Anomalous field dependence of the nuclear-spin relaxation time in the organic conductor $(ET)_4Hg_{2.89}Br_8$

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A linear increase in the rate of spin-lattice relaxation of ^1H nuclei has been observed with increasing magnetic field in the quasi-2*D* conductor $(ET)_4Hg_{2.89}Br_8$ with two incommensurate sublattices.

Several organic conductors based on bis-(ethylenedithio)tetrathiofulvalene (ET) go superconducting at atmospheric pressure.[1,2] Although these compounds, of the type $(ET)_2X$ [$X = I_3$, IBr_2, AuI_2, $Cu(SCN)_2$], exhibit highly anisotropic properties, they are 3D superconductors.[3] The organic conductor $(ET)_4Hg_{2.89}Br_8$, which has two incommensurate sublattices and which exhibit the properties of a 2*D* superconductor with $T_c = 4.3$ K, was recently synthesized.[4,5] As was shown in Refs. 6 and 7, information on the dimensionality of an electron spectrum can be extracted from measurements of the spin-lattice relaxation time T_1 of nuclei in various magnetic fields H. In the present letter we are reporting a study of (a) the static magnetic susceptibility χ over the temperature range 1.3–300 K and (b) the value of T_1 of ^1H nuclei in $(ET)_4Hg_{2.89}Br_8$ over the temperature range 4.5–310 K at frequencies of 33, 45, 64, and 90 MHz ($H = 7.8$, 10.6, 15.0, and 21.1 kOe, respectively). The χ measurements were carried out by the Faraday method in fields up to 10 kOe. The T_1 measurements were carried out on a Bruker SXP pulsed NMR spectrometer. The sample consisted of a set of randomly oriented single crystals with a total mass of 20 mg.

Figure 1 shows the temperature dependence of the spin magnetic susceptibility χ_s, which we found by subtracting from the measured values of χ the diamagnetic component from filled electron shells ($\chi_d = -2.87\times10^{-4}$ cm^3/mole according to the Pascal rules) and the small impurity ferromagnetic component which corresponds to the presence of 6*ppm* Fe in the sample. We see from Fig. 1 that the value of χ_s is a fairly strong function of the temperature, going through a maximum near 30 K. Below 3.5 K, the susceptibility acquires a diamagnetic component, which depends on H and which is evidently related to the onset of superconductivity. The behavior of $\chi_s(T)$ in $(ET)_4Hg_{2.89}Br_8$ is quite different from the corresponding behavior in the isostructural compound $(ET)_4Hg_{3-\delta}Cl_8$ (Ref. 8).

Figure 2 shows the temperature dependence of T_1^{-1} in $(ET)_4Hg_{2.89}Br_8$ in a 21.1-kOe field. Above 170 K the relaxation rate increases rapidly, and it peaks near 290 K. This behavior of T_1^{-1}, which has also been seen in other ET-based organic conductors,[9,10] is related to a modulation of the internuclear dipole–dipole interaction during thermally activated vibrations of the ET molecules. We are more interested in the region $T < 170$ K, where the dominant relaxation mechanism is the interaction of

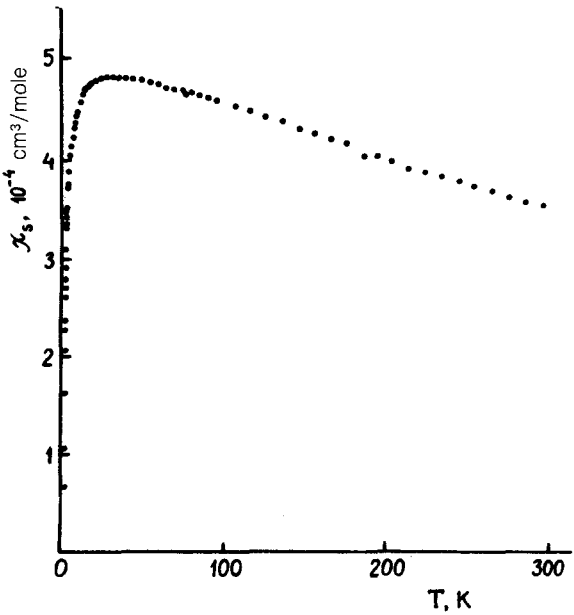

FIG. 1. Temperature dependence of the spin magnetic susceptibility of $(ET)_4Hg_{2.89}Br_8$.

