Fluctuation-induced diamagnetism and dimensionality in superconducting layered compounds: $TaS_2(pyridine)_{1/2}$ and $NbSe_2$†

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(Received 5 January 1977)

The results of an investigation of fluctuation-induced diamagnetism in superconducting layered compounds are presented. These results are used to establish the dimensionality of the superconducting fluctuation effects near T_c. Compounds studied include the intercalated compound $TaS_2(pyridine)_{1/2}$, and unintercalated $NbSe_2$ and $TaS_{1.6}Se_{0.4}$. The susceptibility above T_c, and magnetization in the superconducting state, were measured in fields up to 327 Oe with a superconducting quantum-interference magnetometer suitable for a broad range of sensitive magnetic measurements. The operation and performance of this magnetometer are described. Results for $TaS_2(pyridine)_{1/2}$ indicate that in low fields and near T_c, the fluctuation effects are three-dimensional in nature, where this is established via a comparison with previous results for an isotropic alloy, Pb–5-at.% Tl. This conclusion as to the dimensionality of the superconducting effects is in accord with the qualitative predictions of the Lawrence-Doniach theory for weakly-coupled superconducting layers. Data for $NbSe_2$ have a number of complicating features, and firm conclusions regarding this material could not be drawn.

I. INTRODUCTION

Layered transition-metal dichalcogenides with organic molecules intercalated between the metallic layers form a novel class of superconductors with most unusual structural and superconducting properties.[1] Their structure consists of a crystalline arrangement of thin (~ 6 Å) metallic layers each separated by a layer of organic molecules, as shown in Fig. 1. The separation between metallic layers, δ, can vary from 3 to ~ 50 Å depending on the organic molecule used. These intercalated compounds were first reported to be superconducting by Gamble and co-workers in 1970,[1] and there has been considerable interest in characterizing and understanding the nature of the superconductivity in these layered structures, the dimensionality of the superconducting properties, and the mechanism of superconducting coupling between metallic layers. The layered superconductors have also been of considerable importance as model quasi-two-dimensional superconducting systems, and as such have served to establish some of the general characteristics expected for other superconducting systems of quasireduced dimensionality, for example, the recently discovered quasi-one-dimensional superconductor $(SN)_x$.

In this paper we present the final results of an experimental investigation of the fluctuation-induced diamagnetism above the superconducting critical temperature T_c undertaken to establish the dimensionality of the superconductivity in these superconductors. We also carefully discuss the relevant theoretical issues and the delicate experimental and data-analysis procedures required to use fluctuation effects in superconductors to establish dimensionality. This use of fluctuation effects has proved to be of continuing interest; however, considerable care must be used to obtain sensible and self-consistent results.

The diamagnetic contribution to the susceptibility above T_c of specific concern in this paper is a precursor to the perfect diamagnetism of the superconducting state, and can be understood to arise from small transitory superconducting droplets which exist above T_c due to thermal fluctuations. This effect was first observed in three-dimensional systems by Gollub and co-workers.[2] The results reported here for the fluctuation-induced diamagnetism in layered compounds establish that at least for $TaS_2(pyridine)_{1/2}$, these superconducting fluctuations are three-dimensional

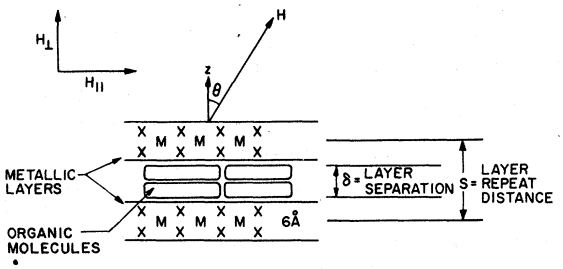

FIG. 1. Schematic of the structure of the intercalated layered compounds, and the definition of field orientations used in this paper. M represents the transition-metal atoms, Ta or Nb and X the chalcogenide atoms, S or Se. The packing structure of the organic molecules has not yet been determined for $TaS_2(pyridine)_{1/2}$.

in nature near T_c, where this is established via a comparison with the earlier results of Gollub. The three-dimensional nature of the superconducting effects near T_c which we observe can be understood to result from the finite *interlayer* coupling, which sufficiently close to T_c leads to superconducting coherence transverse to the layers. Experimental results for the superconducting upper critical fields, which are essential for supplying material parameters used in the comparisons between theory and experiment given below, will be presented in a separate paper.[3]

A number of the features of the superconductivity in layered compounds have been established in previous investigations.[4] A dramatic finding is that T_c is significantly affected by intercalation. For example, the intercalation of pyridine into TaS_2 separates the metallic layers by 6 Å, and increases T_c from 0.8 K for TaS_2 to ~3.5 K for $TaS_2(\text{pyridine})_{1/2}$.[1] It has also been found that T_c depends only weakly on the separation between metallic layers, and that intercalated compounds with the largest layer separations, up to ~50 Å, are superconducting. These findings regarding T_c were of great interest, as it had previously been suggested[5] that such layered structures might exhibit new mechanisms of superconductivity due to interactions between the organic molecules and the electrons in the metallic layers, and that such mechanisms might lead to high superconducting critical temperatures. No evidence has been observed for new mechanisms of superconductivity in the layered compounds studied so far,[6] and it now appears that the enhanced T_c seen for $TaS_2(\text{pyridine})_{1/2}$ is related to the suppression of the low-temperature charge-density-wave state[7] which in TaS_2 occurs below 80 K. The suppression may be due to donation of charge to the metallic layer by the organic molecules.[8]

Another unusual aspect of the superconductivity in layered compounds is the extreme anisotropy of the critical fields,[3,9,10] and critical currents,[11] which depend dramatically on crystal orientation. Orientations of the field perpendicular and parallel to the layers are defined in Fig. 1. Values for $H_{c2\parallel}$ can be very large, with the value for $TaS_2(\text{pyridine})_{1/2}$ exceeding 150 kG. These early measurements established that the properties of layered-compound superconductors were indeed novel, and raised questions as to the effective dimensionality of the superconducting properties and the effect of the quasi-two-dimensional structure on the superconducting properties. However, the early critical-field measurements did not establish explicitly whether the superconducting properties were two-dimensional or three-dimensional in nature, nor did they establish the nature of the superconducting coupling between the metallic layers.

The first evidence regarding the dimensionality of the superconducting properties was provided by measurements of specific heat at the phase transition.[12] Large transition widths were observed for all intercalated compounds, and these were found to be independent of the separation between layers. This result was interpreted as providing qualitative evidence that the phase transition was two-dimensional in character.

Some rather intriguing measurements of magnetic susceptibility above T_c for $TaS_2(\text{pyridine})_{1/2}$ were also reported by Geballe, Menth, and coworkers,[13] who observed a diamagnetic contribution to the high-field magnetic susceptibility which increased as the temperature was decreased from ~40 to 2 K. Since this diamagnetic contribution was observed only for the applied field oriented perpendicular to the layers, it was ascribed to superconducting fluctuations above the transition temperature. The temperature dependence of the diamagnetic susceptibility was found to fit the Curie-Weiss-like theoretical form predicted by Schmid[14] on the basis of the Ginzburg-Landau theory for the fluctuation-induced diamagnetism of a thin film, although the extrapolated divergence of the experimental data was at -0.6 K, and not T_c. Also, as noted in the report of the experimental results, the theoretical form predicted for a two-dimensional system (independent layers) was expected to be valid only for small magnetic fields and near T_c, whereas the measurements were made in large fields (to 8 kOe) and extended to $\sim 10T_c$. Therefore, the significance of these susceptibility results in establishing the dimensionality of the superconducting properties was uncertain.

These early susceptibility measurements did suggest, however, that a quantitative test of the dimensionality of the superconducting properties might be provided by a measurement of the fluctuation-induced diamagnetism in the low-field region near T_c. Such measurements were carried out by the authors for a number of layered-compound superconductors, and have employed an extremely sensitive superconducting quantum-interference magnetometer to study in low fields the diamagnetic contribution to the susceptibility above T_c. Preliminary results of these measurements have been reported previously,[15] and an interpretation in terms of two-dimensional fluctuation effects was presented at that time. In this paper we present more extensive results of these measurements. We also present a revised interpretation of these data, as the theoretical results from the Lawrence-Doniach theory upon which our previous interpretation was based are now known to be inadequate for the temperature range for which com-

parisons were made (see discussion in Sec. II).

The low-field susceptibility data obtained by the authors for $TaS_2(pyridine)_{1/2}$ in fact differed significantly from the high-field data reported by Geballe, Menth, and co-workers. In order to understand these differences, DiSalvo[16] repeated the high-field susceptibility measurements, investigating the field dependence of the susceptibility. His results show that, in large part, the diamagnetic contribution observed at high fields by Geballe *et al.* resulted from an unusual peak in the susceptibility which is observable in pure $2H$-TaS_2 at ~80 K (the onset temperature for the charge-density wave state), and which in $TaS_2(pyridine)_{1/2}$ appears to produce a much weaker magnetic anomaly and a slowly decreasing susceptibility below 80 K. Apparently only a small part of the diamagnetic contribution to the susceptibility at high fields is due to superconducting fluctuations. The measurements reported in this paper, in contrast, are all made in small fields where the contribution due to superconducting fluctuations is expected to dominate.

