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The anomalous mixed state of the C15 Laves phase superconductor $CeRu_2$: a magnetization study

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Abstract. We present a detailed magnetization study of the anomalous (H, T) regime of $CeRu_2$. Using these results as well as a comparative study involving two other type-II superconductors (Bi-2212 and 1% Fe–Nb) showing peak effects, we first show that a picture of dynamic crossover of pinning properties is inadequate to explain the anomalous behaviour in $CeRu_2$. We then argue that a first-order phase transition can explain the observed behaviour and we provide experimental evidence of such a transition in $CeRu_2$ consistent with the Clausius–Clapeyron relation. The applicability of existing theoretical models and the role of magnetism in the anomalous (H, T) regime are discussed

1. Introduction

The C15 Laves phase compound $CeRu_2$ has the highest superconducting transition temperature ($T_C \approx 6.1$ K) [1] amongst those of the Ce-based superconductors. This Laves phase compound has attracted attention almost continuously for the last 40 years due its interesting normal-state properties [2, 3] as well as its superconductivity [4]. In the field of superconductivity, the rare-earth- (RE-) doped $CeRu_2$ alloys have provided a very interesting basis for the study of coexistence of magnetism and superconductivity [4–8]. The recognition of $CeRu_2$ as an intermediate-valence (IV) compound [2, 3], and various studies, both theoretical [9] and experimental [10, 11], have maintained a steady interest in the normal-state properties of this compound. In spite of the work of the last fifteen years, many questions regarding the interesting normal-state properties of $CeRu_2$ are yet to be resolved completely [12].

During the last five years the discovery of an anomalous response in the high-field regime of the superconducting mixed state of $CeRu_2$ has opened up a new area of interest in the superconductivity of this compound. This anomalous behaviour near the upper critical field ($H_{C2}(T)$) line of $CeRu_2$ was first observed in isothermal magnetization (M) versus H plots as an enhanced paramagnetic magnetization [1], and later as an irreversible magnetization [13, 14]. Subsequently anomalous features have also been observed in the same (H, T) regime in various other physical properties, including magnetostriction [15], magnetotransport [16, 17], magnetoelasticity [18, 19] and neutron diffraction [20]. The anomalous irreversibility in the magnetization study resembles the 'peak effect' [21]. The peak effect is actually a generic term used to describe a maximum which usually occurs just below H_{C2} in the critical current (J_C) versus H plots for many hard type-II superconductors. This phenomenon is of interest because it goes against the conventional expectation that the vortex pinning and critical currents should decrease with increasing

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field near H_{C2}. For $CeRu_2$, however, there are quite a few additional features associated with the anomalous behaviour [22, 23], which distinguish this compound from other type-II superconductors.

In spite of much experimental activity during the last five years [15–20, 22–30], a clear understanding of the origin of the anomalous superconducting mixed-state properties of $CeRu_2$ is yet to emerge. At this moment there are two distinct approaches followed in efforts to understand this interesting problem.

The first approach is based on the concept of a dynamic transition involving a crossover from a weak-pinning to strong-pinning regime. This concept was originally due to Pippard [31] and is based on the argument that the shear modulus of the Abrikosov flux-line lattice (AFL) falls to zero quadratically as a function of the applied magnetic field near H_{C2}, i.e. $C_{66} \approx H_{C2}[1 - (H/H_{C2})^2]$, whereas the pinning force density goes to zero linearly as a function of H. This leads to a softening of the AFL near H_{C2} and this softened AFL can be relatively easily pinned by a few weak-pinning centres giving rise to a local enhancement of the magnetic irreversibility and hence also J_C. Such a softening of the AFL was also predicted within the collective pinning model [32], where it causes a rapid decrease in the correlation length of flux bundles. A peak in the pinning force occurs when the correlation length approaches the lattice constant. Experimental support for such a collective pinning mechanism has been obtained through the work on amorphous thin films of Nb_3Ge and Nb_3Si [33]. A similar picture of a dynamical transition has been invoked by various groups [16, 17, 20] in efforts to understand the properties of $CeRu_2$ as well. However, the following characteristic features of $CeRu_2$ distinguish it from various other hard type-II superconductors showing peak effects.

(i) In the M–H plot, the anomalous structure appears in a temperature regime distinctly below T_C [1, 14–16, 23, 24].