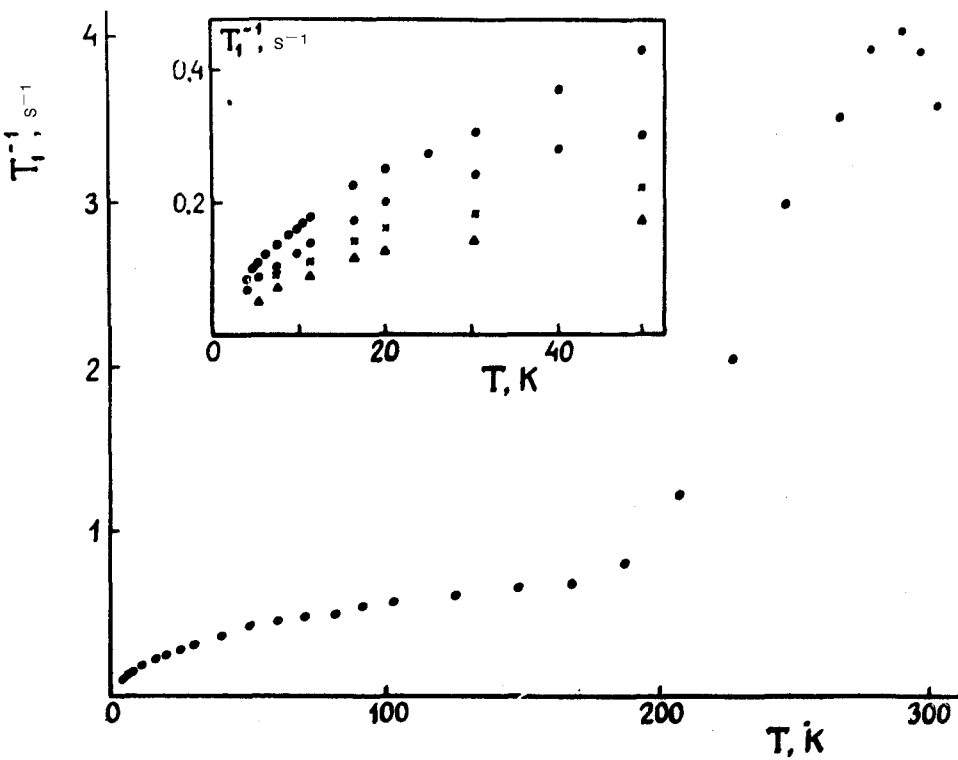

FIG. 2. Temperature dependence of T_1^{-1} of ^{1}H nuclei in a 21.1-kOe field. The inset shows the low-temperature part of the dependence $T_1^{-1}(T)$. ▲—$H = 7.8$; ×—10.6; ○—15.0; ●—21.1 kOe.

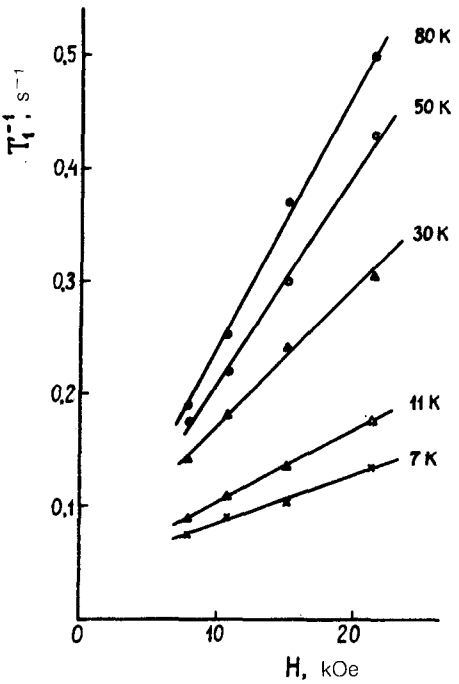

FIG. 3. Dependence of T_1^{-1} on the magnetic field at various temperatures.