The organization of this report is as follows. The Lawrence-Doniach model for layered superconductors and its limiting form near T_c, the anisotropic Ginzburg-Landau theory, are discussed in Sec. II. The theoretical predictions for the fluctuation-induced diamagnetism based on this model, and those based on the microscopic Gor'kov theory, are presented. A description of the superconducting quantum-interference magnetometer used in these measurements is contained in Sec. III. Sample preparation and characteristics are outlined in Sec. IV. In Sec. V we present the experimental results for the compounds studied, $TaS_2(pyridine)_{1/2}$, $NbSe_2$, and $TaS_{1.6}Se_{0.4}$. A discussion of these results and their relation to other experiments is presented in Sec. VI.

II. THEORETICAL CONSIDERATIONS

The Lawrence-Doniach (LD) model[17] for superconductivity in layered compounds pictures a stacked array of thin superconducting layers which are weakly coupled by Josephson tunneling between adjacent layers. This model has proven to be a useful starting point in describing the properties of layered-compound superconductors, and it provides a physical understanding of more recent theoretical work based on the microscopic Gor'kov theory. We shall therefore develop in some detail the predictions of the LD theory, and also present results from the microscopic theory.

A. Lawrence-Doniach model

Within the LD model, the superconducting order parameter Ψ_l within a given layer l is assumed to obey the two-dimensional Ginzburg-Landau (GL) equations within the layer, and to be weakly coupled to the order parameter in adjacent layers. The original equations[17] have been extended[18,19] to include the effects of a large magnetic field parallel to the layers. For the time-independent case, the full LD equation is given as

$$\alpha\Psi_l+\beta|\Psi_l|^2\Psi_l+\frac{\hbar^2}{2m}\left(\vec{\nabla}+\frac{2ie}{hc}\vec{A}\right)^2\Psi_l - \eta(\Psi_{l+1}e^{-2ieA_zs/\hbar c}-2\Psi_l+\Psi_{l-1}e^{2ieA_zs/\hbar c})=0\,. \quad (1)$$

In this equation, α and β are the usual GL material parameters in the dirty limit, $\alpha(T)=\alpha'(T-T_c)/T_c$ and β independent of temperature, and m is the pair mass for motion within the layer; $\vec{\nabla}$ acts in the layer plane; $\vec{A}$ and A_z are the components of the magnetic vector potential parallel and perpendicular to the layers, respectively; s is the layer repeat distance (in the z direction), and η is the tunneling parameter characterizing the strength of the interlayer coupling. Equation (1) can be derived from a microscopic theory in which the single-particle states have the tight-binding form for propagation in the direction perpendicular to the layers.[18]

An important aspect of the theory, which was noted by Lawrence and Doniach, is that as $T\to T_c$, Eq. (1) reduces to the result from the Ginzburg-Landau theory[20] for an anisotropic, three-dimensional superconductor. (We consider a superconductor three-dimensional if its properties can be described in a simple tensorial fashion. The temperature dependence of these properties would be the same as for an isotropic superconductor.) Because (1) reduces to the anisotropic GL result, near T_c all superconducting properties of layered compounds are expected to be three-dimensional in nature, despite the layered structure of the material. This is because near T_c, Ψ varies slowly on the scale of the layer repeat distance s and therefore effectively averages over the finer-scale layered structure. The slow spatial variation of the order parameter near T_c is characteristic of such theories of second-order phase transitions. Since the anisotropic-GL theory provides a good first approximation for describing the properties of the compounds we have investigated, we shall discuss these results first.

To examine the behavior in the region near T_c, the Josephson-tunneling (difference) term in (1) may be expanded in a Taylor series, with the leading term a second derivative. Combining this term with the kinetic energy term in (1) yields the usual anisotropic GL equation[20]:

$$\alpha\Psi+\beta|\Psi|^2\Psi + \frac{\hbar^2}{2}\left(\vec{\nabla}+\frac{2ie}{\hbar c}\vec{A}\right)\cdot\left(\frac{\vec{\vec{1}}}{m}\right)\cdot\left(\vec{\nabla}+\frac{2ie}{\hbar c}\vec{A}\right)\Psi=0, \quad (2)$$

where $\vec{\nabla}$ and $\vec{A}$ are respectively the full gradient operator and magnetic vector potential and $(\vec{\vec{1}}/m)$ is an effective-mass tensor given as

$$\left(\frac{\vec{\vec{1}}}{m}\right)=\begin{bmatrix}\frac{1}{m} & 1 & 1\\ 0 & \frac{1}{m} & 0\\ 0 & 0 & \frac{1}{M}\end{bmatrix}. \quad (3)$$

The pair mass M for propagation in the z direction, normal to the layers, is given by

$$M=\hbar^2/2s^2\eta$$

so that M is inversely proportional to the coupling strength η. For weak interlayer coupling, $M\gg m$.

The anisotropy of the effective mass leads to an anisotropy of the temperature-dependent (GL) coherence length, which sets the characteristic length scale over which significant variation of Ψ may occur without undue energy cost. Taking $\alpha=\alpha'(T-T_c)/T_c$, the coherence length within a layer, $\xi(T)$, is given by

$$\xi(T)\equiv\left(\frac{\hbar^2}{2m|\alpha(T)|}\right)^{1/2}=\xi(0)\left(\frac{T_c}{|T-T_c|}\right)^{1/2},$$

where $\xi(0)$ may be determined by experiment (see below). Typical values of $\xi(0)$ for the layered compounds investigated are 100–200 Å. We note that $\xi(2T_c)=\xi(0)$.

The coherence length $\xi_z(T)$ sets the length scale over which variations of Ψ in the z-direction may occur, and is given by

$$\xi_z(T)\equiv[\hbar^2/2M|\alpha(T)|]^{1/2}.$$

Thus,

$$\xi_z(T)=\xi_z(0)\left(\frac{T_c}{|T-T_c|}\right)^{1/2}=\left(\frac{m}{M}\right)^{1/2}\xi(T). \quad (4)$$

For weakly-coupled layered compounds $\xi_z(0)$ will be considerably smaller than $\xi(0)$, and may even be comparable to s. For those materials with very weak interlayer coupling, away from T_c it is possible that $\xi_z(T)\lesssim s$, and the order parameter may vary significantly from layer to layer. In such cases, the anisotropic GL limit will no longer apply, and the layered nature of the material must be explicitly taken into account. Even for such cases, however, $\xi_z(0)$ may be defined as in (4), although it will not be the only relevent length scale in the z direction. The condition that $\xi_z(T)>s$ in fact describes quite well the extent of the anisotropic-GL region near T_c; nearly all of our measurements of susceptibility above T_c fall in this temperature region.

Measurements below T_c of the upper critical field H_{c2} can provide a way of directly determining the coherence lengths and the mass ratio, M/m. For the field oriented perpendicular or parallel to the layers, $H_{c2\perp}(T)$ and $H_{c2\parallel}(T)$ are given[17] within the anisotropic-GL theory as

$$H_{c2\perp}(T)=\Phi_0/2\pi\xi^2(T)=(T_c-T)\frac{dH_{c2\perp}}{dT}$$

and

$$H_{c2\parallel}(T)=(M/m)^{1/2}H_{c2\perp}(T),$$

where $\Phi_0=hc/2e=2.07\times10^{-7}$ G cm^2 is the superconducting flux quantum. The anisotropy of the critical fields is equal to $(M/m)^{1/2}$, so that a measurement of the anisotropy provides the mass ratio. Measurement of $H_{c2\perp}(T)$ is needed to provide a value for $\xi(0)$. These predictions of the anisotropic GL theory for H_{c2} are found to describe fairly well the critical field behavior near T_c of the layered compounds.[3]

B. LD theory: Results and comparison to other systems of quasireduced dimensionality

The fluctuation-induced diamagnetism of layered superconductors has been calculated[21] in the low-field limit within the LD model, following the approach introduced by Schmid.[14] In this approach, the LD free energy [from which (1) is derived by a variational calculation] is used to calculate the energy associated with each normal mode, and this energy is used in a computation of the partition function Z of the system. The (unrestricted) free energy is given by $F=-kT\ln Z$. The susceptibility above T_c due to superconducting fluctuations, χ', is then given as $\chi'=-(1/V)\partial^2F/\partial B^2$, with V the volume. For layered super conductors, χ' is anisotropic, and we shall focus primarily on the case where the applied magnetic field H is perpendicular to the layers. This is because χ' is maximum for $H_\perp$ and is therefore much easier to measure; sample alignment is also easier. Finally, calculation of χ' is simpler for the perpendicular field orientation.

