

ESR study of the ordering transformation in κ -(BEDT-TTF)₂Cu[N(CN)₂]Br

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Ordering transformation and its effect on the electronic structure of the κ -(BEDT-TTF)₂Cu[N(CN)₂]Br organic superconductor was studied by measuring annealing induced changes in low temperature ESR spectra and spin susceptibility temperature dependence. The transformation is shown to proceed through coexistence of two phases. Besides resistivity decrease, ordering was shown to increase ESR spin susceptibility (below about 160 K) with a tendency for restoration of the temperature independent Pauli term. Gaplike spin susceptibility behavior below 60 K is shown to develop only at some stage of ordering. These effects point to a relationship between temperature dependent spin susceptibility in the salt and incomplete ordering.

INTRODUCTION

Influence of the cooling rate on the superconducting transition temperature T_c of κ -(BEDT-TTF)₂Cu[N(CN)₂]Br was found in one of the first investigations after synthesis of the compound.^{1,2} Recently this effect has been the subject of numerous studies in the salt with both usual H₈-BEDT-TTF and deuterium substituted D₈-BEDT-TTF molecules (which we will subsequently abbreviate as Br and D-Br salts, respectively).³⁻⁸ There is growing evidence that a proper cycling is important for electronic properties.^{3,4,6-8} The effect is related to the phase transition at 80 K, due to the order-disorder transformation of the terminal ethylene groups of the BEDT-TTF molecules.⁹ The ordering is in fact realized through a sequence of phase transformations in approximately the 60 to 90 K range.⁸

It is not clear at present, whether the influence of this transformation on the electronic properties of the salt is limited to disorder induced change of scattering in electronic transport.^{6,10} In D-Br salt the transformation leads to a coexistence of two phases, assigned to magnetically ordered insulator and metal,³ suggesting its importance for the band structure.

Contrary to resistance, spin susceptibility χ is not sensitive to the scattering. In normal metal χ is independent of temperature (Pauli spin susceptibility), reflecting constant density of states at the Fermi level. In contrast, temperature dependent χ was found in the Br salt by static³ and ESR measurements,¹¹⁻¹⁵ the origin of which is not clear at present. The reported $\chi(T)$ measurements, however did not take into account the possible influence of the phase transformations, which are sensitive to the thermal cycle. Study of spin susceptibility as a function of thermal procedure can elucidate the role of the ordering transformation in the electronic properties of the material. Hence, the aim of this article is to study ESR in the salt as a function of sample thermal treatment.

EXPERIMENTAL

Single crystals of Br salt were grown by a standard electrochemical procedure. Two samples were selected for ESR study. They were single-crystalline platelets about 1.5×1 mm² in size, differing in thickness (0.12 mm, No. 1 and 0.05 mm, No. 2). T_c of the specimens was 11.2 K, as determined from the resistance transition midpoint in a 1 K/min cooling run.

ESR measurements were taken using a Bruker ESP 300E X-band spectrometer. A continuous-helium-gas-flow oxford 900 cryostat was used, allowing quenching rates up to 200 K/min. Although precise control of the rate was difficult, between 50 to 200 K/min, no significant effect on the results was observed. Since the resonator of the spectrometer is thermally isolated from the sample room its quality factor does not change during measurements. This is supported by good reproducibility of the ESR spin susceptibility χ measured at room temperature both before [$\chi_i(290$ K)] and after the thermal cycle. Linewidth W and χ were determined by numerical integration of the spectrum.¹⁶ The line shape was found to be Lorentzian at high temperature in both samples. However, it changed to Dysonian at low temperature in the thicker sample No. 1 after slow cooling, suggesting sample volume screening.¹⁷ Therefore we mainly discuss the data for sample No. 2.

Since the main aim of our work was to study the role of thermal procedures, we used a geometry with a static magnetic field normal to the conducting plane (along the b axis). In this configuration W is essentially less than in the a direction,^{14,16} resulting in a higher signal to noise ratio for χ . In addition, it was easier to align the magnetic field along b than the c axis, for which W was nearly the same. Our data measured on slow cooling corresponded closely to that previously reported.¹¹⁻¹⁵ The only notable difference was a small gradual decrease in χ on cooling from room temperature to 100 K, similar to that in static susceptibility measurements.³

