

Observation of the peak effect in the superconductor $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$

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(Received 22 April 1997)

The peak effect in single crystals of the superconductor $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$ has been investigated by dc magnetization, ac susceptibility, electrical resistivity, and critical current measurements in applied magnetic fields. The transition from a weakly pinned region to a strongly pinned region is mapped out in the H - T phase diagram. The results on the superconducting stannides, $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$ and $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$, are found to be similar to that obtained on some heavy fermion and intermediate valence superconductors. [S0163-1829(97)06737-4]

I. INTRODUCTION

$\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$ is a superconductor, with a T_c of ~ 8.2 K and belongs to the family of compounds that exhibit a wide variety of properties.¹ Some members of this family of stannides, exhibit magnetism and the co-existence of superconductivity and magnetism. $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$ crystallizes in the Phase-I structure (primitive cubic) and has the same crystal structure as $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$.² While $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ is sometimes known to adopt slightly different structural modifications of the Phase-I structure due to disorder between the Sn and the Yb sites, $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$ does not suffer from any such disorder, always adopting the Phase-I structure.³

In a recent paper,⁴ we have reported the observation of the ‘‘peak effect’’ in single crystals of the related compound $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$, through dc magnetization and resistivity measurements. An irreversible peak in the magnetization was observed below H_{c2} . This ‘‘peak effect’’ in magnetization has also been observed by Sato *et al.*⁵ previously in $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$. Our study also revealed anomalies in resistance measurements in a magnetic field and from these results, it was possible to map out a region of enhanced pinning in the mixed state of $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$. The results obtained by us for $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ strongly resemble those obtained for CeRu_2 (see for instance, Onuki *et al.*⁷). The ‘‘anomalous peak effect’’ has been observed earlier in CeRu_2 , heavy fermion superconductors such as UPd_2Al_3 , CeCo_2 ,⁷ and superconductors such as NbSe_2 .^{8,9} The peak effect exhibited by these compounds, is different from the peak effect exhibited by conventional dirty type-II superconductors.¹⁰⁻¹² The observations of the hysteretic peak in the magnetization, and a wide variety of magnetotransport, magnetocaloric, and elastic constant measurements in the heavy fermion and intermediate valence compounds have led to a discussion of whether there is sufficient experimental evidence pointing to the existence of the FFLO state in these materials. The FFLO state was proposed by Fulde and Ferrel and Larkin and Ovchinnikov independently.^{13,14} The FFLO state is a partially polarized state that forms at high magnetic fields, the transition from the ordinary superconducting mixed state to this state being of first order. The superconducting order parameter is spatially modulated in this state. The FFLO state has been looked for in vain among the conventional superconductors. The conditions laid down for the existence and observation of the FFLO state are stringent: (i)

the superconductors have to be in the clean limit, $l \gg \xi$ (ii) the superconductors are strongly Pauli limited; (iii) the temperature range over which the state exists is restricted to $T \leq 0.55T_c$.¹⁵ Although the heavy fermion superconductors were originally put forward as the most likely candidates for the existence and observation of the FFLO state, it is now clear that they do not entirely satisfy all the criteria in all cases, the temperature range stipulated in (iii) is much smaller than that observed.

Recently, there have been attempts at explaining the existing experimental evidence in the heavy fermion superconductors as an indication of the existence of a new state called the generalized FFLO (GFFLO) state. The theoretical framework for the GFFLO state was put forward by Tachiki *et al.*^{16,17} and is a more realistic version of the FFLO model. In a few recent publications^{18,19} the first-order transition seen between a weakly pinned state to a strongly pinned state in the heavy fermion superconductors has been interpreted in terms of the GFFLO model, which may allow for a wider temperature region than $T \leq 0.55T_c$ over which this effect may be observed. In most of these compounds, including the superconducting stannides in the present study, the anomalies and the transition to a different pinning region persists in temperature up to T as high as $0.9T_c$.