For H perpendicular to the layers, the fluctuation-induced diamagnetism within the LD model is found to be:

$$\chi'=-\tfrac{1}{6}\pi kT\Phi_0^{-2}\xi(T)(M/m)^{1/2}\frac{1}{\{1+[\frac{1}{2}s/\xi_z(T)]^2\}^{1/2}}, \quad (5)$$

where k is Boltzmann's constant. This result has the characteristics that in the region near T_c, for

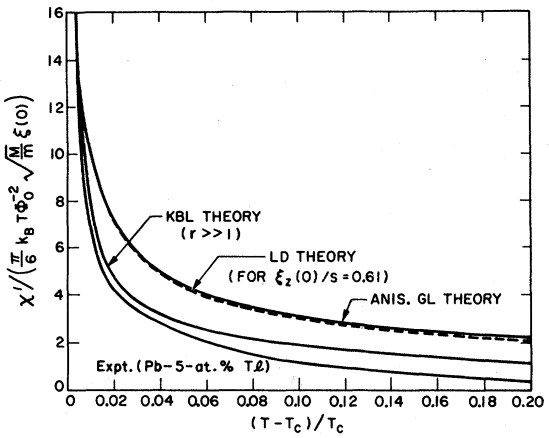

FIG. 2. Fluctuation-induced diamagnetism: theory and experiment. Theoretical curves are the anisotropic Ginzburg-Landau theory, Eq. (6), in the text. The Lawrence-Doniach theory for layered superconductors, Eq. (5), with a value of $\xi(0)/s$ appropriate for TaS_2(pyridine)$_{1/2}$; and the KBL theory for layered superconductors in the isotropic limit ($r \gg 1$). Experimental curve for Pb–5-at.% Tl is from data of Ref. 2 and 28. All curves have been scaled by the same factor, which includes all material parameters and is only weakly temperature dependent.

which $\xi_z(T) \gg \frac{1}{2}s$, χ' reduces to the three-dimensional form,

$$\chi' = -\tfrac{1}{6}\pi k T \Phi_0^{-2} \xi(0)(M/m)^{1/2} \left(\frac{T_c}{T - T_c}\right)^{1/2}, \qquad (6)$$

but enhanced over the result for isotropic systems[14] by the factor $(M/m)^{1/2}$. The prefactor $\frac{1}{2}\pi k T \Phi_0^{-2}(M/m)^{1/2}\xi(0)$ contains all material parameters, while the strongly temperature-dependent factor $[T_c/(T - T_c)]^{1/2}$ is characteristic of the fluctuation susceptibility of three-dimensional systems. Results (5) and (6) are plotted in Fig. 2, with the material parameters for (5) being those appropriate to TaS_2(pyridine)$_{1/2}$, namely $s = 12.0$ Å and $\xi_z(0) = 7.3$ Å (see Table I, below). As seen in Fig. 2, the difference between the full LD result (5) and the anisotropic GL result (6) is small and only marginally significant in the temperature range shown. For the other compounds studied, with even greater values of $\xi_z(0)/s$, the differences between (5) and (6) are completely negligible.

For temperatures well above T_c, and for sufficiently weak coupling such that $\xi_z(T) \ll \frac{1}{2}s$, χ' falls below the three-dimensional prediction (6) and approaches the two-dimensional form:

$$\chi' = -\tfrac{1}{3}\pi k T \Phi_0^{-2} \frac{\xi^2(0)}{s} \left(\frac{T_c}{T - T_c}\right). \qquad (7)$$

Equation (7) is precisely the result obtained by Schmid for the fluctuation susceptibility of a thin film of thickness s. The layer thickness $d = (s - \delta)$ does not appear in (7) because the superconducting layers only occupy a volume fraction of d/s, so that the layer thickness cancels from the final result. Both the temperature dependence and magnitude of this two-dimensional result (7) differ from those of the three-dimensional result (6). The crossover from a three-dimensional to two-dimensional character evidenced by (5) occurs at a temperature T_0 defined by the relation

$$\xi_z(T_0) = \tfrac{1}{2}s. \qquad (8)$$

Since $\xi_z(0)$ depends on the interlayer coupling strength through (4) and the dependence of M on η, T_0 and the width of the three-dimensional region near T_c also depend on the strength of the interlayer coupling. Thus, compounds with weak interlayer coupling will have a very narrow temperature region for three-dimensional behavior, whereas compounds with stronger interlayer coupling, as for example TaS_2(pyridine)$_{1/2}$, can have three-dimensional behavior for a large temperature region above T_c.

The fluctuation-induced diamagnetism for H

TABLE I. Superconducting material parameters for layered compound and alloy samples.

Material	T_c (K)	s (Å)	$\xi_z(0)$ [b] (Å)	$\xi(0)(M/m)^{1/2}$ (from H_{c2} measurements [b]) (Å)	$\xi(0)(M/m)^{1/2}$ (from scaling χ') [a] (Å)
TaS_2 (pyridine)$_{1/2}$	3.45	12.0	7.3	4600–5300	9500
$NbSe_2$	7.16	6.3	26	220	No scaling possible
$TaS_{1.6}Se_{0.4}$	4.1	6.1	18.2	550	d
Pb–5-at.% Tl [c]	7.1	···	···	340	≡340

[a] This work.
[b] Reference 3.
[c] References 2 and 28.
[d] Susceptibility data above T_c not reproducible; see text.

oriented parallel to the layers has been calculated by Tsuzuki,[21] and was found to be very small. Therefore, for H parallel, the fluctuation-induced diamagnetism is expected to be essentially unobservable.

In summary, the LD theory thus predicts that, despite the layered structure of the material, near T_c the fluctuation susceptibility will be that of a three-dimensional system, though anisotropic, while far above T_c, the fluctuation susceptibility for weakly-coupled materials will instead be characteristic of a two-dimensional system. The temperature T_0 where this crossover occurs is given by (8). These characteristics of the fluctuation susceptibility are outlined in Fig. 3. A crossover of dimensionality is also expected for other fluctuation-caused properties such as enhanced conductivity.[17]

Dimensional crossover effects, analogous to those predicted for layered superconductors, are also expected for other systems of quasireduced dimensionality including layered magnets,[22] and coupled one-dimensional superconducting chains of which $(SN)_x$ should be a good example.[23,24] Layered magnets have been investigated extensively, and a lattice-dimensionality crossover directly analogous to that predicted for layered superconductors indeed has been observed in the susceptibilities of a number of quasi-two-dimensional Heisenberg ferromagnets,[22] which have highly anisotropic exchange coefficients. The anisotropy of the exchange coefficients was found to determine the crossover temperature, in analogy to the layered superconductors. In the magnetic systems, there can in addition be spin-dimensionality crossovers (Heisenberg $\rightarrow XY \rightarrow$ Ising) due to the presence of a small amount of XY anisotropy and Ising anisotropy in the spin interactions. There is no analog for this spin anisotropy in the superconducting case.

The experimental situation for $(SN)_x$, the first superconducting polymer, is not yet settled. Measurements of H_{c2} can be interpreted[23] in terms of largely three-dimensional behavior, and consistent with three dimensionality. They yield a value for the coherence length perpendicular to the chain axis of $\xi_\perp(0) \approx 135$ Å, which is much larger than the spacing between polymeric chains ~3 Å. An interpretation in terms of one-dimensional behavior is also possible,[23] leading to a value for $\xi(0) \approx 605$ Å. Results for the excess conductivity above T_c,[24] have also been interpreted in terms of one-dimensional fluctuation effects. Such one-dimensional superconducting behavior is thought to arise due to the fibrous nature of the $(SN)_x$ crystals. Each fiber is believed to have a diameter of a few hundred angstroms. It appears that further work will be required to understand in a self-consistent fashion the behavior above and below T_c in this material. Intrinsic dimensional crossover effects, those associated with the relevant superconducting coherence length being comparable to the interchain spacing, would in any case not be expected for a compound with the material parameters [$\xi_\perp(0)$ and interchain spacing] of $(SN)_x$. Thus the behavior of ideal (nonfibrous) $(SN)_x$, like the *unintercalated* layered compounds, ought to be that of an anisotropic but three-dimensional system.

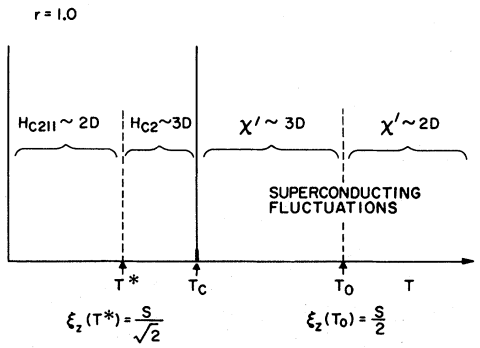

FIG. 3. Schematic diagram of the dimensional character of fluctuation-induced diamagnetism χ' above T_c predicted by the Lawrence-Doniach theory. For $T \rightarrow T_c$, χ' is characteristic of an anisotropic three-dimensional system. For systems with sufficiently weak interlayer coupling, well above T_c, the susceptibility is characteristic of a two-dimensional system (uncoupled layers). The dimensional crossover occurs at T_0, given from $\xi_z(T_0) = \frac{1}{2}s$. As indicated in this figure there also is a dimensional crossover expected below T_c in the behavior of the upper critical field. This interesting effect is discussed in Refs. 3, 18, and 19.

C. Results from microscopic theory

The qualitative predictions of the LD theory serve as a useful guide in understanding the diamagnetic susceptibility above T_c in layered compound superconductors, as they correctly distinguish the temperature region for which the fluctuation effects have a three-dimensional character, and also show how the superconducting material parameters enter into the predictions for χ'. Calculations based on the microscopic Gor'kov theory by Klemm, Beasley, and Luther (KBL)[25] and by Gerhardts,[26] show that the crossover effects predicted by the LD theory do indeed occur, and approximately at T_0. However, the prediction of the LD theory for χ' (5) is found to overestimate the magnitude of χ' except very near T_c. This is because the LD theory is a mean-field theory in its approach and overestimates the contributions to χ' from high-energy, short-wavelength fluctuations. Indeed, this result was found experimentally

for the fluctuation-induced diamagnetism of isotropic superconductors,[2] and extensive theoretical work[27] has served to establish more clearly the limits of a mean-field approach in describing these fluctuation effects. Only very near T_c, for $T - T_c < 0.02\,T_c$, where typical fluctuations have long wavelengths, are the prediction of GL-like theories for isotropic superconductors found to be *quantitatively* correct. This difficulty should be less pronounced for two-dimensional systems, but should still be significant. Since transition broadening in the layered compounds obscures the fluctuation effects in the very narrow region near T_c where the mean-field results are expected to be accurate, our measurements have extended to well above T_c where the more refined microscopic theory is required. We shall use the results of KBL in the following discussion, as they are nearly identical to those obtained by Gerhardts.

