Zero Field Muon Spin Relaxation Study of the Low Temperature State in α-(BEDT-TTF)$_2$KHg(SCN)$_4$

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(Received 23 August 1994; revised manuscript received 22 December 1994)

Zero field muon spin relaxation measurements are reported for the low temperature magnetic phase of the organic metal (BEDT-TTF)$_2$KHg(SCN)$_4$. Steplike changes in the relaxation rate indicate two transitions; the first occurs around 12 K and is accompanied by a change in the shape of the relaxation function. A further increase in the relaxation rate occurs below 8 K. These changes signify the onset of an internal magnetic field distribution below the transition, which is assigned to a spin-density-wave (SDW) ordering with an estimated amplitude of $\sim 3 \times 10^{-3} \mu_B$ below 8 K. This very small value is consistent with the upper limits set by previous magnetic resonance studies and also with a simple mean field description of the SDW transition.

PACS numbers: 75.30.Fv, 76.75.+i

The series of organic metals (BEDT-TTF)$_2$MHg(SCN)$_4$ (M = K, NH$_4$, Rb, Tl) (BEDT-TTF is bisethylenedithiatetrathiafulvalence) [1] have attracted much attention recently as they exhibit a fascinating combination of properties related to the coexistence of quasi-one-dimensional (1D) and quasi-two-dimensional (2D) sections in the Fermi surface (FS). The 1D section consists of a well nested pair of sheets which are expected to be unstable against a periodic modulation of a Peierls type transition [charge density wave (CDW) or spin density wave (SDW)]. In the K salt which we study here, anomalies are observed in many properties in the region of 10 K, which have been associated with such a transition. The presence of new periodicities and a reconstruction of the FS in the low temperature state has been established from detailed magnetotransport studies, e.g., using angle dependent magnetoresistance oscillations which are characteristic of the quasi-1D and quasi-2D sections of FS [2]. High magnetic fields destabilize the low temperature magnetic phase and return the system to a simpler metallic state which appears to be essentially the same as that observed at higher temperatures [3].

The most direct evidence for an SDW ground state up to now comes from the static magnetic susceptibility which becomes anisotropic below about 10 K in the K salt and indicates antiferromagnetic order with an easy axis in the high conductivity plane [4]. It has, however, proved rather difficult to probe the details of the amplitude of this magnetic order using standard magnetic techniques; previous ESR [5] and NMR [6,7] studies have failed to see any large fields associated with SDW ordering and set rather a small upper limit for the modulation amplitude of $0.01 \mu_B$ [6].

Zero field muon spin rotation (ZF-MUSR) is a sensitive technique that is well suited to studying the weak changes in the local field distribution associated with a small amplitude SDW ordering; moments of order $10^{-3} \mu_B$ can typically be detected. Several MUSR studies, for example, on the heavy fermion superconductor URu$_2$Si$_2$ have clearly shown an increase in relaxation rate [8] associated with an SDW having an estimated amplitude of the order of $10^{-3} \mu_B$. In organic metals ZF-MUSR has recently been used to study the SDW in TMTSF$_2$PF$_6$ and related materials [9]. The SDW amplitude is rather larger in these TMTSF systems ($\sim 0.1 \mu_B$) and this leads to a clearly observable precession signal in the ZF-MUSR. No comparable precession signal has so far been seen in (BEDT-TTF)$_2$KHg(SCN)$_4$, however [10]. In the study reported here the weak local fields associated with the SDW are 1 to 2 orders of magnitude smaller than those seen in the established organic SDW systems, and the fields are observed here by their effect on the muon spin relaxation parameters (note that the term relaxation here includes slow precession under the influence of weak internal fields).

The zero field muon spin rotation experiments were carried out at the surface muon beam of the University of Tokyo Meson Science Laboratory at KEK, Tsukuba. The polycrystalline sample used for the experiment was prepared as previously described [11] and consisted of around 200 mg of crystals with typical dimensions $1 \times 0.5 \times 0.5$ mm^3. These crystals were randomly oriented and held in a high purity silver sample cell with a silver window. Any muons stopping in the sample holder or window simply provided a steady background asymmetry and did not affect the determination of the relaxation parameters. The residual field at the sample was reduced below 50 mG using compensation coils, and sample cooling was by a helium flow cryostat with the sample temperature being monitored by a calibrated carbon glass

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resistor. Measurements were made between 5 and 16 K to cover the region of the magnetic transition.