CeRu_2 is known to be a strongly intermediate valence superconductor, while Yb in $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ is thought to be in the divalent state and is therefore not expected to be a valence fluctuating system.²⁰ The similarities in the properties of CeRu_2 and $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ would warrant a study of an analogous compound and we have chosen the nonmagnetic superconductor, $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$ which is identical in all other respects to the Yb compound, for a comparative study. We have carried out an exhaustive study of single-crystal $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$, by performing dc magnetization, ac susceptibility in a magnetic field, resistance measurements, and critical current measurements in a magnetic field. All these measurements show anomalies in the mixed state which can be related to the peak effect. The results obtained on $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$ are similar to those obtained on $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ crystals which in turn strongly resemble those available in the literature for CeRu_2 , as we have shown in our recent paper.⁴ From our comparative study of the two stannides, $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$ and $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$, we conclude that except for a few subtle differences in the nature of the magnetization anomalies observed, the two compounds exhibit

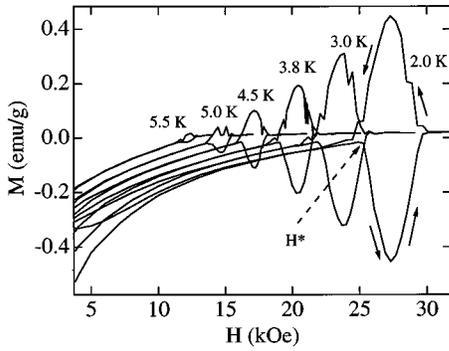


FIG. 1. Magnetization as a function of applied magnetic field at different temperatures for a single crystal of $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$. The arrows indicate the direction of the field variation. H^* is the field at which the onset of the peak in magnetization occurs.

very similar properties. The features in the magnetization, ac susceptibility, and resistivity measurements observed in the mixed state of the superconducting stannides, are in general similar to those observed in the heavy fermion and intermediate valence superconductors.

II. EXPERIMENTAL DETAILS

Single crystals of $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$ were grown by the tin flux method.²¹ dc magnetization measurements were performed using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, USA). A scan length of 2 cm was employed in all the magnetization measurements in order to minimize any artefacts arising from the inhomogeneity of the magnetic field due to the movement of the sample. The ac susceptibility was measured using an induction method with a driving field of $H_{ac} = 2$ Oe (parallel to the dc magnetic field) and a frequency of 113 Hz. A four-probe dc method was employed for measuring the electrical resistance on a small piece of the crystal, with dimensions of $0.23 \times 0.48 \times 3.08$ mm³. The measuring currents were between 1 and 100 mA, where 1 mA corresponds to a current density of $J = 0.9$ A cm². The current was applied perpendicular to the direction of the applied magnetic field. The critical current values (I_c) were obtained from I - V characteristics at a certain temperature and magnetic field using the criteria of the appearance of 1 μ V across the sample.

III. RESULTS AND DISCUSSION

Figure 1 shows the variation of the magnetization as a function of magnetic field at different temperatures for a single crystal of $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$ with a T_c of 8.2 K. The sample was initially cooled down to the required temperature in zero magnetic field and the magnetization was recorded for increasing as well as decreasing magnetic fields. The magnetization curves clearly indicate a sudden increase of magnetization at a certain magnetic field H^* before the upper critical field H_{c2} is reached. As the field is decreased from well above H_{c2} , the magnetization curves are irreversible, until the field H^* is reached and thereafter reversible down to low fields. This irreversible peak observed is typical of superconductors showing the classical peak effect due to the sudden increase in the current density below H_{c2} . This feature is

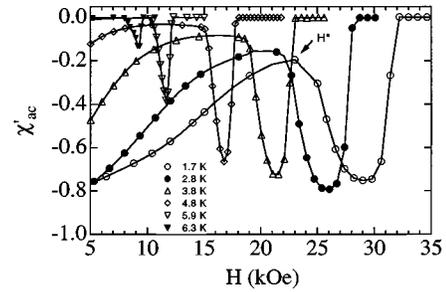


FIG. 2. Real part of the ac susceptibility (χ') as a function of applied dc magnetic field at different temperatures. For increasing as well as decreasing fields, the curves are reversible at all temperatures. Only some of the data points are shown in each curve for clarity. All the curves are normalized with respect to the χ' value at zero field. The field at which the onset of the peak occurs agrees well with the H^* values obtained from the M vs H curves (see Fig. 1).

broadly similar to that seen by us in $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$,⁴ with a couple of differences: (a) the magnetization recorded while the field is being reduced shows a few irregular jumps in the irreversible region. These are probably due to flux jumps, they are seen consistently only for reversing fields at all the temperatures at which the magnetization is recorded; (b) the magnetization curves show a larger reversibility for fields below H^* than that seen in $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$.

