SUPERCONDUCTING DIAMAGNETISM OF $TaSe_3$ AND $NbSe_3$

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ABSTRACT

The superconducting transitions of the highly anisotropic metals $TaSe_3$ and $NbSe_3$ were investigated using SQUID magnetometers. The observed diamagnetic susceptibility showed similar unusual field and temperature dependences for both materials. In particular, the susceptibility of the samples in low fields increased greatly at temperatures far below the transition temperature of the material (as indicated by the onset of temperature dependent diamagnetism and the upper limit of flux trapping). The measurements suggest the presence of a second transition at low temperatures where small superconducting regions of the sample become coupled throughout larger volumes.

INTRODUCTION

Compounds of tantalum and niobium with the chalcogens S, Se, and Te are of interest because the metal ions of these compounds are coupled much more strongly in one or two dimensions than in the remaining dimension(s). Tantalum triselenide and niobium triselenide are of particular interest because they show highly anisotropic metallic conduction to low temperatures. In addition, $NbSe_3$ shows two distinct charge density wave transitions[1] (at 144 and 59 K) while $TaSe_3$ shows none, even though the materials have similar structures.

There is confusion in the literature as to whether or not (or in what way) these compounds become superconducting. $TaSe_3$ has been reported to become superconducting around 2.2K on the basis of resistance and critical field measurements.[2,3] However, many, if not all, of the samples examined exhibited non-zero resistance to the lowest temperatures reached, and the report of superconductivity is in conflict with the reported absence of a diamagnetic transition in $TaSe_3$.[4]

In $NbSe_3$ two low temperature resistive anomalies have been reported.[5] The first is centered at approximately 2 K, the second at about .25 K. Again the possible superconductive nature of these transitions is obscured by the observation of non-zero resistance to the lowest temperatures obtained. Magnetic studies of $NbSe_3$ have been reported[4] which indicate that no diamagnetic transition occurs in this material until pressures in excess of .5 Kbar are applied.[6] Finally there has been a recent report[7] of a sharp resistive drop at about 1.5 K in $NbSe_3$ which has been alloyed with 5% $TaSe_3$. While a residual resistance apparently remained below this transition, on the basis of critical field studies this alloy material was labeled an anisotropic three-dimensional superconductor.

In this paper we describe the results of high resolution magne-

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tization measurements of $TaSe_3$ and $NbSe_3$ in the temperature range of the low temperature resistive anomalies. In the case of $NbSe_3$ resistive measurements have also been made as a function of temperature, magnetic field and current density. Diamagnetism associated with these anomalies has been observed which clearly is due to the existence of superconducting long range order within these materials. However, the nature of these transitions is not in accord with that of bulk homogeneous superconductors.

In the first section of this paper the materials and samples are described, and the experiments are briefly explained. The second section presents observations of the diamagnetic transitions in the two materials. In the third section mechanisms are suggested which could account for the unusual diamagnetism.

SAMPLES AND EXPERIMENTAL TECHNIQUES

Tantalum and niobium triselenides are grown by heating stoichiometric amounts of the elements in an evacuated quartz tube for several weeks.[8] The materials form long, fine fibers (millimeters long and tens of micrometers cross-dimension) in which the long dimension coincides with the direction of high conductivity (crystallographic b-axis). Structural determinations show that the compounds can be thought of as chains of the metal ions (each at the center of a triangular prism defined by six half selenium atoms) linked most strongly along the fiber axis. The unit cell of $TaSe_3$ contains[9] four such chains while that of $NbSe_3$ contains six.[10] The compounds are expected to be highly anisotropic in the plane perpendicular to the b direction.

The $TaSe_3$ examined here was grown by W. Fisher. The composition was checked by x-ray diffraction for the presence of $TaSe_2$ and none was found. Under an optical microscope the material appeared as small clusters (0.5 to 3 mm diameter) of randomly oriented interpenetrating fine needles and striated ribbons. These crystals varied from 0.1 to 3 mm length, with cross-dimensions from 1 to 20 micrometers. The ends of the ribbons were generally split. About 100 mg of this material was loosely assembled in a volume approximately 1.5 x 3 x 8 mm. In analyzing the data the magnetization was referred to the sample volume, and no filling fraction correction was applied.