The forward-backward asymmetry of the detected positron emission following muon decay under zero external magnetic field is shown in Fig. 1. This asymmetry directly measures the time dependence of the implanted muon spin polarization under the influence of the local field at the muon site. It can clearly be seen that the relaxation becomes faster at lower temperatures and also that there is some change in the shape of the relaxation function with temperature. No fast large amplitude oscillations are observed here, in contrast to the earlier measurements on the SDW state of the TMTSF salts [9]; this is consistent with a much weaker amplitude of SDW in the present system. The asymmetry data measured in this experiment were found to be well fitted by the function

$$a(t) = a_0 e^{-(\sigma t)^\beta} + a_{bg},$$

where β is a variable shape parameter, which is 2 for the Gaussian (static) limit and 1 for the Lorentzian (dynamic) limit, and σ is a general line-shape independent relaxation rate parameter. The fits to the data using this function are shown as solid lines in Fig. 1. The temperature dependences of β and σ are shown in Fig. 2. It can be seen from the relaxation rate plot Fig. 2(a) that on cooling there are two temperatures where a sharp increase of relaxation rate occurs. The first is around 12 K and the second just below 8 K. At the 12 K transition there is also a change in the line-shape parameter [Fig. 2(b)]. We note that the 12 K transition corresponds to the temperature at which the g factor as measured by ESR starts to change [5], whereas 8 K is the point at which the large magnetoresistance appears [11] and the magnetic susceptibility falls rapidly in the high conductivity plane [4].

In the higher temperature region above the magnetic transitions, relaxation due to dipolar interaction with nuclear moments surrounding the muon site is expected. This would give a relaxation function that is initially Gaussian. The fact that β is less than 2 in the region above 12 K therefore suggests there is also some contribution to the relaxation due to electronic spin fluctuations, which, however, disappears on going through the 12 K transition. The square of the relaxation rate is proportional to the second moment of the local field distribution, and we can express the measured relaxation rate σ in terms of a nuclear contribution and an electronic SDW contribution

$$\sigma^2 = \sigma_N^2 + \sigma_{\mathrm{SDW}}^2 .$$

In the region above 12 K we assume no static contribution from the SDW and the measured relaxation rate determines the nuclear term with corresponding local field $\sigma_N/\gamma_\mu = 2.4$ G. This nuclear contribution is assumed to remain constant with temperature. The increased relaxation rate in the 8–12 K region can then be related to the appearance of an additional 2.2 G contribution from the SDW; in the region below 8 K the total electronic contribution increases to 3.2 G.

In order to relate these fields to the SDW we need to have some idea of the muon site. Positive muons in normal metals usually come to rest at an interstitial site of minimum potential. If the muon were to behave in the same way in this system then it would be expected to come to rest in the loosely packed layer of negatively charge SCN^{-1} ions where the electrostatic potential minimum is expected (site A, Fig. 3). However, the molecular system here is rather unlike a conventional inorganic metal, having a very nonuniform charge distribution with many covalent bonds, and it is quite likely that such simple electrostatic considerations are not the main factor determining the muon site. The nuclear dipole field distribution seen by the muon, however, provides an important constraint on the possible sites. The dominant nuclear spin contribution to the local field seen by the muon will be from the ethylene group protons at the ends of the BEDT-TTF molecules. The measured value of 2.4 G corresponds to the four protons of an ethylene group at a range of ~2.2 Å which would be consistent with site A. However, another site more closely coupled to the molecule and associated with the large outer ring (site B, Fig. 3) would also be consistent with this nuclear field value. The position of the muon site with respect to the spin distribution on the molecule is important if we want to make a quantitative estimate the amplitude of the SDW from the MUSR data. The spin distribution of the highest occupied molecular orbital of the BEDT-TTF molecule is mainly concentrated at the

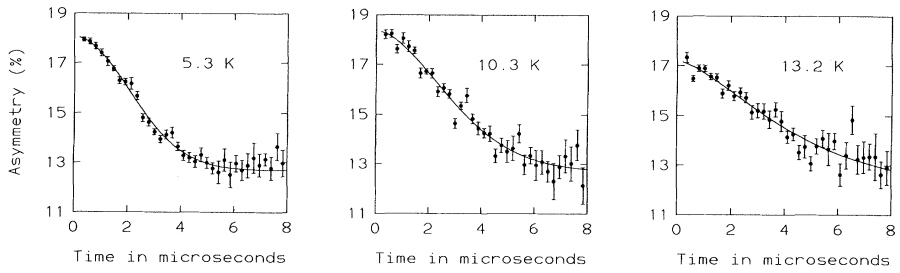

FIG. 1. Forward-backward asymmetry at several temperatures with solid lines showing the fitted relaxation function as described in the text.