In order to further investigate this anomaly in magnetization, ac susceptibility measurements were carried out as a function of temperature as well as applied dc magnetic field. The sample was initially cooled in zero field to the required temperature and χ' was measured for increasing and decreasing magnetic field values. The magnetic-field variation of the real part of the ac susceptibility (χ') is shown in Fig. 2 for various temperatures. As the dc magnetic field is increased, χ' shows a monotonic decrease up to a field value H^* . As the field value is increased further, χ' shows a sudden increase, goes through a maximum, and then decreases as H_{c2} is approached. The field values H^* are almost the same as those where the peak is observed in the dc magnetization data. The peak positions in χ' were found to be independent of the magnitude of the ac field, as well as the frequency. Also, the curves were almost reversible for increasing and decreasing fields. The peaks in χ' could be traced up to 7.3 K ($\sim 0.9T_c$) from the lowest temperatures (1.7 K in our measurements).

In order to investigate whether the anomalies occurring in the dc magnetization and ac susceptibility are related to increased pinning (as is the case for superconductors exhibiting the classical peak effect), electrical resistance as a function of field and temperature as well as the I - V characteristics were measured. Figure 3 shows the temperature variation of the electrical resistance for different applied magnetic fields for a fixed measuring current, $I=100$ mA. For zero applied magnetic field, the superconducting transition is observed as the resistance dropping to zero and staying at zero down to the lowest temperature measured. As the field is increased, a small but measurable rise in the resistance is observed for a certain range of magnetic fields, after the onset of the superconducting transition, before reaching the $R=0$ state. This sudden increase in the resistance is ob-

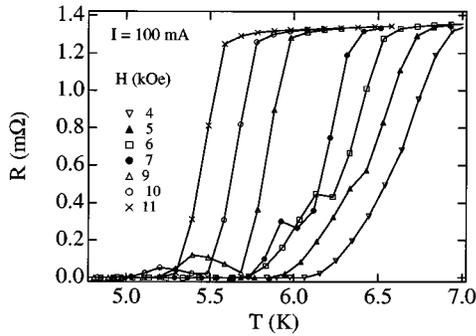


FIG. 3. Resistance as a function of temperature for different applied magnetic fields for a measuring current of 100 mA. For certain field values, the resistance shows an anomalous rise in the superconducting state.

served for fields between 5 and 10 kOe at this measuring current. For fields of 9 and 10 kOe, the resistance falls to zero and as the temperature is lowered further, it shows a reentrance. These curves are reversible for increasing and decreasing temperatures.

The anomalies in the resistance are seen more clearly in the resistance variation as function of magnetic field at different temperatures, and are shown in Fig. 4, at $T = 6.63$ K. The temperatures and magnetic fields at which these anomalies appear are strongly dependent on the measuring current. The curves have been recorded for various values of the measuring current to map out the field and temperature region over which this anomalous increase in the resistance in the superconducting state is observed.

The observation of the resistance anomalies coupled with the irreversible peak seen in the magnetization curves, reflect a change in the pinning properties at characteristic applied fields. This field is H^* , derived from the magnetization measurements at different temperatures. In the resistance measurements, the field at which a resistance anomaly is first seen for the lowest measuring current used would be the field required to bring about a movement of the flux lines due to the Lorentz force at a given temperature. This flow of flux causes a dissipation and is seen as a rise in the resistance. In our previous investigation of the anomalies in the resistance in $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$,⁴ we have shown how the fields at which

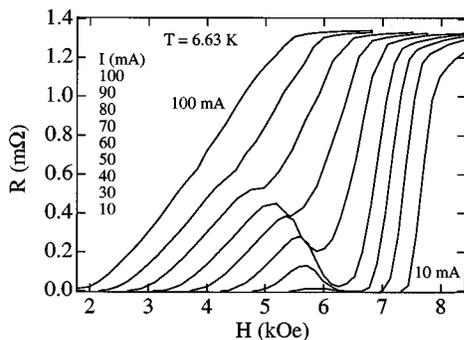


FIG. 4. Resistance variation as a function of applied magnetic field for different measuring currents at $T = 6.63$ K. The appearance of the anomalous increase in resistance strongly depends on the measuring current, which in turn depends on the critical current density of the sample.

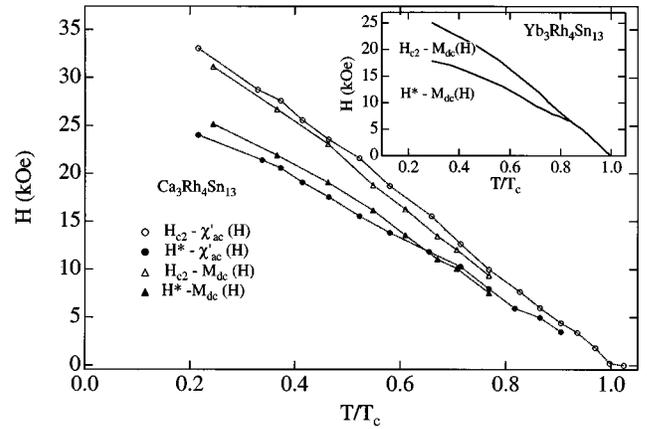


FIG. 5. H - T phase diagram for $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$ obtained from dc magnetization and ac susceptibility measurements. H^* , the field value at which the onset of the peak effect appears, is plotted from both measurements. Inset shows the H - T phase diagram obtained for $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ [see Tomy *et al.* (Ref. 4)] for comparison.