Three samples of $NbSe_3$ were prepared from material grown in this lab to investigate the effect of changing the sample morphology. The material as grown appeared similar to $TaSe_3$ under an optical microscope: clumps of randomly oriented long narrow ribbon-like crystals. Under an electron microscope these ribbons appeared to be composed of fibers on the order of several hundred angstroms wide: crystal ends were always frayed into these smaller fibers. From this material three samples were made:

Sample A: 94 mg of the material as-grown, loosely assembled into a volume 3 x 4 x 10 mm.

Sample B: 90 mg of the material compacted using an hydraulic press to form a cylinder 3 mm long x 2.5 mm diameter.

Sample C: 135 mg of similarly compacted material, but the fibrous $NbSe_3$ was etched in dilute H_2SO_4, rinsed, and dried before compaction.

The magnetic susceptibilities of these samples were measured using SQUID magnetometers in two separate cryostats, one cooled with a ^3He pot, the other by a dilution refrigerator. The static magnetization, M_{dc}, was measured by sweeping temperature in constant magnetic field H; the static susceptibility is defined as M_{dc}/H. The temperature and field dependent ac susceptibility χ_{ac} was determined by measuring the magnetization response to a small ac field ($\leqslant$ 2 mOe at 0.08 Hz) applied parallel to the static field with a separate small solenoid.

Conventional four probe low frequency ac resistance measurements were made on single ribbons of $NbSe_3$ as a function of temperature, applied magnetic field, and current density. Although these samples appear visually and in an SEM to be single crystals the microscopic morphology has not been fully elucidated. The current direction in all cases was along the crystallographic b axis (the high conductivity direction) and magnetic fields up to 40 kOe were applied parallel to the b axis and to the a* axis.

EXPERIMENTAL RESULTS

The low temperature diamagnetic susceptibilities of $TaSe_3$ and $NbSe_3$ are quite similar, and appear to depend strongly on the sample morphology. Important features common to both materials are 1) the susceptibility is very small near the temperature where the (upper) resistive transition is observed (below 2.5 K), 2) the susceptibility increases strongly at temperatures far below this transition temperature, 3) the ac susceptibility is much greater than the dc susceptibility (as defined above) at low temperatures, and 4) χ_{dc} decreases very quickly with increasing field while χ_{ac} is affected only slightly by small fields, falling to half its zero field value around 100 Oe.

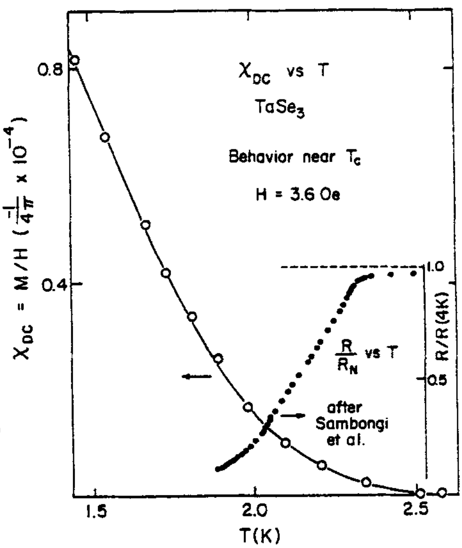

Figure 1. Onset of temperature dependent diamagnetism in $TaSe_3$ shown with the first published resistive transition drawn to the same temperature scale. The resistance does not drop to zero (baseline of graph). The solid line guides the eye. $-1/4\pi$ represents total flux exclusion from the sample.

As samples of $TaSe_3$ and $NbSe_3$ are cooled below the temperature where the resistive transition is observed to begin (~2.5K) a small diamagnetic susceptibility is observed. Figures 1 and 2 show this onset. The susceptibility shows no thermal hysteresis, but flux

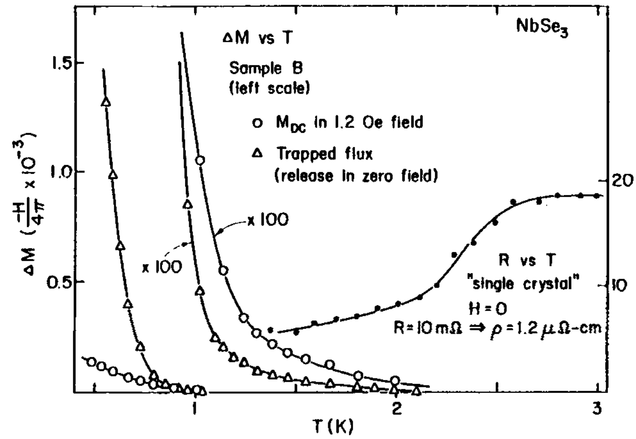

Figure 2. M_{dc} traces flux expulsion from the compacted sample of $NbSe_3$ during cooling. Below 0.5 K the field was removed. As the sample was warmed, trapped flux was released (same ΔM scale). Also shown is low temperature resistive anomaly measured on a crystal grown in this lab. The lines guide the eye.

trapping has been observed in all samples. Flux trapping is shown in Fig. 2 for one of the $NbSe_3$ samples, where it is seen to persist to above 2 K. Such flux trapping is proof of the existence of long range phase coherence and hence of the existence of superconductivity in $NbSe_3$.