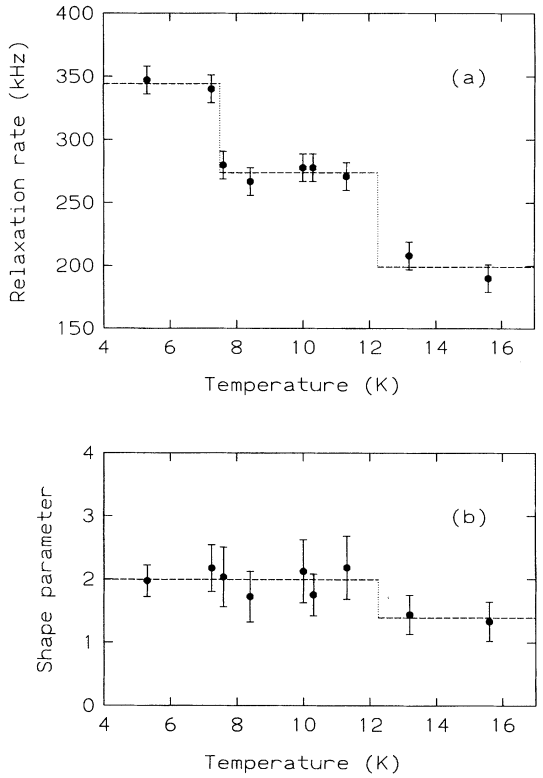

FIG. 2. The temperature dependence of the relaxation rate σ (a) and the shape parameter β (b). The dashed lines indicate the average values for different temperature regions.

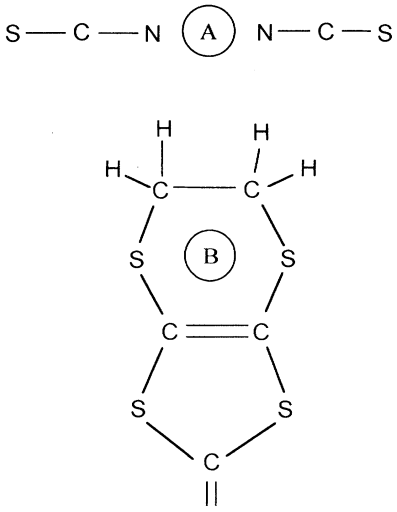

FIG. 3. An illustration of the two possible muon sites considered in the text; site A in the SCN anion layer and site B associated with the outer ring of the BEDT-TTF molecule.

center with a maximum on the innermost sulfur atoms [12]. Taking into account this molecular spin distribution, we estimate that the field produced by a $1\mu_B$ spin on the molecule nearest the muon would be 25 G at site A and 1.6 kG at site B. The observed low temperature electronic field contribution of 3.2 G thus implies an amplitude of $(0.1-0.2)\mu_B$ if the muon is in site A compared with only $2.9 \times 10^{-3}\mu_B$ if the muon is at site B. Previous NMR measurements, however, set an upper limit for the SDW amplitude of $\sim 0.01\mu_B$ [6] so we conclude that only site B is consistent with both MUSR and NMR measurements.

Although the previously reported proton NMR study set an upper limit around $0.01\mu_B$ for the SDW amplitude [6], the fraction of molecular spin density at the protons is not very large. The spin density is actually much stronger at the central sulfur and carbon atoms, and thus ^{13}C NMR of the central carbons should be a more sensitive experiment to probe for the SDW. This experiment has been carried out recently by Kanoda *et al.* [7] and changes are clearly observed in their NMR spectra on going into the low temperature phase. The observed low temperature line broadenings of a few kHz for magnetic field parallel to the conducting layers are entirely consistent with the local fields of a few G seen by our muon experiments. Unfortunately Kanoda *et al.* so far have not provided any analysis of their line shapes which would give useful quantitative information about the low temperature state.

