Precursor Effects of Superconductivity up to 35°K in Layered Compounds*

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Diamagnetic anisotropy associated with the transition into the superconducting state in intercalated TaS_2 crystals is seen above 35°K. The anisotropy grows inversely with temperature obeying roughly a diamagnetic Curie law. It seems plausible to ascribe it to electron correlations which at lower temperature are responsible for the superconductivity.

We have studied the magnetic susceptibility in layered crystals of $TaS_2(\text{pyridine})_{1/2}$ and $TaS_2(\text{aniline})_{3/4}$ as a function of temperature and orientation. The preparation, structure, and superconducting properties of the crystals have been recently described.[1-3] Briefly, they consist of metallic TaS_2 layers 6 Å thick separated by organic layers that are ordered and 6 Å thick in the case of pyridine, and disordered and 12 Å thick in the case of aniline. Both the pyridine and aniline crystals have been shown to be bulk superconductors with the onset of superconductivity near 3.7 and 3.1°K as determined by heat-capacity and ac susceptibility measurements.[3] We were led to the present study hoping to find anisotropic effects associated with crystal structure that might not be so sensitive to crystal defects as the electrical conductivity. As can be seen in Fig. 1, the anisotropy is strongly temperature dependent, and it seems to be associated with the superconducting transition. This association is made firm by the fact that a number of samples with different organic intercalates have been studied and they all show the same kind of behavior. Some other possible spurious causes of the observed temperature dependence have been considered and eliminated as discussed below.

Gollub, Beasley, and Tinkham[4] studied fluctuation phenomena in bulk lead using very sensitive equipment. These authors observed a diamagnetic contribution to the susceptibility up to 16°K $\approx 3T_c$. Current theories[5] suggest that in samples with confined geometry like thin films, a stronger temperature dependence of the susceptibility may occur. The small volume of such samples makes detection of the effect very difficult. In our crystals this aspect is circumvented since

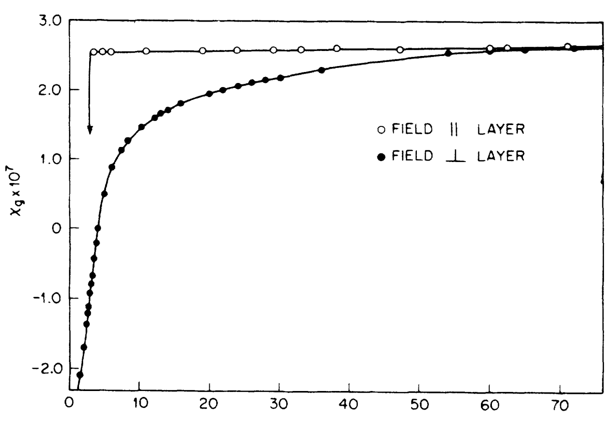

FIG. 1. Magnetic susceptibility per gram of $TaS_2(\text{pyridine})_{1/2}$ as a function of temperature. $\chi_\perp$ ($\chi_\parallel$) was measured with the applied field perpendicular (parallel) to the layers. The points above 5°K were taken from several samples and field values between 1 and 8 kOe. No magnetic field dependence within experimental errors (size of the dots) was observed.

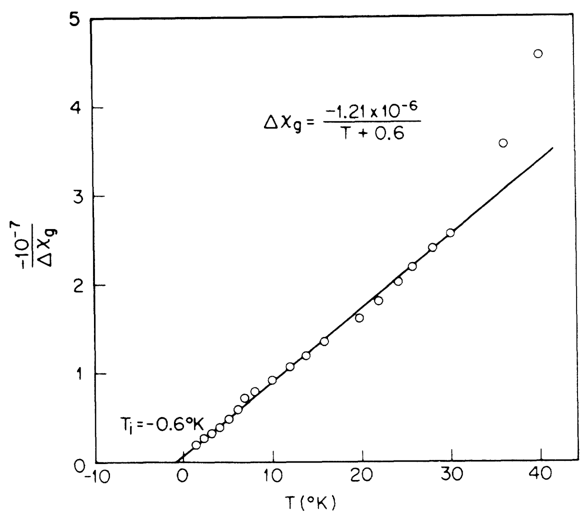

FIG. 2. Inverse of the difference between $\chi_\perp$ and $\chi_\parallel$ plotted as a function of temperature.

there are typically at least 10^6 layers. The surprising feature of the intercalated system is that the fluctuations appeared to persist even in fields up to 10 kOe thus making the experiment possible with conventional means. Theories[5] predict a diamagnetic Curie law (diamagnetism inversely proportional to temperature) but are only applicable near T_c and not in the range of our measurements.[6] We therefore do not attempt to fit the data with any theoretical function. However as discussed below, and illustrated in Fig. 2, the anisotropy is roughly fitted by a diamagnetic Curie law.

The data were taken in a Faraday balance of high sensitivity. The magnetic field and gradient were produced by an electromagnet so that a horizontal field of from 0.4 to 8 kOe could be used.