The general idea behind the thermal cycles used was to

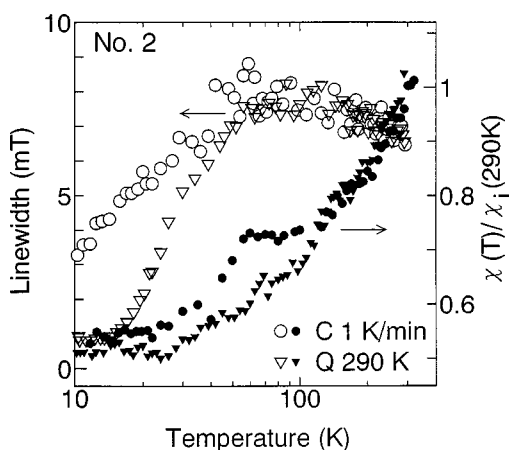


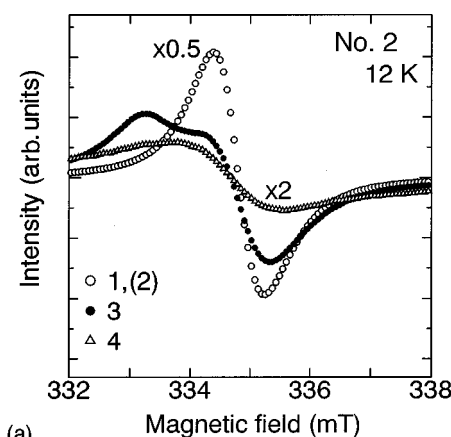
FIG. 1. Temperature dependence of the ESR linewidth (open symbols) and of the ESR spin susceptibility (closed symbols), normalized by the value at room temperature before thermal cycles $\chi_i(290)$, after slow cooling (circles) and quenching (triangles) from 290 K. The data were taken in identical run on slow warming (1 K/min) from 4.2 K.

alter the degree of ethylene ordering. It was decreased by quenching from high temperature and increased by either slow cooling (0.5 to 1 K/min), or by changing the duration and temperature T_A of annealing within the 60 to 90 K range.⁸ In both cases the states were characterized by their low temperature ESR spectra (taken at 12 K to exclude from consideration the effects associated with the superconducting state, which are beyond the scope of this article) and spin susceptibility temperature dependence. $\chi(T)$ was measured in a standard 1 K/min warming run from 4.2 K, hence any difference observed is due to the preceding cooling and/or annealing cycle.

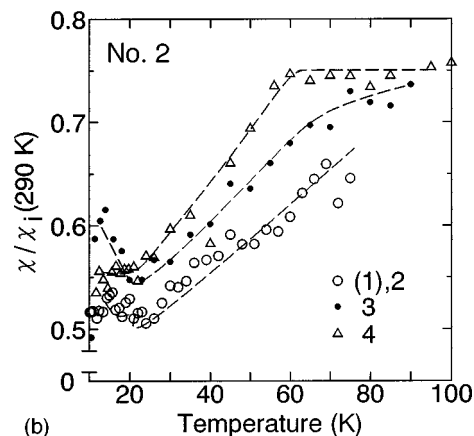
RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the ESR linewidth $W(T)$ and of the normalized spin susceptibility (taken on warming) after quenching from 290 K and after cooling at a rate of 1 K/min. In both samples after quenching the line is narrow and symmetric. It remains symmetric after slow cooling in No. 2, but becomes slightly asymmetric in No. 1. The difference in $W(T)$ between quenched and slowly cooled states is observed until entering the transformation range, above about 60 K. It is difficult to follow the transformation *in situ* since the line is broad at this high temperature. However, W is small at low temperatures, giving high resolution, which enables study of the transformation by fixing its intermediate stages with quenching. For this purpose we used step-by-step annealing of the sample, quenched from room temperature. As shown in Fig. 2(a), curve 3, annealing in the transformation range results in the appearance of two distinct lines, representing two phases. The respective splitting is practically erased at the high temperature boundary of the transformation range (curve 4). This result is quite similar to the experimental observation in the D-Br salt³ and is also in line with the ethylene ordering model,¹⁸ predicting transformation through coexistence of two phases.

It should be noted that the line splitting of Fig. 2(a) directly shows a difference in g factors of the two phases. It is



(a)



(b)

FIG. 2. Transformation of the low-temperature ESR spectrum (a) and spin susceptibility temperature dependence (b) of the quenched sample No. 2 with successive annealing at increasing T_A : (1) after initial quenching from room temperature to 4.2 K; (2) followed by annealing at 50 K for 4 h and quenching at 4.2 K; (3) followed by 4 h annealing at 75 K and quenching to 4.2 K; (4) followed by 1 h annealing at 90 K and quenching to 4.2 K. Curves 2(a) and 1(b) are not shown, since they are very close to those of 1(a) and 2(b), respectively.