As the temperature is decreased the susceptibility continues to increase (with positive curvature in the χ vs T plots) to temperatures far below the onset temperature. This continuous increase in susceptibility correlates well with the continuous decrease in resistivity reported in $NbSe_3$ (Fig. 3). Low temperature measurements have not been reported for $TaSe_3$. Figure 3 also shows that the size and temperature dependence of the susceptibility depends on the morphology of the sample. The corresponding curve for the sample of etched and compacted material is similar in shape to that of sample B, but χ_{dc} is larger and shows some indication of beginning to level out for $T < 100$ mK (Figure 4).

The temperature dependence of the ac susceptibility is very similar to that of χ_{dc} in $TaSe_3$ (Figs. 5 and 7), and in the several samples of $NbSe_3$ (Figures 4 and 6). However, χ_{ac} is much larger than χ_{dc} except in the limit of very small applied fields.

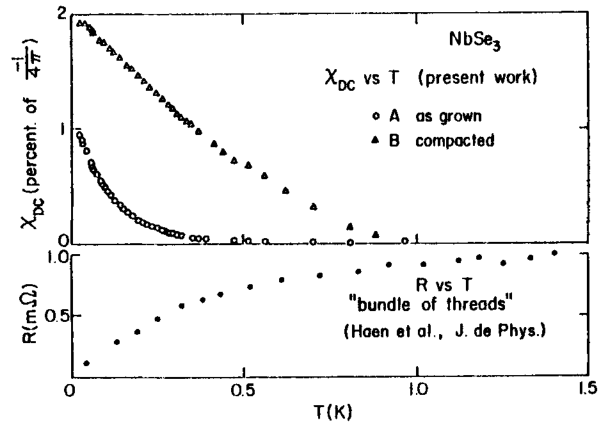

Figure 3. Upper portion shows low temperature increase of diamagnetic susceptibility of $NbSe_3$. Measurements were made below 1 K and the zero offsets determined by matching measurements made in the ^3He cryostat. Susceptibility of the as-grown material above 0.5 K is small but not zero. Lower portion of the figure reproduces the second low temperature drop in resistance for the lowest current density (1.3 mA/mm^2) reported by Haen et al.

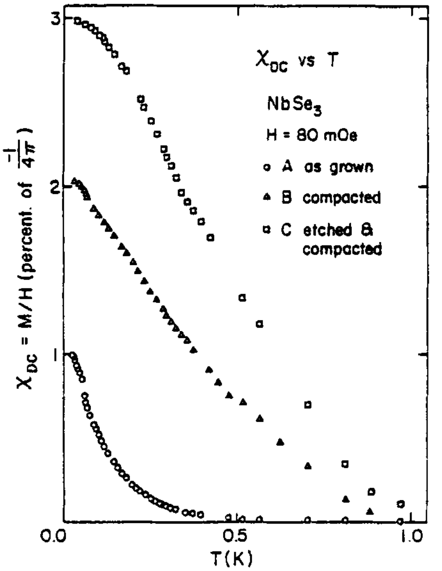

Figure 4. Low temperature increase of diamagnetic susceptibility for three samples of $NbSe_3$ (see text).

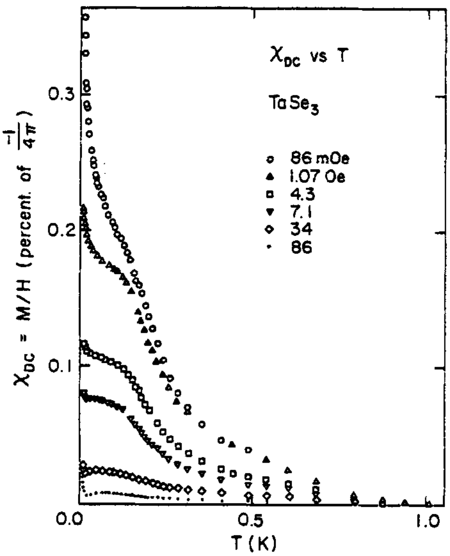

Figure 5. Low temperature increase of diamagnetic susceptibility for $TaSe_3$ (as grown material) in several dc fields.

