonon interaction cannot explain the behavior of m_c^* under pressure [24,25], the main contribution to m_c^* is likely the electron-electron interaction. Since the details of the electron-electron interaction are not yet known, it is important to reveal the nature of this interaction.

NMR (nuclear magnetic resonance) is an important experimental probe that can be used to obtain the local spin susceptibility from the Knight shift K , and the magnetic fluctuation from the spin-lattice relaxation time, T_1 . Although, many NMR studies have assessed the effects of chemical pressure [2,7,8,11], few have been used to measure the effects of physical pressure [9]. To determine the pressure dependence of the electron correlation, we determined the ^{13}C -NMR spectrum and T_1 of κ -(BEDT-TTF) $_2\text{Cu}(\text{NCS})_2$ as pressure was increased from ambient pressure to 0.9 GPa using the NiCrAl clamp cell with Daphne 7373 oil. The low-temperature structure of κ -(BEDT-TTF) $_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ salt has disorder that originates from a glass transition in the ethylene group of BEDT-TTF, which causes the abnormal line broadening in the NMR spectrum [9,10]. On the other hand, κ -(BEDT-TTF) $_2\text{Cu}(\text{NCS})_2$ does not have such a structural disorder. Hence it is expected that the line width is still narrow at low temperatures and we can evaluate the NMR shift precisely.

To prevent from the Pake doublet effect, we enriched one side of the central $\text{C} = \text{C}$ with ^{13}C nuclei [Fig. 1(a)] [2]. The external magnetic field parallel to the a axis was 9.4 T, with a resonant frequency of 100.71 MHz. Under these conditions, the superconducting state is suppressed. Determination of the NMR spectrum of this salt at ambient pressure showed two dimers per unit cell with two crystallographically independent central $\text{C} = \text{C}$ sites (i.e., inner and outer sites) [4]. Indeed, four peaks, labeled peaks A through D, were observed at 210 K [Fig. 2(a)]. Previous results indicate that peaks A and B are inner sites and peaks C and D are outer sites [9,10,26]. To quantitatively determine spin susceptibility under pressure, we needed to determine the hyperfine coupling constant a and the chemical shift σ . The NMR shift δ_{ij} , of the ^{13}C nuclei at the i -h dimer, j th site in the molecule can be expressed

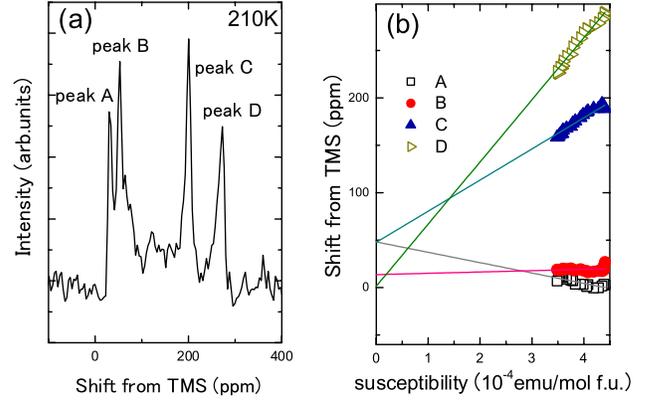


FIG. 2 (color online). (a) Spectrum at ambient pressure. (b) $\delta - \chi$ plot at ambient pressure.

using the equation $\delta_{ij} = K_{ij} + \sigma_i = a_{ij}\chi + \sigma_i$, where χ is spin susceptibility. Although the Knight shift depends on the crystallographic environment, the chemical shift is not sensitive to differences between inner and outer sites. The chemical shift is due to the coherent shielding current on the nuclei.

Therefore, we can evaluate the spin susceptibility under pressure using a and σ . We measured the temperature dependence of the NMR shift at ambient pressure, and obtained a $\delta - \chi$ plot for each site [Fig. 2(b)]. Using this plot, we calculated a as $-0.61 \text{ kOe}/\mu_B$ and σ as 48.15 ppm for peak A, a as $0.08 \text{ kOe}/\mu_B$ and σ as 13.44 ppm for peak B, a as $2.02 \text{ kOe}/\mu_B$ and σ as 34.56 ppm for peak C, and a as $3.69 \text{ kOe}/\mu_B$ and σ as -1.11 ppm for peak D, respectively. Since the chemical shift is not sensitive to inner and outer sites, we assigned peaks A and C to one dimer and peaks B and D to the other dimer. We estimated the pressure dependence of spin susceptibility from peak D, because its hyperfine coupling constant was the largest of the four. Figure 3(a) shows the pressure dependence of spin susceptibility, as estimated by