thought that the BEDT=TTF molecule and its orientation in the crystal mainly determine the g factor in organic charge transfer salts.¹⁷ Hence, the g factor change could indicate a change of molecular orientation in the lattice. However, this is not the only possibility. The temperature dependence of both the linewidth and g factor was discussed by Kataev *et al.*,^{12,13} although the origin of this behavior is still controversial. W strongly decreases with sample quenching. Since ESR signal in this system is due to conduction electrons, W can be determined by the Elliott mechanism.¹⁹ In this model W is determined by the spin-lattice relaxation time T_1 as $W = 1/\gamma T_1 = \alpha(\Delta g)^2 \tau^{-1}$, where γ is the gyromagnetic ratio, α is a numerical factor of the order of 1/30, $\Delta g = (g - 2.0023)$ is the deviation of the g factor from that of the free electron, and τ^{-1} is a scattering rate of any origin, causing relaxation of conduction electrons. Within this model both the g factor and W are related to resistivity. Therefore the difference in the g factors could be due simply to the difference in conducting properties. This seems to correspond to the parallel increase of both W and resistivity with temperature. However, W decreases on quenching in sharp contrast with the increase of resistivity. Another possibility

to explain the decrease in W is to assume an increase of the Fermi velocity due to partial gapping of the Fermi surface (FS).¹² This idea seems to be in line with restoration of spin susceptibility upon increase of the degree of ordering [see Figs. 1 and 2(b) below].

Figure 1 shows $\chi(T)$ of the sample in the states with strongly different ordering. $\chi(T)$ measured on warming after slow cooling resembles basically that obtained in static susceptibility measurements.³ Susceptibility decreases nearly linearly on cooling, approximately 20% decrease of χ from 290 to 100 K, which is a little greater than the 15% decrease reported in the literature.³ Figure 2(b) shows the effect of annealing on $\chi(T)$ in a temperature range, limited to that below and in the ordering range. In each cycle the data was taken on 1 K/min warming to the next T_A . The annealing induces gradual increase of the spin susceptibility. The gap-like behavior is not typical for the quenched state (curve 1). It evolves only at a definite stage of general χ increase upon annealing (curves 3 and 4), showing its close relation to the ordering transformation.²⁰⁻²³

Actually annealing is influencing $\chi(T)$ both below and above low temperature transformation range (Fig. 1). In the latter case the effect is mainly kinetic in origin and is caused by existence of the sample in a thermodynamically nonequilibrium state. We checked that tempering of annealing in intermediate states gives $\chi(T)$ curves lying between the two curves shown in Fig. 1. The curves coincide at approximately 160 K, however, diverge slightly above 200 K again. Comparison of the curves obtained after slow cooling and after quenching actually gives the high temperature limit of the stability of quenched phase. This limit corresponds approximately to 160 K, and meets reasonably the temperature of ethylene ordering change, as established in annealing studies.^{24,8}

As we can see, by improving the order of the ethylene groups with annealing, χ of the sample can be increased. Notably, the temperature range in which the difference is observed is close to that in which incommensurate ethylene superstructure was detected by high resolution NMR studies,²⁵ pointing to an interaction of the superstructure with the electronic system (at least below 160 K).

Since degree of ordering influences spin susceptibility, we have to conclude influence of the molecule conformation change on the band structure. Several alternatives could be mentioned for the mechanism of this influence. The ethylene groups do not carry sizable electronic density. Therefore they

can influence the electronic system only indirectly, by either changing the transfer integrals between the molecules or/and introducing charge modulation through distortion of the anion layer. The uniform increase of the interdimer transfer integrals can drive the system to the Mott transition from the insulating to the metallic state on cooling.³ If the change of transfer integrals is periodic due to the superstructure, the modulation can act similar to a charge density wave (CDW), provided the superstructure wave vector q meets nesting conditions $q = 2k_F$ somewhere at the Fermi surface. CDW-like behavior is also possible for modulation of the ion positions within the anion layer. In the case of random change of the transfer integrals due to disorder, an Anderson localization can be observed.

It is clear that lattice shrinking on ethylene ordering should be favorable for the Mott transition. Assuming that χ decrease on cooling is due to Mott transition,³ increase of ordering should then lead to *simultaneous* resistivity and susceptibility decrease, which is in contrast to our observation. A decrease of χ resulting from partial decrease of the density of states at the Fermi surface is more consistent with our data. In this model the susceptibility should be Pauli-like in the disordered metallic state at high temperature and resistivity decrease should be accompanied by susceptibility increase, in line with our experimental observation.

CONCLUSION

Phase transformation in the 60 to 90 K range in the organic superconductor κ -(BEDT-TTF)₂Cu[N(CN)₂]Br proceeds through coexistence of two phases, in line with the prediction of the model for ethylene ordering. An increase in the degree of the ordering leads to a general increase of spin susceptibility. This observation points to a decrease in the density of states at the Fermi surface due to incomplete order as one of the main reasons for the temperature dependence of spin susceptibility.

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¹BEDT-TTF stands for bis(ethylenedithio)tetrathiafulvalene.

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