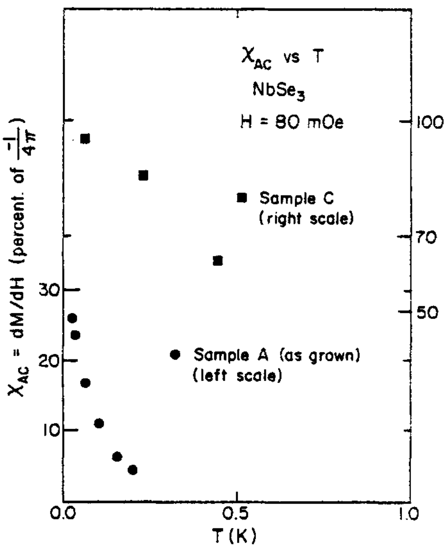

Figure 6. ac susceptibility of two samples of $NbSe_3$ at low temperature. χ_{ac} and χ_{dc} plots are similar in shape, but $\chi_{ac} >> \chi_{dc}$. The baseline is zero for both vertical scales.

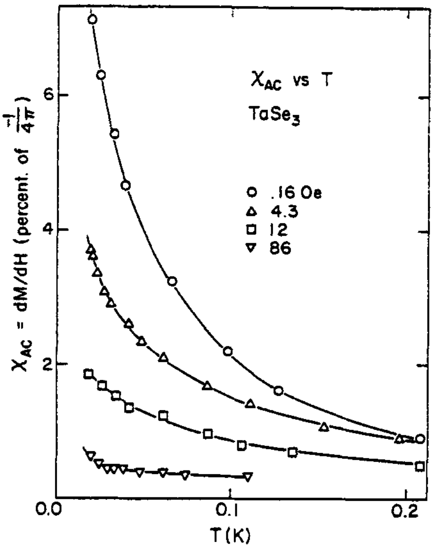

Figure 7. Low temperature ac susceptibility of $TaSe_3$ in several applied dc fields. χ_{ac} is larger than χ_{dc} and increases strongly at lower temperatures. Note different temperature scales for Figs. 5 and 7.

The shape of χ_{dc} vs T for $TaSe_3$ may be influenced by background, as the signal was quite small. A curie term has been added to the data which amounts to .12%/Oe at 10 mK (using the units of Fig. 5). This Curie term is several times larger than the background of the empty magnetometer, and suggests paramagnetic impurities in the $TaSe_3$. However, the large increase in χ_{dc} at very low temperatures is present in low fields even in the uncorrected data. Background is entirely negligible in the ac measurements.

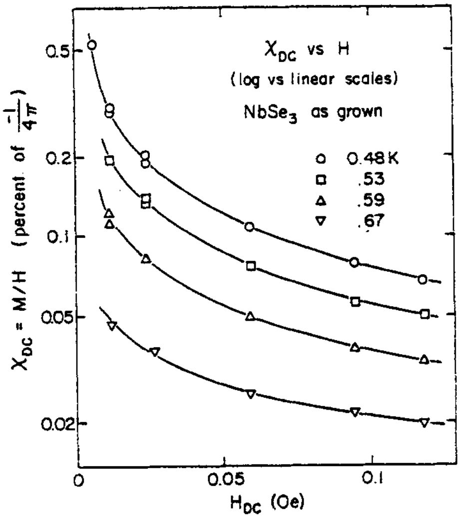

Figure 8. χ_{dc} vs H_{dc} curves for $NbSe_3$ constructed from χ_{dc} vs T measurements. χ_{dc} is not constant in low fields. Vertical scale is logarithmic.

The effect of increasing magnetic field is to decrease the susceptibilities, particularly the dc susceptibility. The measurements of χ_{dc} vs T in various fields can be replotted as χ_{dc} vs H for several temperatures. This has been done in Fig. 8 for low field measurements in $NbSe_3$ (as-grown), and is clearly not constant, even in fields of 20 mOe. The applied field diminished χ_{ac} much less than χ_{dc}, as shown in Fig. 9. Measurements are shown for two samples of $NbSe_3$, and the etched and compacted sample maintains χ_{ac} nearly constant to a dc field much larger than the field which begins to diminish χ_{ac} in the as-grown sample. The sample of $TaSe_3$ (not shown) behaved much as the corresponding (as-grown) sample of $NbSe_3$.