the anomalies are observed in the resistance at different temperatures correspond to the fields H^* at which the peak in the M vs H curves is seen, in the limit of zero measuring currents. This illustrates that we are sampling the same feature, i.e., changes in the pinning strength over a fixed field and temperature region, in both the magnetization and resistance measurements. The same holds true in our present study on $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$ as well. The H^* values obtained from the M vs H curves correspond well with the field values obtained from an extrapolation to zero current from the resistance measurements. Resistance anomalies of the type observed in these compounds have been previously observed in CeRu_2 ,²² NbSe_2 ,^{23,8} and by us recently in $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$.⁴

Based on the magnetization, ac susceptibility, and the resistance measurements on $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$, it is now possible to construct a H - T phase diagram. This is shown in Fig. 5. The H_{c2} values obtained from both the dc magnetization and ac susceptibility measurements are plotted along with the H^* values obtained from each of these measurements. The inset shows the H - T phase diagram obtained by us from dc magnetization measurements for $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$.⁴ The H^* - T line in the phase diagram therefore separates two regions: a weakly pinned region for fields below H^* , where there is easy movement of flux lines and a strongly pinned region for fields above H^* , where the flux lines are pinned to an energetically favorable arrangement. It is only when the Lorentz force due to the applied magnetic field overcomes the pinning force in the weakly pinned regime, that there is a dissipation due to the flux flow, which causes a voltage to appear across the sample and is seen as the resistance anomaly. The phase diagram obtained by us here for the two superconducting stannides is very similar to that reported in the literature for CeRu_2 . Both in CeRu_2 and in UPd_2Al_3 , the H^* - T line extends to $\sim 0.9T_c$ as in the present study.

A measurement of the critical current was carried out as a function of applied magnetic fields. Figure 6(a) shows the I - V characteristics measured at a fixed temperature ($T = 5.7$ K) for various applied magnetic fields. It is seen that for a particular range of the applied magnetic field within a particular temperature range, the behavior deviates from the normal I -

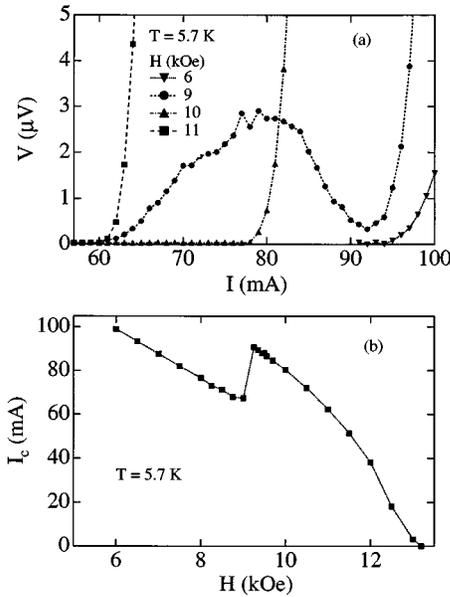


FIG. 6. (a) I - V characteristics at a particular temperature for different applied magnetic fields. For certain applied magnetic fields the I - V curves show a deviation from the normal characteristics. One such curve is shown in the figure for a field of 9 kOe. (b) The critical current (I_c) as a function of magnetic field. I_c is defined as the current at which a voltage of 1 μ V first appears across the sample. The field at which the sudden rise in I_c occurs, agrees well with the field H^* at which the onset of the peak in the M vs H curves occur.

V characteristics. Such anomalies are observed for fields between 6 and 10 kOe and a typical curve of this behavior is shown in the figure for a field of 9 kOe. From these I - V characteristics taken at different temperatures and fields, the critical current is extracted and plotted in Fig. 6(b) for one temperature, $T = 5.7$ K. A sharp rise in the critical current is seen at ~ 9 kOe. The field at which the sharp increase in critical current occurs at any given temperature, corresponds well with H^* , the field at which the peak in the magnetization occurs (see Fig. 1).