The KBL prediction for $\chi'(T)$ for small fields shows the same crossover as for the LD theory. To distinguish these two regimes, KBL introduce a parameter r, defined as

$$r = (4/\pi)[\xi_z(0)/\tfrac{1}{2}\vec{s}]^2 . \tag{9}$$

For $r \gg 1$, the fluctuation susceptibility will be essentially that of a three-dimensional system at all temperatures, while for $r \ll 1$, the fluctuation susceptibility will be two-dimensional in character except very near T_c. Using material parameters derived from the critical field measurements, values of r are found to be 1.9 for $TaS_2(\text{pyridine})_{1/2}$, 4.5 for $TaS_{1.6}Se_{0.4}$, and ~90 for $NbSe_2$. Therefore, except for $TaS_2(\text{pyridine})_{1/2}$ at temperature $> 1.5\,T_c$, the experimental results for $\chi'(T)$ should have essentially the three-dimensional form. This can also be seen from the data in Table I, where values of $\xi_z(0)$ and s are given for the compounds studied. The three-dimensional form ($r \gg 1$) of KBL is plotted in Fig. 2 for the dirty limit (mean free path $l \ll \xi_0$), which is appropriate for the layered compound studied.[3] We can infer from the close agreement of the previous GL and LD results for $TaS_2(\text{pyridine})_{1/2}$ that the KBL result for $r = 1.9$ would not be significantly different from the plotted result for $r \gg 1$. For the KBL result, all material parameters can be included in the same scaling factor as in the LD result, namely, $\frac{1}{6}\pi kT\Phi_0^{-2}(M/m)^{1/2}\xi(0)$.

The prediction for χ' in the three-dimensional limit by KBL and Gerhardts avoid certain of the approximations used in earlier calculations[27] based on the microscopic theory. The KBL predictions can be compared to the experimental results obtained by Gollub for a Pb–5-at.% Tl superconducting alloy,[2,28] which are also shown in Fig. 2. The KBL result is much closer to the Pb-Tl data than is the GL three-dimensional result, which is given by (6) with $M/m = 1$. However, for $(T - T_c)/T_c > 0.05$, even these most recent predictions of the microscopic theory exceed the experimental data. Since the susceptibility of this Pb-Tl sample was studied with particular care and found to be field-independent for $H \leq 10$ G, and for $(T - T_c)/T_c < 0.2$, the experimental results are believed to be quite accurate. The disagreement between the experimental results and theory for isotropic superconductors is not fully understood. The theoretical results do give an excellent account of the scaling field which describes the field dependence of the magnetization at T_c, $M'(T_c)$, for moderate and large fields. However, the theory overestimates both $M'(T_c)$ for small fields and also χ' away from T_c, as seen in Fig. 2. It thus appears that further refinements will be required in the theoretical calculations for these regions. We shall therefore use the Pb-Tl results, scaled as suggested by the theory, in comparisons with our data for the layered compounds. The scaled Pb-Tl data will be taken to define behavior characteristic of a three-dimensional system and thus will serve to test the dimensionality of $\chi'(T)$ for the layered compounds.

KBL and Gerhardts have also calculated the field dependence of $M'(T_c)$ for the layered compounds. These calculations show that a measurement of this field-dependent quantity would provide additional information on the behavior of the high-energy fluctuations and might also show dimensional-crossover effects. However, these field-dependent effects are most dramatic for $H \geq 0.5H_{c2\perp}(0)$. Since the maximum practical field of the magnetometer was ~300 G [$\leq 0.03H_{c2\perp}(0)$], such measurements were not possible.

III. SQUID MAGNETOMETER SYSTEM

An extremely sensitive magnetometer, using a superconducting quantum-interference device (SQUID) as a field sensor, was used to measure changes of sample magnetization as a function of temperature. The original version of this magnetometer system was constructed by J. P. Gollub and one of the authors (MRB) to measure fluctuation diamagnetism in bulk superconductors, and a full description of the construction and operation of the original magnetometer has been given by Gollub.[2] We shall therefore outline rather briefly the design and operation of this SQUID magnetometer system, and discuss some of the design improvements undertaken for this work. A more detailed discussion of the design of the present SQUID magnetometer system has been given elsewhere.[29]

A simplified diagram of the magnetometer is

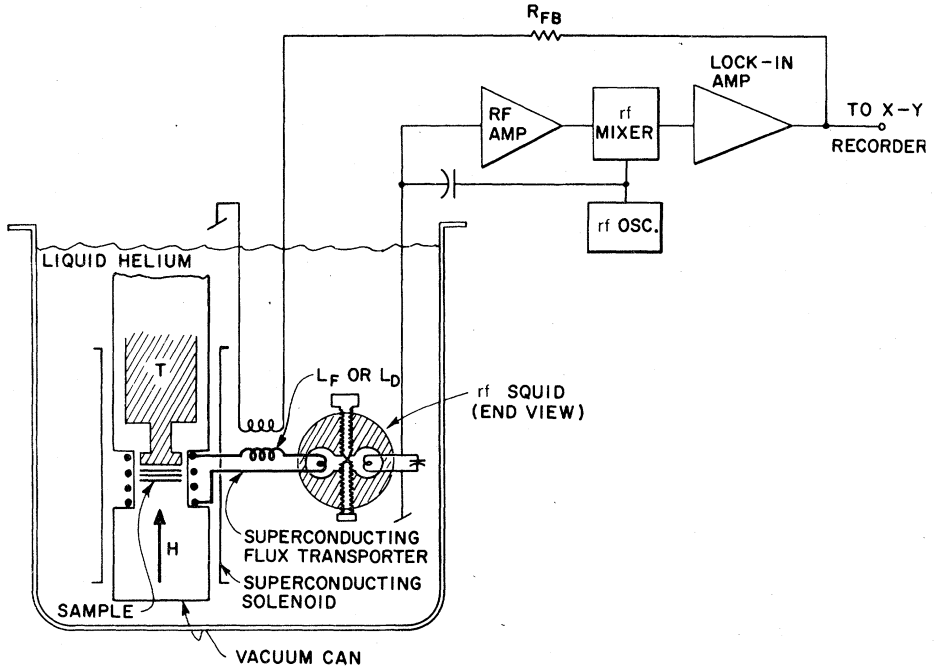

FIG. 4. SQUID magnetometer system. Sample is glued to a variable-temperature copper holder. Changes of sample magnetization are coupled to the SQUID sensor via superconducting flux transporter. The feedback circuit nulls the current in the flux transporter, and provides an output voltage which is proportional to the magnetization change. Mechanical superconducting switches for inserting L_d in place of L_f are not shown. Superconducting *Pb* shield can around the entire low-temperature apparatus and a high-permeability magnetic shield outside the Dewars are also not shown.

shown in Fig. 4. The basic arrangement used is to maintain the SQUID magnetic flux detector at a fixed temperature in a liquid-helium bath, and to vary only the temperature of the sample, which is thermally isolated in a vacuum can. The SQUID used was an rf SQUID,[30] rather than the double-point-contact dc SQUID employed by Gollub. The SQUID was machined from Nb-Ti rod stock. Commercially available SQUID sensors (if operable, between 1 and 4.2 K) and commercial rf detection electronics would also be satisfactory. The sample is in a stable magnetic field H_a produced by a superconducting niobium solenoid operating in the persistent mode. Changes of sample magnetization are sensed by a superconducting pick-up (primary) coil wound around the sample chamber; these induce a persistent circulating current in the superconducting dc flux transporter. Magnetization changes are thereby coupled to the SQUID. With this arrangement, the thermal and magnetic environments of the sample and SQUID may be controlled and optimized independently. Feedback to the flux transporter is used to cancel flux changes sensed by the SQUID. Mechanical superconducting switches (not shown) also permit a much larger superconducting inductor to be inserted into the transporter circuit, in place of L_F. This reduces the amount of flux sensed by the SQUID, and thus extends considerably the dynamic range of the magnetometer system. This low-sensitivity mode of operation is useful in measuring the large flux change at the superconducting transition. Two concentric Moly-Permalloy shields surround the Dewar and reduce the background magnetic field to ~1 mOe. In addition, the entire low-temperature magnetometer is enclosed in a superconducting lead can to shield spurious field changes. Experiments were carried out in a rf shielded room.

The sample, typically a stack of 6-10 single-crystal flakes, is inside the vacuum can, thermally bonded with GE 7031 cement to a high-purity copper mount, which is in turn screwed into a variable-temperature high-purity copper bar. The temperature of the copper bar is measured with a Solitron germanium resistance thermometer. The thermometer calibration was checked with a commercially calibrated Cryocal germanium thermometer and found to be accurate to 0.02 K.