The inset to Fig. 10 shows the typical ρ(T) behavior. The "knee" between 2 and 2.5 K has been observed, in zero field, in all crystals examined (12 samples from two different batches). Below

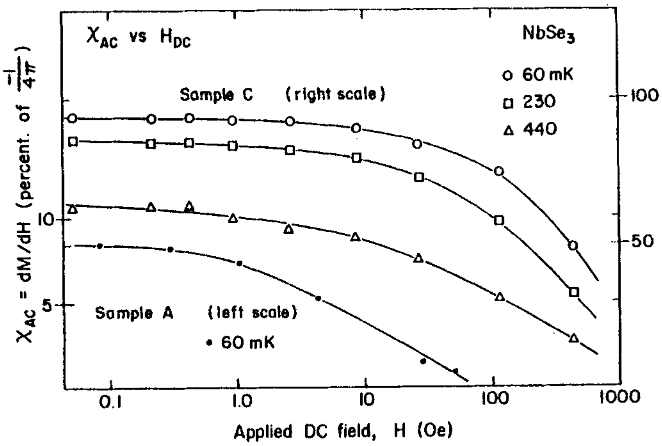

Figure 9. χ_{ac} vs H_{dc} for two samples of $NbSe_3$ at 60 mK, and for the etched and compacted sample at several temperatures. χ_{ac} is unchanged by fields less than 1 Oe, in marked contrast to χ_{dc}. Horizontal scale is logarithmic.

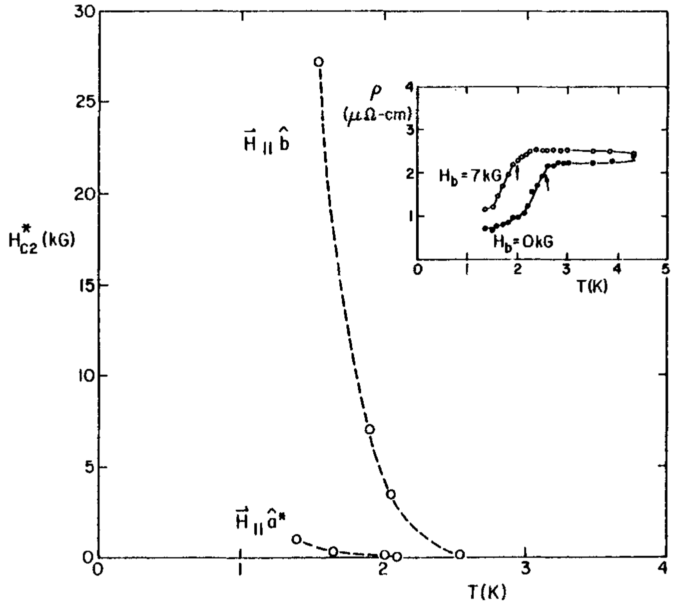

Figure 10. Effective parallel (H||b) and perpendicular (H||a*) critical fields $H^*_{c2}(T)$ for $NbSe_3$. The inset shows how the resistive anomaly is depressed in a field (H||b) and indicates the temperature at which a 10% drop in resistance has occurred. This temperature is used to construct the main figure.

2 K the resistance levels off at a value which is highly sample dependent, varying from 30% to 90% of the 4.2 K resistance. So far no correlation has been found between the magnitude of the resistance drop and any other property of the samples, e.g. crystal dimensions, room temperature resistance, residual resistance ratio, history, etc.

The temperature at which the knee occurs is depressed by a magnetic field. The value of the field, H^*_{c2}, required to lower the temperature of the anomaly is depicted in Fig. 10. There is considerable anisotropy in this field dependence, characteristic of superconductors of reduced dimensionality. Fig. 11 shows the field