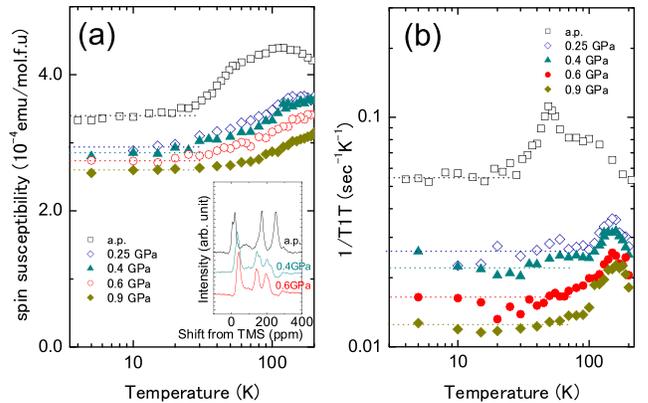


FIG. 3 (color online). (a) Temperature dependence of spin susceptibility under pressure (inset: the spectrum at 40 K under several pressures), (b) pressure dependence of $1/T_1T$.

the Knight shift. The inset of Fig. 3(a) shows the NMR spectrum at 40 K under several pressures. The abnormal line broadening as in κ -(BEDT-TTF)₂Cu[N(CN)₂]Br was not observed and we could estimate the spin susceptibility precisely. At ambient pressure, a broad maximum was observed at 100 K. Application of pressure, however, shifted this peak to higher temperatures, a finding corresponding to the pressure suppression of the hump structure of electric conduction [22]. By applying more pressure, spin susceptibility was suppressed at all temperatures. At all pressures and at low temperatures, spin susceptibility showed almost temperature independent behavior, strongly suggesting the suitability of the Fermi liquid framework at low temperatures. The spin susceptibility we observed is proportional to the density of state at the Fermi level, $N(E_F)$. While m_c^* is reduced 40% at 0.4 GPa, $N(E_F)$ is reduced only 15%.

NMR also detects the spin fluctuation from T_1 . Figure 3(b) shows the pressure dependence of $1/T_1T$. Findings on the inner and outer sites were proportional to each other, and the scale factor could be examined by differences in off-diagonal terms of the hyperfine coupling tensor. We therefore decided to measure the inner site (peaks A + B), because the spectrum of this site was sharper than that of the outer site (peaks C + D). Similar to previous findings, $1/T_1T$ was maximal at 55 K [7,11], the so-called T^* . As shown in Fig. 3(b), a steep decrease was observed as the temperature was reduced from T^* , and almost temperature independent behavior was observed at low temperatures. When pressure was increased to 0.25 GPa, the maximum $1/T_1T$ was around 150 K. But T^* was not so greatly altered at pressures above 0.4 GPa, and its behavior corresponds to the suppression of maximum spin susceptibility. At low temperature and under all pressures, $1/T_1T$ showed temperature independent behavior. When pressure was increased to 0.25 GPa, $1/T_1T$ decreased about 50% and slightly decreased above 0.4 GPa. Similar to the Knight shift, the temperature independence of $1/T_1T$ suggests a Fermi liquid picture at low temperatures. In a Fermi liquid, the following Korringa relation is satisfied, $(T_1T)K^2 = F\mathcal{K}^{-1}(\frac{\gamma_e}{\gamma_I})^2 \frac{\hbar}{4\pi k_B}$ where γ_e and γ_I are gyro-magnetic ratios of electron and ¹³C nuclei, \hbar is Planck's constant, k_B is Boltzmann constant, F is the form factor due to the anisotropic hyperfine coupling constant, and \mathcal{K} is the Korringa factor, respectively. The Korringa factor of this material was previously estimated to be about 7–9 at ambient pressure [11]. Therefore, we can evaluate the Korringa factor from the Knight shift and T_1 , as the Korringa factor at ambient pressure can be normalized to 8 below 20 K.

The pressure dependence of spin susceptibility and of the Korringa factor are shown in Fig. 4. Increasing pressure from ambient pressure to 0.25 GPa, decreases spin susceptibility about 15%, whereas, over 0.25 GPa, spin susceptibility decreases very slowly [Fig. 4(a)]. This behavior is