To calibrate the magnetometer for sample magnetization changes ΔM, it was necessary to determine the coupling factor F_c between the sample and the primary coil. The flux sensed by the primary coil is given by $\Delta\Phi = 4\pi\Delta MAF_c$, with A the sample area. Since each layered compound sample had somewhat different dimensions, we determined F_c for each sample. To do this, we used measurements of the full superconducting transition when χ goes from $-1/4\pi$ to essentially zero above T_c. At low temperatures a known dc field was applied, and the flux change as the sample was heated to above T_c was measured. (The flux expulsion upon cooling, and for subsequent temperature cycles, was smaller than that obtained for the initial

warming, due to flux trapping effects.) To include demagnetizing effects present when the sample is superconducting, we modeled the sample as an ellipsoid with a demagnetizing factor n along the direction of the applied field H_a. The field H_i inside the sample is given by $H_i = H_a - 4\pi nM$, so that the sample magnetization given by

$$M = \chi H_i = \chi H_a/(1+4\pi n\chi). \quad (10)$$

The magnetization change when χ changes from $1/4\pi$ to zero is thus given by (10) as $\Delta M = -H_a/4\pi(1-n) = \Delta\chi H_a/(1-n)$. When χ changes between two *small* values, however, the magnetization change is given instead by $\Delta M = \Delta\chi H_a$. Thus, although we may use the full superconducting transition to provide a known susceptibility change, $\Delta\chi = -1/4\pi$, to calibrate the magnetometer for small susceptibility changes, we also need to know the value of $(1-n)$ for each sample. Values of n were estimated from measured sample dimensions, and ranged from 0.44 to 0.6. The resulting values of F_c were of the order of 0.2. The approximation of treating the somewhat irregularly shaped samples as ellipsoids in order to estimate the demagnetizing factor introduced the largest uncertainties into the calibration procedure. An alternate calibration procedure, using a small solenoid of the same volume but only roughly the same shape as the sample to simulate the sample's magnetization, led to a value of F_c which was ~30% smaller. This indicates that errors of the calibration factor may unfortunately be as large as ~30%. The basic problem is that the (irregularly shaped) sample cannot be treated as a point dipole, as it fills a substantial volume of the superconducting transporter primary or "pick-up coil."

The sensitivity of the SQUID magnetometer system is excellent, and a variety of other measurements have also been made with this system, including measurements on amorphous semiconductors[31] and on random multifilamentary superconducting wire.[32] This magnetometer is most suited for measurements of susceptibility *changes* as a function of temperature; total sample susceptibility can be measured, though with reduced sensitivity, by withdrawing the sample from the pick-up coil. The major factors limiting magnetometer sensitivity at reasonably large fields (> 10 g) for swept temperature operation are spurious dc flux changes at the transformer primary coil due to field drifts. These appear identical to changes in sample susceptibility, and thus cannot be discriminated. These field drifts are apparently due to changes in the (temperature-dependent) susceptibility of some construction materials of the magnetometer used near the primary coil; these are caused by changes of the bath temperature. Indeed, electronic regulation of the temperature of the superfluid helium bath was found to substantially reduce magnetometer drift. With the bath temperature regulated magnetometer sensitivity and stability are excellent, and one can detect susceptibility *changes* at low temperatures of ~10^{-12} emu/cm^3 in a 1 cm^3 insulating sample (which has no Johnson noise currents). The optimum sensitivity for detecting susceptibility changes occurs for fields between 10 and 100 G, and for sample temperatures below ~20 K. Except at low fields (< 10 G), field drifts, and not broadband SQUID noise, limit magnetometer sensitivity.

The performance outlined above represents a considerable improvement upon the performance of the original version, particularly in terms of the field stability at high fields and high temperatures. Two changes were made in the design of the original magnetometer to obtain this improved field stability. First, the thermal link between the heater rod and the bath, a copper braid, was made significantly weaker so that much less power was required to heat the copper rod above the bath temperature. This change significantly reduced the heating of the helium bath. Reducing the heater power also reduced the thermoelectric currents generated in the copper rod by small temperature gradients. The field from these thermoelectric currents had been sensed at the pick-up coil. Second, superconducting lead shielding was used in the vicinity of the heater to provide additional reduction of the spurious flux changes associated with the thermoelectric currents. Together, these changes substantially improved magnetometer performance.

With these improvements in magnetometer design, measurements can be carried out to over 40 K, with somewhat increased field drift over that below 20 K. Also, measurements may be made in fields up to ~330 G. Above this field level, performance degrades significantly, possibly due to flux creep in the magnet. We hope to solve this problem in future magnetometer designs.

IV. SAMPLE PREPARATION AND CHARACTERISTICS

The layered-compound samples studied were as-grown single-crystal flakes, with typical dimensions of $3\times3\times0.2$ mm^3. All crystals used in this work were produced at Stanford University by one of the authors (R.E.S.). Single crystals were required because the fluctuation susceptibility is highly anisotropic. As the preparation and structural properties have already been reported in detail for TaS_2 compounds and $NbSe_2$,[1,8,16,33] and for the $TaS_{1.6}Se_{0.4}$ compounds,[34] we shall only briefly

outline the procedures followed, using the preparation of $TaS_2(pyridine)_{1/2}$ as an example.

Crystals of TaS_2 are obtained by chemical vapor transport of prereacted TaS_2 powder, using iodine as a transporting agent. The resulting crystals are annealed at 800 °C for a few days and cooled slowly (~ 1 week) to room temperature. As the crystals cool, they transform from the high-temperature (nonsuperconducting) $1T$ polytype[16] to the $2H$ two-layer hexagonal polytype, which is superconducting below 0.8 K and is the polytype used. All TaS_2 crystals were produced in an identical fashion from the same spool of tantalum wire and quantity of sulfur, and thus the resulting intercalated compounds can be directly compared. Great care was taken to avoid iron contamination.

Intercalation of pyridine is achieved by heating TaS_2 crystals and pyridine liquid in a sealed tube at 200 °C for up to one month. The progress of intercalation can be monitored by measuring T_c. The crystals from each separate intercalation tube were labeled by the batch number for that tube so that the consistency of the superconducting properties for different intercalation batches could be established. X-ray studies of the structure of $TaS_2(pyridine)_{1/2}$ which is intercalated with *pure* pyridine indicate that two molecular stacking arrangements are possible in these crystals; a mixture of the layer separations with $\delta = 5.85$ Å and $\delta = 6.01$ Å usually results for this compound, which we denote as mixed phase. A single-phase compound, with $\delta = 6.01$ Å only, can be obtained by intercalating TaS_2 with pyridine which contains dissolved sulfur.[35] Saturating the pyridine with sulfur before intercalation apparently prevents the removal of sulfur from the TaS_2 crystals during the intercalation process. In our measurements we have used only such single-phase $TaS_2(pyridine)_{1/2}$ except as noted. Among the compounds investigated, only $TaS_2(pyridine)_{1/2}$ is known to have such problems with a mixed-phase compound resulting from intercalation of the pure organic compound. A detailed explanation of the difference in structure between the two phases, and how saturating the pyridine with sulfur favors only one phase, is not yet available.

For the compounds which have been prepared as crystals, the one with the largest layer separation is $TaS_2(aniline)_{3/4}$ with $\delta = 12$ Å. Because the larger organic molecules do not intercalate as readily, so far only TaS_2 powders have been intercalated to achieve layer separations greater than 12 Å. Even the $TaS_2(aniline)_{3/4}$ crystals are quite small, typically $1 \times 1 \times 0.1$ mm^3. The related compound $TaS_{1.6}Se_{0.4}(aniline)_{3/4}$ is unfortunately not superconducting.[36]

The samples used in these measurements are of excellent quality, and their properties are generally quite reproducible. The only major problem we have encountered with these samples is that the TaS_2 crystals are usually slightly wrinkled, and this leads to problems in measuring the angular dependence of the critical field H_{c2} near the parallel orientation, and would also lead to problems in measuring χ' for the parallel field orientation. The wrinkling appears to be present in the unintercalated crystals, and is likely caused by strains resulting from a change in the volume of the unit cell during the transformation from the $1T$ polytype to the $2H$ polytype. Smaller TaS_2 crystals would probably be less wrinkled. The $TaS_{1.6}Se_{0.4}$ crystals appear to be free of wrinkling, and can be readily intercalated. They may thus represent an optimum choice for intercalation of organic molecules. $NbSe_2$, which forms the most perfect crystals, can be intercalated only under extreme conditions.[37]

V. EXPERIMENTAL RESULTS

Measurements of the dc magnetization in the superconducting state, and of the fluctuation-induced diamagnetism above T_c, were carried out for samples of $TaS_2(pyridine)_{1/2}$, $NbSe_2$, and $TaS_{1.6}Se_{0.4}$. Each sample consisted of a stack of single crystals glued together. Four samples of $TaS_2(pyridine)_{1/2}$, two of the single-phase compound and two of the mixed-phase compound, two samples of $NbSe_2$, and one sample of $TaS_{1.6}Se_{0.4}$ were run. Measurements of the full superconducting transitions were made for each sample in order to provide a measure of sample quality and transition broadening, and to gauge sample inhomogeneity as indicated by flux trapping effects. Data which were presented in a preliminary report[15] of this work are the same as those presented here.