nuclear spins with conduction electrons. Ordinary metals exhibit a Korringa temperature dependence ($T_1^{-1} \propto T$) in this region, and the relaxation rate is independent of the magnetic field. A Korringa behavior of T_1^{-1} at low temperatures has also been observed in the ET-based organic conductors studied previously.[9,10] For $(ET)_4Hg_{2.89}Br_8$ the temperature dependence of T_1^{-1} is nonlinear; furthermore, there is a rapid increase in T_1^{-1} with increasing H (see the inset in Fig. 2). It can be seen from Fig. 3 that over the range of magnetic fields studied the dependence $T_1^{-1}(H)$ can be approximated by linear functions at various temperatures.

This field dependence of the spin-lattice relaxation rate in a metal is quite unusual. Other relaxation mechanisms which might be operating (e.g., mechanisms associated with low-frequency fluctuations of the hyperfine magnetic fields or the presence of paramagnetic impurities) could only result in a decrease in T_1^{-1} with increasing H. The particular features of spin diffusion in quasi-1D and quasi-2D metals[6,7] should also lead to a decrease in T_1^{-1} with increase in H. To obtain additional information about the spin-lattice relaxation mechanism, it is useful to analyze the experimental data on the basis of the generalized Korringa relation

$$T_1^{-1} = \frac{4\pi k_B T}{(g\mu_B)^2 \hbar} \chi_s^2 a_H^2 F , \qquad (1)$$

where a_H is the hyperfine interaction constant, g is the electron g-factor, μ_B is the Bohr magneton, and F is the amplification factor. The temperature dependence of χ_s

at $T > 30$ K can explain (at least qualitatively) the deviations from a linear $T_1^{-1}(T)$ dependence. If we use the estimate[10] $a_H \approx 1$ Oe, we find $F \gtrsim 3$ from (1) at low temperatures and at $H = 21.1$ kOe. On the other hand, if we extrapolate the data on T_1^{-1} to $H = 0$, we find values $F < 1$, which are characteristic of both ordinary metals and the $(ET)_2X$ organic conductors which have been studied previously.[10] It can thus be concluded that a relaxation amplification mechanism whose effectiveness increases with increasing magnetic field is operating in $(ET)_4Hg_{2.89}Br_8$.

An increase in T_1^{-1} with increasing H has been observed previously only for ^{199}Hg nuclei in the quasi-2D metal $Hg_{3-\delta}AsF_6$ with an incommensurate mercury sublattice.[11] A mechanism involving an amplification of T_1^{-1} due to a cyclotron motion of electrons in orbits of very small radius has been propsoed[11] in order to explain those results. These orbits would arise because of the incommensurate nature of the Hg chains. We would like to point out that a mechanism of this sort could operate only in pure metals, where the condition $\omega_c \tau > 1$ would hold (ω_c is the cyclotron frequency, and τ the relaxation time of the electron momentum). Although the compound $(ET)_4Hg_{2.89}Br_8$ is also a quasi-2D conductor, and although it has an incommensurate mercury sublattice, its conductivity is low,[4] and the condition which we just specified should not hold for it. For highly disordered conductors, T_1^{-1} is typically amplified with increasing resistance,[12] but an increase in T_1^{-1} with increasing H is not predicted. The observed field dependence of T_1^{-1} in $(ET)_4Hg_{2.89}Br_8$ could thus hardly be explained on the basis of the models which have been discussed in the literature. The incommensurate nature of the two sublattices in this compound is apparently playing an important role here. Because of this situation, the Fermi surface should be complex. It is possible that the amplification of T_1^{-1} with increasing H is caused by the effects of a partial localization of electron states of the incommensurate 2D metal in a magnetic field. Further information on the relaxation mechanism may be provided by measurements of T_1 in stronger magnetic fields.

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