The upper curve in Fig. 1 is the magnetic susceptibility for the magnetic field parallel to the layers, $\chi_\parallel$, and the lower curve for the field perpendicular to the layers, $\chi_\perp$. Above 50°K both orientations show a slightly temperature-dependent paramagnetism which, within the present experimental limit, is the same. Below 50°K a diamagnetic component in $\chi_\perp$ appears and grows. The total change in $\chi_\perp$ shown in Fig. 1 is quite small and amounts to about 0.01% of a full superconducting transition. Consequently all possible contributions to the susceptibility must be considered. The pyridine and aniline used in the preparation of the complexes have been separately measured and found to have negative susceptibilities with small positive temperature dependences between room temperature and 4°K. The crystals of TaS_2 starting material (2*H* phase) show a small increase of χ with decreasing *T*.[7] The intercalation complexes were prepared as previously described[2] by heating the TaS_2 and organic liquid in sealed Pyrex tubes at 150°C for several days. The observed diamagnetic contribution as the temperature is lowered below 40°K is a property of the intercalated crystal, not the starting materials. Of the many different contributions to the magnetic susceptibility of metal-organic compounds, none are known to have the observed temperature dependence. The temperature dependence could be due to a sluggish low-temperature phase transition from a paramagnetic to a diamagnetic state. However, there is no observable dependence of the measured susceptibility upon either the rate or the direction of temperature change. The data for $\chi_\perp$ in Fig. 1 are for three batches of pyridine intercalated crystals of different sizes and shapes. Other intercalation compounds also show roughly the same diamagnetic component although results at present are not complete.

In view of the above we feel justified in relating the decrease of the susceptibility below 40°K for $\chi_\perp$ to the superconducting transition. In order to isolate the superconducting component of the susceptibility it is necessary to draw a base line which includes all the other contributions. This is not possible to do from first principles. The usual practice in isolating any temperature-dependent term in the susceptibility is to subtract out a base line extrapolated from a region where there is little or no temperature dependence. The anisotropic nature of the complexes makes it possible for us to be somewhat less arbitrary. Since above 60°K the slope and magnitude of $\chi_\parallel$ and $\chi_\perp$ are equal within experimental error and intuitively no enhanced contributions to $\chi_\parallel$ are expected above T_c, $\chi_\parallel$ is chosen as the baseline. In fact we find that $\chi_\parallel$ maintains its high-temperature slope down to 4°K. Figure 2 shows that Curie-Weiss-like diamagnetic behavior is roughly followed over the whole temperature range below 30°K. The oscillations around the straight line may be of significance but there remains a large experimental uncertainty in the highest-temperature points due to the choice of base line. The data for the aniline compound also show a Curie-Weiss diamagnetic behavior with a slope smaller by about 25%.

No magnetic field dependence of the pyridine sample susceptibility was observed above 4°K.

The points shown in Fig. 1 are for fields from 1 to 8 kOe. This result was unexpected and may ultimately prove important in establishing a detailed model. It is perhaps not so surprising however to find that fluctuations which exist so far above T_c can also exist far above $H_{c2\perp}$. $H_{c2\perp}$ was determined to be 900 ± 200 G at 1.6°K for the pyridine crystal by taking a magnetization curve using a modified version of the Faraday balance with reduced sensitivity. $H_{c2\parallel}$ at the same temperature was found in the same apparatus to be >18 kOe, the limit of the measuring field. We found a higher limit for H_{c2} by observing that the resistive transition is only depressed by 0.5°K in 60 kOe. This value of $[dH_c/dT]_{T=T_c}$ is greater than that for any known superconductor and suggests that intercalation compounds may have useful high-magnetic-field properties. The effects of higher magnetic fields are being pursued. It seems clear, however, that the anisotropy ratio of H_{c2} is >100. The theory of Lawrence and Doniach[8] relates this ratio to the square root of the conduction-electron effective masses in the two directions and hence to the electrical conductivity.

Evidence of fluctuation effects has also been seen in conductivity measurements along the layers of one $TaS_2(\text{pyridine})_{1/2}$ crystal up to 10°K. However the results to date are sample dependent, apparently being quite sensitive to sample perfection.[3] Hake[9] has reported evidence for fluctuation effects from measurements of magnetoresistance of short-coherence-distance alloys at $\sim 3T_c$ and in fields as high as 40 kOe.

One of the motivations of our study of superconductivity in layered structures was to examine the properties of electrons constrained to flow in two dimensions. The present work shows that under such constraints the electron correlations which eventually cause superconductivity give rise to a measurable diamagnetic term at unexpectedly high temperatures and rather high applied magnetic fields.

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[5]See, for example, A. Schmid, Phys. Rev. 180, 527 (1969).

[6]Application of the model of B. R. Patton, V. Ambegaokar, and J. W. Wilkins [Solid State Commun. 7, 1287 (1969)] suggests that the diamagnetic fluctuations will maintain a Curie-Weiss-like behavior for $T \gg T_c$ and $H \gg H_{c2}$ if the effective fluctuation cutoff energy is sufficiently large. S. Doniach, private communication.

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