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Superconductivity in Layered Compounds with Variable Interlayer Spacings*

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The superconducting heat-capacity anomaly of intercalated $\mathrm{TaS_2}$ compounds is independent of the spacing between the $\mathrm{TaS_2}$ layers when the spacing is varied between 3 and 30 Å. We conclude that the entropy associated with the anomaly arises mainly from two-dimensional correlations.

We have studied the heat capacity and low-frequency magnetic susceptibility of a number of superconducting layered compounds as functions of the interlayer separation. The results show that the superconductivity is a bulk property, that is, all the conduction electrons take part in the superconducting transition, and furthermore they suggest that the superconducting heat-capacity anomaly is mainly a two-dimensional phenomenon.

Superconductivity in the layered compound $\mathrm{TaS_2(pyridine)_{1/2}}$ has been reported previously.[1] The preparation and some of the chemical and physical properties of this and other intercalation compounds has also been studied.[2] Briefly, when $\mathrm{TaS_2}$ is treated with molecules that are sufficiently strong Lewis bases, the molecules penetrate between the individual $\mathrm{TaS_2}$ layers (intercalate) and form a periodic structure. The separation δ of the 6-Å-thick metallic $\mathrm{TaS_2}$ layers depends upon the molecule used and in some cases the particular intercalation conditions, but the $\mathrm{TaS_2}$ layer itself remains intact with intraplanar spacings almost unchanged. The intercalation compounds are usually stoichiometric and possess a high degree of registry from layer to layer in all three dimensions, indicating that the organic molecules are also ordered between the $\mathrm{TaS_2}$ planes.[3] However, in some compounds specifically noted below, the $\mathrm{TaS_2}$ layers are randomly placed over each other; the spacing δ between the layers is still uniform but the layers have no horizontal registry. This randomness in the $\mathrm{TaS_2}$ stacking indicates a high degree of disorder in the organic molecular arrangement and is also reflected in the fact that the disorder compounds are generally nonstoichiometric.

As would be expected from their structure, the physical properties of these materials are quite anisotropic. But because large, good, single crystals have not been prepared, the measurements of anisotropy can only place limits on the ratio of particular properties along the planes ($\parallel$) to those perpendicular ($\perp$). For example, in $\mathrm{TaS_2(pyridine)_{1/2}}$ ($\delta \sim 6$ Å) the critical field ratio $H_{c2\parallel}/H_{c2\perp}$ at $T = 1.5$°K is > 80 with $H_{c2\parallel}(T = 1.5\text{°K}) \gg 60$ kG.[4] The Ginzburg-Landau parameter κ is also anisotropic and can be estimated from measured H_{c2} and H_{c1} values, $\kappa_\perp \simeq 1.5$ and $\kappa_\parallel \simeq 15$. The resistance ratio is harder to determine because our imperfect crystals apparently have some very small interlayer shorts and cracks; however, we believe that $\rho_\perp/\rho_\parallel > 10^4$. The critical current-density ratio is probably quite unreliable because of these shorts but $J_{c\parallel}/J_{c\perp}$ is at least 10^3. To our knowledge these superconducting compounds are the most anisotropic known.

The ac magnetic susceptibility (~18 Hz) is measured in low fields (0.05–5.0 G) by the usual low-frequency inductance method.[5] The heat capacity was measured from 1 to 10°K on small amounts (~100 mg) of the material by a method developed in our laboratory.[6] The accuracy of a given datum point in this particular set of measurements is $\simeq 2\%$.

$\mathrm{TaS_2}$ in the 2H phase is superconducting (T_c

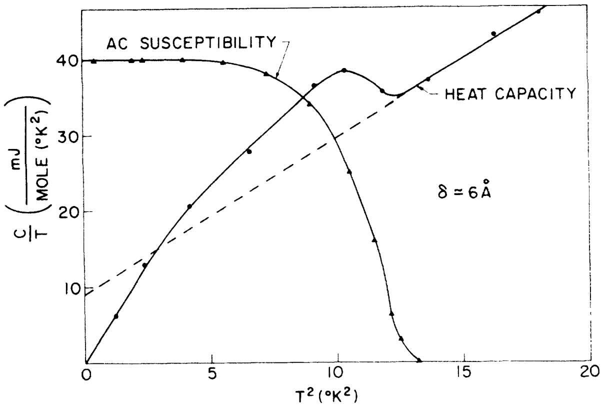

FIG. 1. The measured heat capacity and magnetic susceptibility of $TaS_2(pyridine)_{1/2}$ from 1 to 4.5°K. The normal-state extrapolation is shown as a dashed line.