A. Intercalated compounds: $TaS_2(pyridine)_{1/2}$

Full superconducting transitions of single-phase $TaS_2(pyridine)_{1/2}$ are shown in Fig. 5 for the dc field oriented perpendicular to the layers, $H_\perp$, and for the field oriented parallel to the layers, $H_\parallel$. Both single-phase and mixed-phase compounds showed similar behavior. In obtaining these curves, the sample was cooled in zero applied field, the field was applied, the sample was then heated to above T_c, and finally cooled below the transition. The direction of each temperature sweep is indicated in the figure. These results show that the field applied at low temperatures is fully shielded from the interior of the sample by lossless surface currents. When the sample is warmed to above T_c, the field enters the sam-

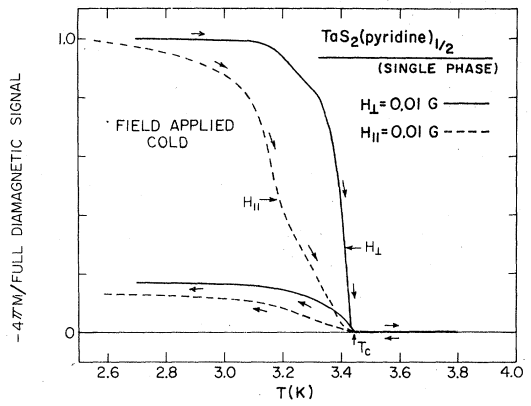

FIG. 5. Full superconducting transitions of single-phase TaS_2(pyridine)$_{1/2}$, for fields perpendicular and parallel to the layers. The field was applied with the sample cold; the direction of each temperature sweep is indicated in the figure. The expulsion of flux upon cooling is not complete because of flux-trapping effects. Subsequent warming and cooling cycles retrace the lower (cooling) curve. Curves represent the low-field behavior. The value of T_c noted is obtained by extrapolating major portion of curve to $M=0$. Fluctuation-induced diamagnetic susceptibility above T_c shown in Fig. 6, is seen by increasing magnetometer sensitivity by $\sim 10^5$.

ple; when the sample is cooled to below T_c, only a fraction of the flux is expelled.

These results confirm that at least a partial Meissner effect does occur in these compounds, as a material with only zero resistance would not expel *any* flux upon cooling. The expulsion is incomplete because of flux-trapping effects, which were even larger in some of the isotropic alloy samples studied by Gollub *et al.*[2] The flux expulsion observed for $H_\parallel$ also indicates that the individual metal layers must be coupled together, as the diamagnetism expected[38] for uncoupled 6-Å-thick layers is orders of magnitude smaller than that observed. The apparent absence of any Meissner effect in previous experiments[1] on TaS_2(pyridine)$_{1/2}$ was undoubtedly due to the large measuring fields used in those experiments.

The transitions seen in Fig. 5 are reasonably compact, and both their width and shape depend strongly on sample orientation. The transitions shown in Fig. 5 all represent the behavior observed in the limit of zero applied field, and therefore the broadening observed is not due to passage through the mixed state, nor to broadening introduced by sample demagnetizing effects. In contrast, the full superconducting transitions of the unintercalated layered compound $NbSe_2$ are much sharper, with widths of ~ 0.04 K, and do not show a pronounced anisotropy. We believe that the broadening below T_c seen in Fig. 5 for TaS_2(pyridine)$_{1/2}$ is caused by regions of the sample which are not completely intercalated, and have T_c's somewhat lower than that of the fully intercalated compound. (Unintercalated TaS_2 has a T_c of 0.08 K.) Indeed, while the measured transitions for TaS_2(pyridine)$_{1/2}$ are not sharp, they do exhibit a well defined onset temperature of 3.45 K which is independent of sample orientation, and is the same for the two different intercalation batches we have measured. The full transition for a sample from the other batch of TaS_2(pyridine)$_{1/2}$, however, does show significant broadening, but only on the *low-temperature* side of the transition. We therefore believe that the onset temperature of this transition may be reliably identified as the superconducting critical temperature T_c for the fully intercalated (single-phase) compound. Additional evidence supporting this identification is obtained from the susceptibility measurements above T_c, in which the fluctuation diamagnetism is found to diverge at this same temperature, 3.45 K.

The full superconducting transition for mixed-phase TaS_2(pyridine)$_{1/2}$ is similar to that of the single-phase compound, although the transition temperature of the mixed-phase compound is ~ 0.5 K higher than that of the single-phase compound. The transitions are also much broader. The higher transition temperature observed for the mixed-phase compound is probably characteristic of the regions with a layer separation of 5.8 Å. This difference in values of T_c may reflect a different arrangement the pyridine molecules for the 5.8-Å phase.

The diamagnetic contribution to the susceptibility above T_c for single-phase TaS_2(pyridine)$_{1/2}$ is shown in Fig. 6 for $H_\perp = 3.27$ and 327 G, and for $H_\parallel = 3.27$ G. Susceptibility is here defined as M/H. In plotting Fig. 6, we have subtracted a small background signal due to the magnetometer, which was present even in zero field. With this subtraction made, the baseline of the data was chosen by estimating the level at which the temperature dependence of the fluctuation diamagnetism was negligible. This procedure subtracts the normal state susceptibility which is presumed to be temperature independent, and the notation χ' indicates that we measure susceptibility *changes* relative to this high-temperature value.

As seen in Fig. 6, the fluctuation diamagnetism observed for $H_\parallel$ is smaller than that for $H_\perp$, and this is consistent with the behavior expected in such an extremely anisotropic superconductor, whether two- or three-dimensional. This anisotropy indicates that the large enhancement observed for $H_\perp$ does *not* arise from transition broadening, but is intrinsic. The value of T_c noted on the graph, 3.45 K, is that derived from the full

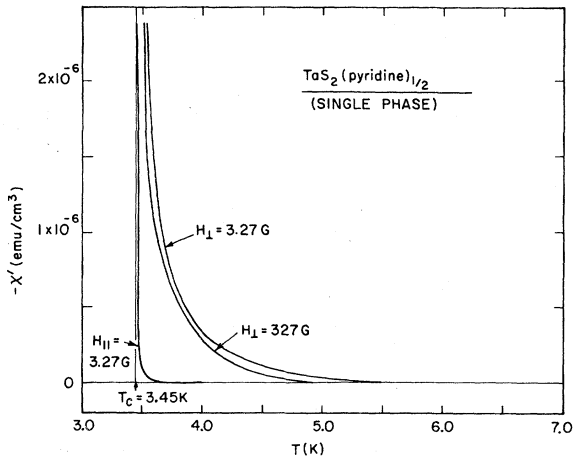

FIG. 6. Diamagnetic susceptibility above T_c of single-phase TaS_2(pyridine)$_{1/2}$ for fields perpendicular and parallel to the layers. No hysteresis is observed for $T > T_c$.

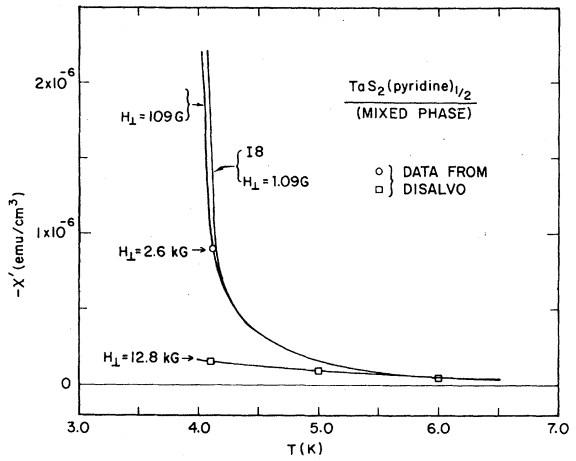

FIG. 7. Diamagnetic susceptibility above T_c of mixed-phase TaS_2(pyridine)$_{1/2}$ for fields perpendicular to the layers, compared to data for high fields from DiSalvo, Ref. 16. At the largest field, 12.8 kG, the superconducting transition would be fully suppressed.

superconducting transition (Fig. 5). Comparing susceptibility curves for different field values, the susceptibility measured for $H_\perp = 327$ G is seen to be nearly identical to that measured for 3.27 G, except for a slight shift of the 327-G curve to lower temperatures. Presumably this is due to the depression of the superconducting transition with increasing field. Except for this slight shift, the susceptibility was found to be virtually field-independent up to 327 G, and the curve for 3.27 G represents the limiting behavior as $H \to 0$.

Measurements made on single-phase TaS_2(pyridine)$_{1/2}$ sample from a second intercalation batch led to very similar results. We have also repeated the susceptibility measurement for the sample of Fig. 6 one year after the first measurements, and the results were identical.

Fluctuation susceptibility was also measured for two mixed-phase TaS_2(pyridine)$_{1/2}$ samples, and the results for one sample are shown in Fig. 7. The data for this sample are similar to those of the single-phase sample (Fig. 6). The susceptibility diverges at a temperature somewhat above the full transition of this mixed-phase sample, and this is indicative of some transition broadening, which would be expected from the rather broad full transition for this compound.

The high-field susceptibility results reported by DiSalvo[16] for another mixed-phase TaS_2(pyridine)$_{1/2}$ sample, measured in fields of 2.6 and 12.8 kG, are also shown in Fig. 7. The high-field data have been offset so as to match the low-field data at 7 K. At the larger field used, the superconducting transition is completely suppressed. We see in the figure that when the smaller magnetic field is used, $\chi'(4.2\ \mathrm{K})$ approaches the low-field value and although the field ranges do not overlap, we conclude that the high-field data is probably consistent with the data for low-fields. There may, however, still be some small differences between the two samples due to different methods of preparation.