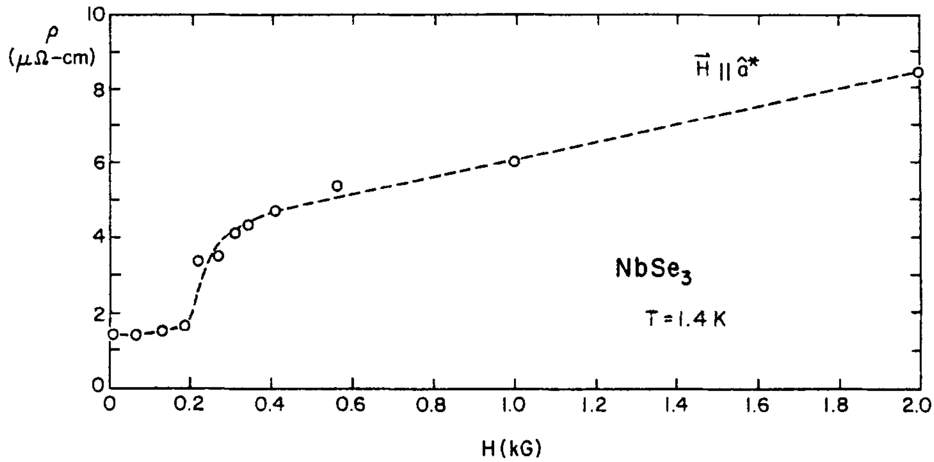

Figure 11. Field dependence (H||a*) of the resistivity of $NbSe_3$ at 1.4 K. Current density was 5×10^{-3} A/cm^2.

dependence of the resistivity at a fixed temperature of 1.4 K. There is a well defined transition to normal state behavior at a field of 200 Oe applied perpendicular to the current. The corresponding transition is at a field of order 10 kOe for the parallel field, and is much broader.

It should be emphasized that all these measurements were made using currents less than 500 nA in samples of about 10^{-5} cm^2 cross-section (i.e. current densities less than 5 x $10^{-2} A/cm^2$). Non-linear I-V characteristics are observed for current densities in excess of 10^{-1} A/cm^2 (i.e. 1 μA).

DISCUSSION

The onset of temperature dependent diamagnetism with the resistivity drop near 2.5 K indicates a superconducting transition in both $TaSe_3$ and $NbSe_3$ at this temperature. This is made certain by the observation of flux trapping in all samples. However, the temperature and field dependence of the susceptibility cannot be explained simply in terms of a superconducting transition near 2.5K. While the non-constancy of the dc susceptibility in weak fields and the difference between the ac and dc susceptibilities could be interpreted as extreme type II behavior, such an interpretation would explain neither the positive curvature of χ vs T nor the strong increase of χ at temperatures far below the superconducting transition temperature.

The observations are suggestive of a transition in which separate small regions of dimension much smaller than the supercondu-ting penetration depth are individually superconducting below about 2.5 K and become coupled over much larger regions when the thermal energy k_BT becomes less than the coupling energy between regions. Two possibilities are coupling between portions of a single crystal and coupling between the small crystals which make up the sample.

Yamamoto[3] has suggested on the basis of critical field anisotropy measurements that a crystal of $TaSe_3$ is best thought of as consisting of uncoupled thin layers parallel to the bc plane. The crystallography of $NbSe_3$ suggests that it might also be considered to have a planar structure. While critical field measurements have not yet been completed on $NbSe_3$ the preliminary measurements reported above indicate an anistropy similar in character to that found by Yamamoto in $TaSe_3$ but even more extreme. This severe anisotropy suggests that two transitions could occur in a single crystal: first, one where the planes would become (individually) superconducting, and second, a lower temperature transition when the weak Josephson-like coupling between the 2-d planes is strong enough to overcome thermal fluctuations. Thus the low temperature transition is a transition from 2-d to 3-d superconducting behavior in the crystal. Such a transition would be of the paracoherent-coherent variety suggested by Deutscher et al.[11]

In the case of the diamagnetic measurements a similar argument also gives the possibility of two transitions in a sample of many weakly coupled crystals. In this model the first transition occurs when individual crystals become superconducting, the second when the inter-crystal superconducting coupling becomes established. While this second possibility cannot be ruled out, its likelihood is diminished by the requirement that the penetration depth of these materials must be very large, greater than 10 μm, in order to explain the small diamagnetism near the first resistive anomaly. This latter explanation also does not account for the non-zero residual resistance routinely observed in these materials.

While not conclusive, the experimental evidence tends to support the concept of weakly coupled 2-d superconducting planes within the $TaSe_3$ and $NbSe_3$ crystals. If so, the inter-phase coupling is much weaker than that normally found in the dichalcogenides with the 3-d ordering here occurring far below T_c. Thus these materials may well be the best examples available of 2-d superconductivity. Further work on these materials is in progress.

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