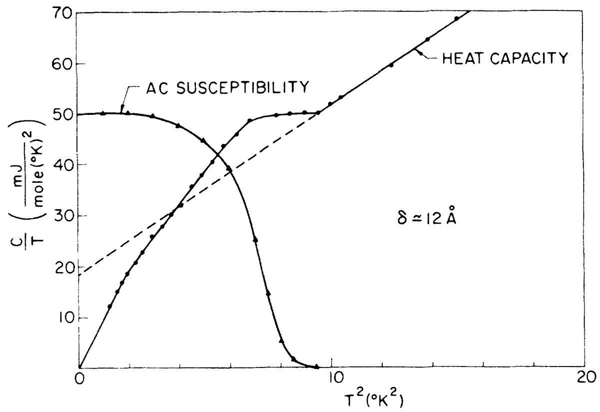

FIG. 2. The measured heat capacity and magnetic susceptibility of $TaS_2(aniline)_{0.75}$ from 1 to 4.5°K. The specific-heat anomaly appears smaller in this sample than in $TaS_2(pyridine)_{1/2}$ for two reasons: The contribution to the background is larger because there is more organic material per TaS_2 and the normal-state extrapolation (shown as dashed line) is not valid for this sample (see text). In fact the two anomalies are quite similar.

= 0.8°K) and the smoothed heat-capacity measurements from 1 to 10°K are fitted by C (mJ/mole °K) = $8.50T + 0.370T^3 + 1.4\times10^{-4}T^5$. The data from 1 to 4.5°K for two intercalated samples are shown in Figs. 1 and 2. In Fig. 1, C/T (mJ/mole °K^2) and the ac magnetic susceptibility are plotted versus T^2 for the sample $TaS_2(pyridine)_{1/2}$. (At low T the sample is completely diamagnetic.) In this compound two molecular packing arrangements are possible, one with $\delta \simeq 5.8$ Å and the other with $\delta = 6.0$ Å; interlayer order is observed in both. This sample had about an equal amount of both phases. The electronic specific-heat coefficient γ is obtained from the intercept of the normal-state heat capacity extrapolated from above the transition; the low-temperature phonon heat-capacity coefficient β is obtained from the extrapolated line slope. Only a small part of the normal region can be used in this extrapolation because the phonon part of C above 5°K varies as T^2, indicating a soft branch (as in the other two-dimensional structure, graphite[7]). The γ and β obtained from extrapolation are consistent with the third law of thermodynamics in that the same entropy above the transition is calculated when using either the extrapolated normal-state heat capacity or the measured superconducting heat capacity.

In Fig. 2 the same plot is shown for $TaS_2(aniline)_{0.75}$. In this compound the TaS_2 planes are ordered only in one dimension ($\delta = 12.1$ Å), thus the organic layers must be highly disordered or "amorphous." The entropy calculated from a straightforward extrapolation of the normal-state curve is much larger than that calculated from the superconducting state. Consequently, the extrapolation from above T_c is not valid for this sample. In fact the extrapolated normal-state intercept on the C/T axis is about twice that obtained for the three-dimensionally ordered compounds.

For all the samples C/T vs T^2 in the superconducting state extrapolates to zero (or at least $<0.05\gamma$) at $T = 0$. It is clear that the normal linear electronic term is not present and that a gap has been introduced into the electron excitation spectrum. To the extent that the extrapolated value is zero, all the conduction electrons must take part in this transition; the superconductivity is a *bulk* property.

In the single-phase intercalated TaS_2, the transitions observed in both the heat capacity and susceptibility measurements are broad. Even though there is no clear way to compare quantitatively the transition widths observed in these two measurements, the susceptibility transition is at least as broad as the heat-capacity transition. Also, we have observed the susceptibility transition in over 100 single-phase intercalated samples prepared in different ways with different molecules and layered superconductors, and have always found a width of 0.5 to 1.0°K.[8] The transition temperature and shape are independent of interlayer spacing (see below and Ref. 2), and in the two-phase samples (different δ's present) the width is about the same as in the single-phase samples. Consequently, it appears that even in

TABLE I. Samples used in heat-capacity measurements. The columns list the organic intercalate (molecule), the ratio of molecules to TaS_2 (x), the separation between the TaS_2 layers (δ), the temperature at which the onset of the anomaly is observed in these heat-capacity measurements (T_{onset}), the electronic and phonon specific-heat coefficients γ and β, the maximum height of the heat-capacity anomaly $\Delta C/\gamma T_{onset}$, and the TaS_2 stacking arrangement.