B. Unintercalated compounds: $NbSe_2$ and $TaS_{1.6}Se_{0.4}$

The full superconducting transition for $NbSe_2$ is shown in Fig. 8. The transition seen for this compound is quite sharp, with a width [(10–90)%] of only 0.04 K, indicative of good sample quality. We attribute the small residual broadening observed to inhomogeneities, strains, and other imperfections within the crystal, which lead to the more symmetrically broadened transition, as would be usual for ordinary superconducting metals. A value of $T_c = 7.16$ K is obtained by extrapolating to $M = 0$ in Fig. 8.

Results for the susceptibility above T_c for $NbSe_2$ are shown in Fig. 9. Data obtained for a second sample were nearly identical. A significant temperature-dependent ($1/T$-like) paramagnetism was detected at high temperatures (to 12 K) and is believed to be due to paramagnetic impurities in the sample. This contribution was subtracted from the raw data. Both the raw and the corrected data are shown in Fig. 9 to illustrate the magnitude of the correction, which is indeed quite large. We note that the diamagnetic susceptibility for TaS_2(pyridine)$_{1/2}$ with $H_\perp$ is almost two orders of magnitude larger, and no paramagnetic contribution is observed for that compound. For TaS_2(pyri-

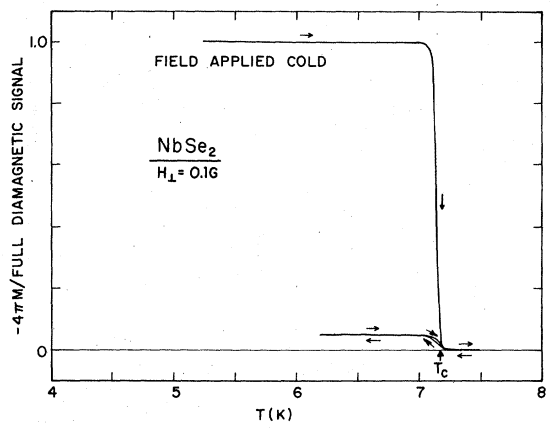

FIG. 8. Full superconducting transition of $NbSe_2$, in a perpendicular field of 0.1 G. The field was applied with the sample cold; the direction of each temperature sweep is noted in the figure.

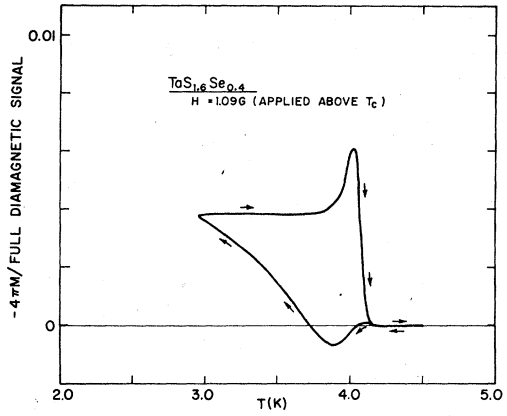

FIG. 10. Magnetization near T_c of $TaS_{1.6}Se_{0.4}$, in a perpendicular field of 1.09 G, showing unusual paramagnetic dip and large hysteresis. The field was applied with the sample above T_c. Scale of magnetization is 100× more sensitive than for previous plots of full transitions, Fig. 5. Behavior seen in Fig. 10 was not observed for any of the other compound studied. See text for discussion.

dine)$_{1/2}$, the much larger fluctuation diamagnetism may mask any small paramagnetic contributions.

The full superconducting transition for $TaS_{1.6}Se_{0.4}$ looks similar to that of $NbSe_2$. However, when viewed with increased sensitivity, the sample magnetization as shown in Fig. 10 has a number of very unusual features. These include a region below T_c in which the total magnetization is paramagnetic, and a large diamagnetic peak near T_c. We tentatively attribute this unusual behavior to the effects of surface superconductivity,[38] as Gollub *et al.*[2] have observed qualitatively similar features for an alloy sample, and were able to establish that the effects they observed were due to surface superconductivity. Due to problems with the fluctuation susceptibility data for $TaS_{1.6}Se_{0.4}$ we did not study further the behavior of this sample, and the susceptibility above T_c for $TaS_{1.6}Se_{0.4}$ will not be reported. The characteristics of surface superconductivity in layered superconductors would be of interest, and this compound might be a good candidate for such experiments.

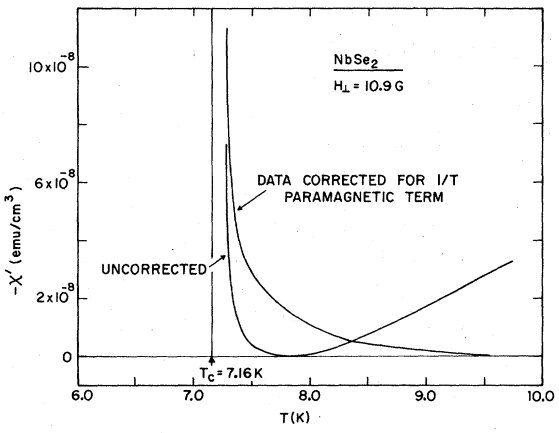

FIG. 9. Susceptibility above T_c of $NbSe_2$ in a perpendicular field of 10.9 G. Recorded data extended to 12 K. A paramagnetic contribution proportional to $1/T$ was observed at high temperatures (> 9 K), and subtracted from the raw data to obtain the corrected curve.

VI. DISCUSSION

The experimental results presented in the previous section show that a temperature-dependent diamagnetic susceptibility is observed above T_c for the layered compounds TaS_2(pyridine)$_{1/2}$ and $NbSe_2$, and appears to be due to superconducting fluctuation effects. For TaS_2(pyridine)$_{1/2}$ these effects are relatively large, while for $NbSe_2$, the diamagnetic susceptibility is quite small, and a rather large correction must be made to the raw data to subtract a $1/T$-like paramagnetic susceptibility. Results for $NbSe_2$ will therefore be scrutinized with special care.

In order to understand the susceptibility results for the layered compounds, we shall compare these results with the susceptibility data for an isotropic superconducting alloy of Pb-Tl obtained by Gollub *et al.*[2,28] Susceptibility data will be scaled as suggested by theory to emphasize the essential temperature dependence. The scaled susceptibility data for this Pb-Tl sample will be used to define behavior characteristic of three-dimensional systems, as discussed in Sec. II. In order to clearly establish the three-dimensional nature of the fluctuation effects in the layered compounds, we shall

require agreement of *both* the temperature dependence and the magnitude of the enhanced diamagnetism. For Pb–5-at.% Tl, the scaling factor near T_c has a value of

$$\tfrac{1}{6}\pi k T_c \Phi_0^{-2} \xi(0) = 4.1 \times 10^{-8} \text{ emu/cm}^3,$$

with parameters of $\xi(0) = 340$ Å and $T_c = 7.1$ K.

A. TaS_2 (pyridine)$_{1/2}$

The scaled susceptibility above T_c for TaS_2(pyridine)$_{1/2}$ is plotted in Fig. 11, along with data for Pb-Tl. The scaling factor

$$\tfrac{1}{6}\pi k T \Phi_0^{-2} \xi(0)(M/m)^{1/2}$$

for TaS_2(pyridine)$_{1/2}$ was treated as an adjustable parameter for this graph, and the value of $\xi(0)(M/m)^{1/2}$ was chosen to obtain a "best fit" to the scaled Pb-Tl curve. The value of T_c of 3.45 K is that derived from the full superconducting transition. We find that *all* the data for TaS_2(pyridine)$_{1/2}$ can be scaled to follow quite accurately the three-dimensional temperature dependence over the full temperature range shown, using a value of $\xi(0)(M/m)^{1/2} = 9500$ Å. That the sharp divergence of χ' is seen at the bulk T_c indicates that transition broadening *above* T_c is not a serious problem for this compound, and further strengthens our identification of 3.45 K as the true critical temperature.

The value of the parameter $\xi(0)(M/m)^{1/2} = 9500$ Å derived from the scaling procedure differs from the value of $\xi(0)(M/m)^{1/2}$ derived from critical-field measurements (see Table I). The value derived from critical field measurements is in the range 4600 to 5300 Å.[39] (The small spread in values reflects small variations in properties of the individual single-crystal flakes studied.) We believe that the discrepancy between the values of $\xi(0)(M/m)^{1/2}$ derived from the two different experiments can be understood to arise on the one hand from inaccuracies of the calibration of the SQUID magnetometer and on the other hand from some uncertainties in the determination of $(M/m)^{1/2}$ from the critical field data.[3] As discussed in Sec. III, the calibration factor for sample susceptibility changes may be in error by as much as 30% for the layered compound samples. In addition, the critical field measurements probably underestimate the value of $H_{c2\parallel}$ somewhat, and hence also underestimate $(M/m)^{1/2}$; this is due to complications in the critical field data which arise due to small regions which are misaligned relative to the whole crystal. The true values of $\xi(0)(M/m)^{1/2}$ derived from the critical field measurements would therefore be somewhat larger. (The results for χ' should be much less affected by any misoriented regions, as their volume contribution to the susceptibility would be negligible.) Considering these uncertainties, we conclude that the magnitude of the fluctuation-induced diamagnetism observed for TaS_2(pyridine)$_{1/2}$ is reasonably consistent with that predicted on the basis of the superconducting material parameters derived from critical field measurements.