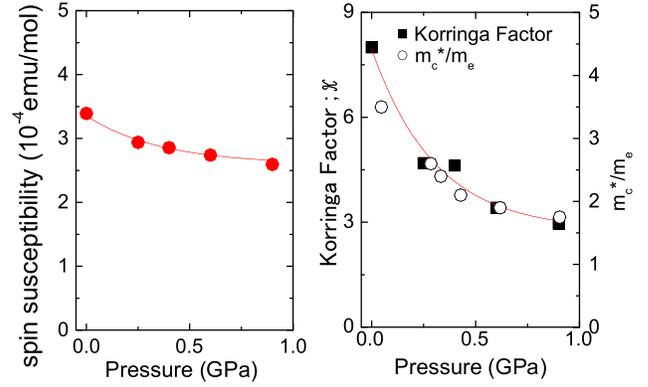


FIG. 4 (color online). (a) Pressure dependence of spin susceptibility. (b) Pressure dependence of Korringa factor and the effective cyclotron mass [23].

consistent with the thermodynamic effective mass m^* from the density of states calculated from the band structure under pressure [25]. As m^* is proportional to spin susceptibility, Fig. 4(a) shows the pressure dependence of $N(E_F)$. These findings differ from the m_c^* obtained from the SdH effect. The enhancement of m_c^* was not due to $N(E_F)$.

In contrast, increasing pressure, from ambient pressure to 0.25 GPa, decreases the Korringa factor by 50%, whereas additional pressure caused a further slow decrease [Fig. 4(b)]. This behavior of the Korringa factor is similar to the pressure dependence of m_c^* shown in Fig. 4(b). The Korringa factor characterizes the type of electron correlation. When $\mathcal{K} = 1$, the system is regarded as a simple metal; when, $\mathcal{K} > 1$, an antiferromagnetic contribution is expected; and when $\mathcal{K} < 1$, a ferromagnetic contribution is expected. The behavior of $\mathcal{K} > 1$ in κ -(BEDT-TTF)₂Cu(NCS)₂ suggests the existence of an additional antiferromagnetic contribution. In this case, \mathcal{K} can be expressed as $\mathcal{K} \approx 1 + A \text{Im} \bar{\chi}(\mathbf{Q}, \omega_N) / \omega_N$, here ω_N is the Larmor frequency and $\bar{\chi}(\mathbf{Q}, \omega_N) = \chi(\mathbf{Q}, \omega_N) / \chi^2$ is the dynamic susceptibility with \mathbf{Q} vector normalized by the spin susceptibility, which corresponds to the antiferromagnetic fluctuation. From $T_c \propto \exp(-1/c\lambda^*)$ and the similarity of the pressure dependence between $m_c^*/m_e = 1 + \lambda^*$ and \mathcal{K} , we can get the relationship between T_c and $\bar{\chi}(\mathbf{Q}, \omega_N)$ as $T_c \propto \exp(-1/c' \text{Im} \bar{\chi}(\mathbf{Q}, \omega_N))$.

This relationship suggests that superconductivity is quantitatively related to antiferromagnetic fluctuations. The antiferromagnetism in κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl [8] suggests the superconductivity mediated by the antiferromagnetic fluctuation in κ salts, giving rise to many theoretical predictions. However, there is as yet no experimental evidence showing a relationship between T_c and antiferromagnetic fluctuation. The results presented here show a similarity between m_c^* and the Korringa factor, suggesting a relationship between superconductivity and antiferromagnetic fluctuation. In contrast, the symmetry of superconductivity expected from STM [27] and thermal conductivity [28] may differ from that

expected from the antiferromagnetic structure of κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl [17]. Since our results also showed that this material changed from a bad metal to a Fermi liquid at T^* , we cannot conclude that fluctuation at low temperature is the same as fluctuation in κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl. That is, another antiferromagnetic fluctuation with a different \mathbf{Q} vector may be related to superconductivity in this material.

The contribution of antiferromagnetic fluctuation to m_c^* , however, is less clear theoretically. We believe our experimental results enable more quantitative theoretical investigations and may contribute to the elucidation of the mechanism of superconductivity in a strongly correlated electron system.

In summary, we measured the ¹³C-NMR spectrum of κ -(BEDT-TTF)₂Cu(NCS)₂ with ¹³C substituted on one side of central C = C, while increasing pressure up to 0.9 GPa. The temperature independent behavior of K and $1/T_1T$ at low temperature suggests that it behaves as a Fermi liquid at low temperature under all pressures. The Korringa factor is sensitive to pressure with a pressure dependence similar to that of m_c^* . It is strongly suggested that antiferromagnetic fluctuation contributes to the mechanism of superconductivity in this material. Determination of T^* showed that the temperature dependence of $1/T_1T$ was maximal around 50 K at ambient pressure; application of pressure, up to 0.25 GPa, shifted T^* to around 150 K, whereas application of pressure above 0.4 GPa had little effect on T^* . We confirm that this material changes from a bad metal to a Fermi liquid at T^* .

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