$(\text{Molecule})_x$	δ (Å)	T_{onset} (°K)	γ (mJ/mole °K^2)	β (mJ/mole °K^2)	$\Delta C/\gamma T_{onset}$	Interplanar stacking
Pure TaS_2	0	0.8	8.5 ± 0.1	0.370	...	ordered
$(\text{2, 6-dimethylpyridine})_{1/5}$	3.55	2.8	9.5 ± 0.4	1.65	0.65 ± 0.07	ordered
$(\text{pyridine})_{1/2}$	5.8[a] 6.0	3.7	8.9 ± 0.4	2.07	0.8 ± 0.1	ordered
$(\text{3-ethylpyridine})_{0.29}$	5.3	3.2	...	...	0.8 ± 0.15	random
$(\text{aniline})_{0.75}$	12.1	3.06	...	...	0.7 ± 0.15	random
$(\text{octadecylamine})_{0.58}$	29[a] 45	3.05	...	...	0.8 ± 0.2	random

[a] Two molecular stacking arrangements are observed in these compounds. These different phases can be labeled by different δ's.

the two-phase materials, the transition width is not due to different molecular arrangements. It remains a remote possibility that *all* of these intercalated superconductors have some undetected inhomogeneities that cause a broadened transition; however, we believe that most of the broadened transition is intrinsic to these materials.

Some of the parameters extracted from data taken on six samples are given in Table I. T_{onset} is the temperature at which the beginning of the anomaly is observed in these heat-capacity measurements. The γ and β obtained by extrapolation from above T_{onset} are shown only if this extrapolation of the normal-state data is consistent with the third law. We have not defined a critical transition temperature because there is no sharp singularity in either the specific heat or the susceptibility. To do so would imply that there was a phase transition at that temperature into the superconducting state.

From the table several things may be noted. First, the T_{onset} does not correlate with δ. Second, those samples for which γ could not be obtained by extrapolation of the normal-state heat capacity have highly disordered molecular layers while the ordered intercalated materials have γ values only slightly higher than the unintercalated TaS_2. Note in particular that the two samples with δ approximately 6 Å have about the same T_{onset}, but in the disordered material the extrapolation is not valid. We believe the extrapolation fails to be consistent with the third law because the phonon part of the heat capacity in the disordered materials increases somewhat faster than T^3 in a part of the region 0–4°K. This is an unusual occurrence in solids, previously observed only in bulk amorphous glasses and polymers.[9,10] We suggest, then, that it is the disordered molecules in these materials that cause this noncubic temperature dependence.[11]

Since the measured γ value in the ordered intercalates is practically insensitive to δ, we assume that γ for the disordered materials is $\simeq 9.5$ mJ/mole °K^2, as for the ordered compounds. If we further make the reasonable assumption for the disordered materials that just below T_{onset} the normal-state heat capacity does not markedly deviate from the extrapolation from above T_{onset}, we can roughly estimate the maximum size of the heat-capacity anomaly $\Delta C/\gamma T_{onset}$ due to the superconducting transition. From the table it is apparent that within the rather large estimated errors $\Delta C/\gamma T_{onset} \approx 0.7$, independent of δ. The usual BCS result $\Delta C/\gamma T_c \simeq 1.43$ is measured in other bulk or "three-dimensional" superconductors at the transition temperature T_c where the heat capacity shows a discontinuous jump and is the result obtained for pure TaS_2.[12] The maximum in the heat-capacity anomaly is observed in all the samples at about 0.4 ± 0.1°K below T_{onset}.

Since the approximate width and shape of the heat-capacity anomaly are independent of δ, we believe that most of the entropy associated with the heat-capacity anomaly arises from two-dimensional correlations. Evidence for two-dimensional diamagnetic fluctuations is found well above T_c in these compounds.[4,13] Although the other measured physical properties are highly anisotropic, they (like the critical current density) show that there is some weak coupling between the layers. At small enough δ there can be Josephson tunneling and in all of these materials there are apparently a few very small interlayer "shorts." However, these possible coupling mechanisms have little effect upon the heat-capacity transition when $3 < \delta < 30$ Å.

This work raises a number of experimental and theoretical problems. Is it necessary that a three-dimensional ordering or phase transition take place for "superconducting-like" properties to be observed, such as apparent zero or immeasurably low resistance with large upper critical fields? If the interlayer coupling is necessary, how strong must it be? If this coupling occurs, a sharp or λ-like anomaly should be associated with it, but will there be enough entropy for the anomaly to be observable? In a somewhat analogous situation, inelastic neutron scattering shows that in the planar antiferromagnet K_2NiF_4, coupling in the third dimension, however weak, seems necessary for the phase transition to occur, and that magnetic fluctuations that are two-dimensional in character can be followed considerably above the Néel temperature.[14]

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