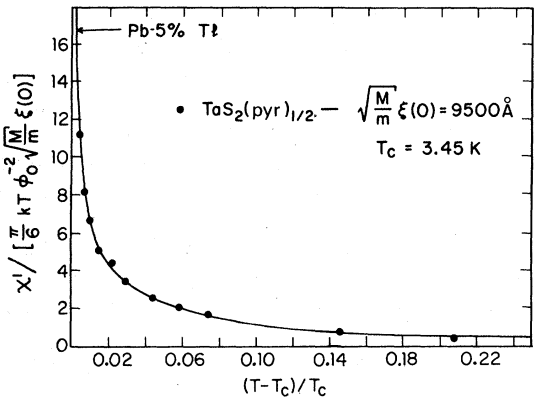

FIG. 11. Scaled susceptibility above T_c of single-phase TaS_2(pyridine)$_{1/2}$, (measured in a perpendicular field of 3.27 G), compared with scaled low-field susceptibility of a superconducting alloy, *Pb*–5-at.% Tl, measured by Gollub, Ref. 28. Value of $\xi(0)(M/m)^{1/2}$ shown for TaS_2(pyridine)$_{1/2}$ was determined by scaling that data to obtain a "best-fit" to the scaled Pb-Tl data, which is used to define three-dimensional character. Value of scaling factor at T_c for TaS_2(pyridine)$_{1/2}$ so derived is $\tfrac{1}{6}\pi k T_c \Phi_0^{-2} \xi(0)(M/m)^{1/2} = 5.5 \times 10^{-7}$ emu/cm^3.

Data were also obtained at higher temperatures for TaS_2(pyridine)$_{1/2}$, and some deviations from three-dimensional behavior might be observable at these higher temperatures. Unfortunately, the low-field Pb-Tl data were not sufficiently reliable at these higher temperatures and reliable comparisons were not possible. Thus, the dimensional-crossover effects above T_c predicted by the LD theory could not be investigated. Evidence suggestive of crossover effects below T_c has been obtained from measurements of H_{c2}.[3]

In view of the excellent agreement of the temperature dependence of the scaled susceptibility data with that of the Pb-Tl data, and the reasonable consistency of the observed magnitude with that expected, we conclude that the superconducting fluctuation effects in TaS_2(pyridine)$_{1/2}$ are three-dimensional in nature over the temperature range investigated. This finding is in accord with the qualitative prediction of the Lawrence-Doniach theory that the weak coupling between superconducting layers will result in three-dimensional behavior near T_c. With the experimentally determined material parameters for TaS_2(pyridine)$_{1/2}$, this three-dimensional region is expected to extend over the full temperature range for

which comparisons with the alloy data have been made.

B. $NbSe_2$

Scaled susceptibility data for $NbSe_2$ and Pb-Tl are plotted in Fig. 12. The value of $T_c = 7.16$ K shown is that derived from the full superconducting transition (Fig. 8); $\xi(0)(M/m)^{1/2}$ was treated as an adjustable parameter for this graph. It was found that there is no value of this parameter for $NbSe_2$ which makes the scaled data agree with that for Pb-Tl; the value derived from the H_{c2} results, $\xi(0)(M/m)^{1/2} = 220$ Å is therefore used in Fig. 12. As seen in the figure, the curve for the susceptibility above T_c of $NbSe_2$ has a different temperature dependence than that of Pb-Tl. The $NbSe_2$ curve diverges approximately 0.12 K above T_c, at $(T - T_c)/T_c \cong 0.2$, and falls below the Pb-Tl data at high temperatures. The disagreement between the two curves is significant, and cannot be explained in terms of instrumental calibration factors, which would affect only the magnitude of the curves.

The most likely explanation of the disagreement apparent in Fig. 12 is that *symmetric* broadening of the full transition, seen in Fig. 8, leads to small regions of the sample with a local of T_c as much as ~0.1 K higher than the mean value of T_c.[40] Since the fluctuation-induced diamagnetic susceptibility is very small, of order 10^{-7} cm^{-3}, the contribution to the total susceptibility from even a minute fraction of the sample in the Meissner state ($\chi = -1/4\pi$) would dominate over intrinsic fluctuation effects. Considering the transition broadening observed, we believe that the discrepancy between the scaled susceptibility data for Pb-Tl and $NbSe_2$ is largely due to a broadened transition in $NbSe_2$. Another factor which probably contributes to the discrepancy is the temperature dependence of the normal-state susceptibility, which cannot be easily separated from the temperature-dependent diamagnetism due to superconducting fluctuations. While we have subtracted a $1/T$-like contribution from the raw data (Fig. 9), there may be other temperature-dependent contributions to the normal state susceptibility, such as from the growth of a charge-density wave. In $NbSe_2$, the charge-density-wave state occurs below ~35 K. The predicted fluctuation susceptibility for $NbSe_2$ is so small, [almost two orders of magnitude smaller than in $TaS_2(\text{pyridine})_{1/2}$] that such temperature dependent contributions to the normal-state susceptibility could be significant. In $TaS_2(\text{pyridine})_{1/2}$, by contrast, the diamagnetic susceptibility due to superconducting fluctuations clearly dominates in low fields, as is evident in Fig. 6.

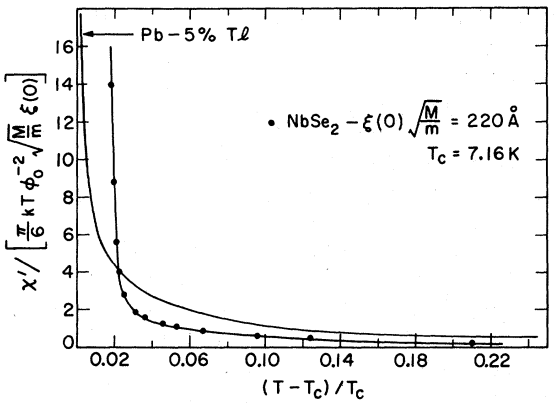

FIG. 12. Scaled susceptibility above T_c of $NbSe_2$ (measured in a perpendicular field of 10.9 G), compared with scaled low-field susceptibility of a superconducting alloy, Pb–5-at.% Tl, measured by Gollub, Refs. 2 and 28. Value of $\xi(0)(M/m)^{1/2}$ shown for $NbSe_2$ was obtained from measurements of H_{c2}, as no satisfactory fit to the scaled Pb-Tl could be obtained with any value of $\xi(0)(M/m)^{1/2}$. The value of the scaling factor for $NbSe_2$ at T_c is $\frac{1}{6}\pi k T_c \Phi_0^{-2} \xi(0)(M/m)^{1/2} = 2.65 \times 10^{-8}$ emu/cm^3. See text for discussion of discrepancy between curves.

In conclusion, we find that the results for $NbSe_2$ are at present not definitive, and attribute this to the effects of transition broadening in this compound, combined with the large size of the background correction and the unknown effects of the charge-density wave on the susceptibility. Since the critical field results below T_c for $NbSe_2$ establish clearly that, as expected, the properties near T_c are three-dimensional in character, the problems with the susceptibility results for this compound can probably be discounted. Thus, the conclusion for $TaS_2(\text{pyridine})_{1/2}$ that the fluctuation-induced diamagnetism has a three-dimensional character appears to be generally valid. We thus conclude that even for these quasi-two-dimensional superconducting systems, weak interlayer coupling leads to a phase transition with a three-dimensional nature. Future work directed toward observation of a dimensional crossover effect would require a layered system with anisotropy significantly greater than that of any compounds studied to date.

ACKNOWLEDGMENTS

We would like to thank Professor M. Tinkham, Professor A. Luther, and Dr. R. A. Klemm for many useful discussions and suggestions, and Dr. R. L. Green and Professor C. Elbaum for discussions regarding $(SN)_x$. Helpful suggestions

from Dr. P. A. Lee and Professor T. H. Geballe are also gratefully acknowledged. We greatly appreciate the continuing support of and interest in these experiments of Professor M. Tinkham.

The National Science Foundation and the Schlumberger Foundation have provided fellowship support for one of us (D.P.) during the course of this research.

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†Research supported in part by the National Science Foundation, the Office of Naval Research, and the Advanced Research Projects Agency.

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[39]Measurements of specific heat at the superconducting transition for TaS_2(pyridine)$_{1/2}$, $TaS_{1.6}Se_{0.4}$, $TaS_{1.6}Se_{0.4}$(pyridine)$_{1/2}$ and $NbSe_2$ by R. E. Schwall, G. R. Stewart, and T. H. Geballe [J. Low Temp. Phys. 22, 557 (1976)] have also been used to determine $H_{c2\perp}(T)$ and thereby $\xi(0)$. Values of $\xi(0)$ so determined were ~ (10–20)% larger than those obtained in Ref. 3, wherein ac susceptibility measurements were employed. The small differences in the values for $\xi(0)$ appear to result only from slightly different methods of analysis of the broad transitions observed and are not considered to be significant. For both ac susceptibility and specific-heat measurements, the actual transitions measured in a perpendicular field roughly overlay on each other.

Values of $dH_{c2\parallel}/dT$ are also given in the paper by Schwall *et al*. These were derived from the high-frequency ac susceptibility data of Ref. 10. In interpreting our data on fluctuation diamagnetism, we have used the values of $dH_{c2\parallel}/dT$ derived in Ref. 3, as these were measured on the same crystal batches, and for both parallel and perpendicular orientations. Also, the same data interpretation scheme was used for both field orientations.
[40]The obvious source of broadening here is the dependence of T_c on stoichiometry.