One of the requirements for the existence of the FFLO state is that the superconductors are strongly Pauli limited. Both UPd_2Al_3 and CeRu_2 appear to exhibit large spin susceptibilities at low temperatures. The dc magnetic susceptibility was measured on a crystal of $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$ and is shown in Fig. 7. To arrive at the Pauli susceptibility, we have subtracted the contribution due to the diamagnetic cores from the observed high-temperature susceptibility, taken as the temperature independent part, χ_0 . An estimate of the contribution from the diamagnetic cores²⁴ gives χ_{dia} to be -1.3×10^{-6} emu/cc for $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$. The Pauli susceptibility $\chi_p = \chi_o - \chi_{\text{dia}} = 3.29 \times 10^{-6}$ emu/cc for $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$. This value is an order of magnitude less than those estimated for CeRu_2 (Ref. 6) (2.2×10^{-5} emu/cc) and UPd_2Al_3 (Ref. 19) (3.2×10^{-5} emu/cc). A detailed analysis of the susceptibility of the stannides is underway, but from the above estimates, it is clear that the stannide crystal in the present investigation is characterized by a significantly smaller spin

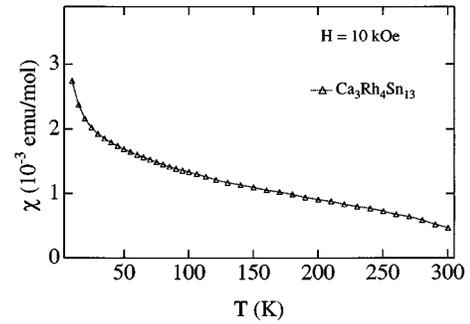


FIG. 7. Measured dc magnetic susceptibility of $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$, $H = 10$ kOe.

susceptibility than the heavy fermion and intermediate valence superconductors.

The features appearing in the dc magnetization and χ' are observed in many conventional superconductors, heavy fermion compounds (e.g., UPd_2Al_3 , CeRu_2 , and CeCo_2). In conventional superconductors, these peaks are explained as arising due to a sudden increase in the critical current below H_{c2} , due to the flux-line lattice distorting to match pinning sites. This stems from Pippard's original explanation for the observation of the peak effect¹¹ and holds good for dirty type-II superconductors. In the heavy fermion superconductor UPd_2Al_3 and the intermediate valence superconductor CeRu_2 , which are all classified as being in the clean limit, i.e., $l \gg \xi$, the observation of the peak effect coupled with anomalies in magnetocaloric, elastic constants, and dilatometric measurements have been taken as evidence for the existence of the FFLO state^{19,25} or more recently, the GFFLO state.^{16,17} From the results presented here for $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$ and from our earlier study⁴ of $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$, it is clear that these compounds do not satisfy any of the criteria put forward for the observation of the FFLO state; i.e. they are not in the clean limit, they are not strongly Pauli limited, and the temperature region where the effects are seen is wider than $T \leq 0.55T_c$. This temperature range (T up to $0.9T_c$) is larger than that predicted by models assuming quasifree electrons.^{13,14} It is thought possible that band-structure effects and the presence of antiferromagnetic exchange interactions could enhance the field region of the GFFLO state.^{16,26}

$\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$, is similar to the Yb analog in most respects, except that the Ca system appears closer to the clean limit than the Yb compound — magnetization is more reversible for fields below H^* for $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$. However, our mean-free-path estimate for $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$ from the normal-state resistivity is ~ 90 Å, comparable to that of $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$, and l and ξ are also of comparable magnitude. The crystal of $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$ that was used in our experiments had a RRR of ~ 10 . The fact that $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$ does not suffer from any crystallographic disorder between the Sn and the Ca sites probably makes it a more ordered system than $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$.

The anomalous pinning properties exhibited by the stannides appear to predict that the unusual peak effect seen in these compounds is probably more prevalent among type-II superconductors than was previously thought to be. It is however surprising that this family of superconductors

should exhibit very similar characteristics to superconductors such as CeRu₂, which are considered to be “exotic.” It is still not clear whether models such as those describing the GFFLO state need to be invoked in order to understand the anomalous features seen in the mixed state of these superconductors. More detailed investigations, in the form of magnetocaloric, elastic constants, and dilatometry measurements of the stannides will throw more light on the exact nature of their mixed state and their pinning properties. A small-angle neutron-diffraction study of the flux-line lattice

will reveal the distribution of the flux lines and the quality of the flux line lattice and is to be undertaken.

ACKNOWLEDGMENTS

We would like to thank the IRC in Superconductivity, Cambridge, for the use of the SQUID and Doug Astill for his help during these measurements. This work was supported by a grant from the EPSRC, UK.

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