In order to understand the small size of the SDW amplitude we note that the main parameter limiting the amplitude is the effective on-site Coulomb interaction U_{eff}. The SDW amplitude is given by [13]

$$\mu/\mu_B = 4\Delta/U_{\text{eff}}, \tag{1}$$

where 2Δ is the SDW gap. The gap is difficult to measure directly here, e.g., from conductivity, as its effects are reduced by the presence of the metallic 2D electrons, but a BCS relation to the transition temperature can be assumed, i.e., $2\Delta = 3.53 k_B T_{\text{SDW}}$. Taking $T_{\text{SDW}} = 7.5$ K and $\mu/\mu_B = 2.9 \times 10^{-3}$ we obtain $U_{\text{eff}} = 1.6$ eV, which is quite reasonable, since values for Hubbard U_{eff} in BEDT-TTF salts estimated from the optical properties, although somewhat model dependent, typically fall between a strongly dimerized limit of ~ 1 eV and the uniform limit of ~ 1.8 eV (see, e.g., [14]). We note for comparison that in the case of $TMTSF_2PF_6$, where $T_{\text{SDW}} = 11.5$ K [15] and $\mu/\mu_B = 0.08$ [16], Eq. (1) gives a value $U_{\text{eff}} \sim 0.1$ eV which is considerably lower than the expected value, which, being a molecular parameter, should be comparable to that in BEDT-TTF. This shows clearly that the SDW state in our system has more in common with classical metallic SDW systems such as chromium [17] than it does with the simple open Fermi surface organic SDW systems, where the ground state is an insulator and the SDW amplitude is anomalously large [13].

No information can be obtained from this muon study about the possible existence of a CDW, the muon being fundamentally a magnetic probe. In general, a $4k_F$ CDW

is expected to accompany a $2k_F$ SDW, but such a CDW is expected to be rather weak [18]; certainly it so far has not been possible to detect any evidence for a CDW by charge sensitive probes such as x rays [19].

Next we consider more closely the origin of the two transitions seen in the relaxation rate and their relation to other measurements and the magnetic phase diagram of this material. The most detailed information already available concerning the phase diagram comes from the magnetoresistance. On cooling in zero field, a step anomaly was observed in the resistance between ~10 and 7 K which becomes a region of rapidly increasing resistance as the temperature is lowered under an applied magnetic field [11]. On either side of this region the temperature dependence of the resistance is similar. Thus the two transitions seen in the MUSR relaxation rate seem to correspond closely to the boundaries of this strongly increasing resistance region. MUSR being a rather local probe cannot distinguish easily between short and long range order, but below 12 K it is clear that some SDW order that is at least short range must be present and that it is fairly constant down to 8 K, below which temperature the SDW becomes stronger with modulation amplitude increasing by ~50%. In the light of all this experimental evidence we propose that the 12 K transition represents the onset of 2D SDW ordering (which may be short or long range) and that the 8 K transition produces a 3D long range ordered SDW state via interlayer coupling of the 2D order parameter. This proposal is strongly supported by recent ultrasonic velocity measurements of Kamio *et al.* [20] which provide a sensitive probe of the coupling in different directions. In these measurements for longitudinal polarization in the interlayer direction a sharp change is seen only at 8 K, whereas the intralayer velocity shows a broad transition with an onset around 11 K and no anomaly at 8 K.

In conclusion, using zero field MUSR we have detected the appearance of a weak local field distribution in the low temperature state of (BEDT-TTF)$_2$KHg(SCN)$_4$, which we have associated with a very small amplitude SDW. The onset is at 12 K, and the SDW amplitude becomes stronger following a secondary transition just below 8 K. The amplitude of the SDW below 8 K is estimated to be $3 \times 10^{-3} \mu_B$, a value which is broadly consistent with a mean field theory for the SDW transition. We propose that the two transitions are associated with intralayer and interlayer modes of SDW ordering. The detailed nature of the SDW states associated with the two transitions is, however, uncertain and remains a subject for further investigations.

F. L. P. gratefully acknowledges the support of the Japan Society for the Promotion of Science.

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