(ii) The estimated volume-pinning force F_P, when plotted against the reduced field H/H_{C2} at various values of T, does not scale into a universal curve [22, 23].

(iii) The increase in the volume-pinning force in the peak effect region is by more than one order of magnitude [34].

(iv) The onset field for the anomaly is distinctly different in the ascending- and the descending-field cycles [15, 16, 18, 22, 23].

All of these observations have led to the usage of the terminology 'anomalous peak effect' to describe the anomalous behaviour in $CeRu_2$ [34].

In the second approach the peak effect in $CeRu_2$ is thought to be associated with a first-order transition to a superconducting state with a new order parameter. Various studies including ones based on magnetization [15, 22], magnetostriction [15, 22] and magnetoelastic measurements [18, 19] support such an idea. In a recent study [35, 36] of minor hysteresis loops (MHL) in the anomalous (H, T) regime of $CeRu_2$, we have argued that the observed magnetic response at the onset of the anomalous regime supports the idea of a first-order transition into a new superconducting state with enhanced pinning. We then presented results of equilibrium magnetization measurements that are consistent with the existence of a first-order phase transition described by the Clausius–Clapeyron relation [35].

All of these studies taken together provide substantial evidence against a picture of a dynamic crossover of pinning properties. In this paper we shall elaborate further on this theme, by making a comparative study involving two other hard type-II superconductors showing the peak effect, namely the high-T_C compound BSCCO (Bi-2212) and 1% Fe-doped Nb. We shall see that, as far as the anomalous superconducting response is concerned, the behaviour of $CeRu_2$ remains quite distinct from those of the other two superconductors.

The rest of the paper is organized in the following way. In section 2 we give details of the preparation and characterization of the $CeRu_2$ samples used in the present study, as well as details of the dc magnetization measurement. In section 3 we first present a comparative study of (i) minor hysteresis loops in the peak effect regime and (ii) the field dependence of the pinning force density in $CeRu_2$, Bi-2212 and 1% Fe-doped Nb. Then we provide experimental evidence of a first-order transition in $CeRu_2$ consistent with the Clausius–Clapeyron relation. The applicability of various theoretical models and the role of magnetism in the anomalous (H, T) regime are discussed. Finally a conclusion is drawn, favouring the existence of a first-order transition in $CeRu_2$.

2. Experimental procedure

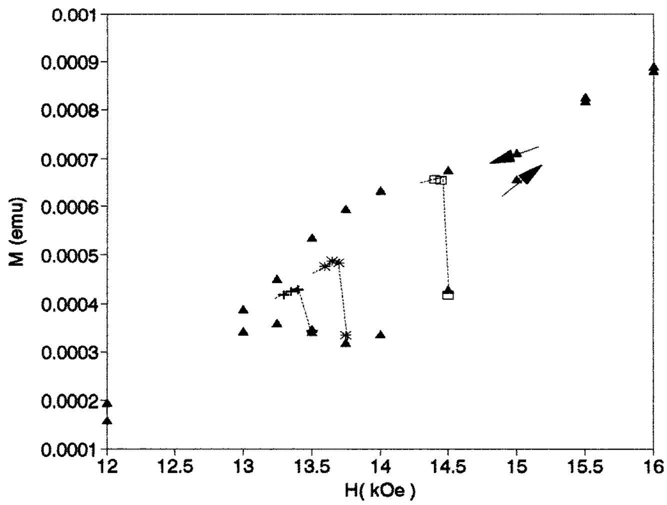
In the present study, we have used polycrystalline samples of $CeRu_2$ and Nd-doped $CeRu_2$ obtained from various sources (Imperial College, University of Kentucky and Los Alamos National Laboratory). (It is already established that the polycrystalline and Nd-doped $CeRu_2$ samples show all of the characteristic features of the anomalous superconducting mixed state observed in a good quality single-crystal sample [28, 29].) These samples were characterized using x-ray diffraction study and metallography. The sample from Los Alamos was subjected to more detailed characterization and had been used in earlier measurements [7]. Unless otherwise mentioned, all of the results to be presented in this paper were obtained for this particular sample. We assert that the results obtained are qualitatively similar for all of the samples. For comparison, we studied a single-crystal sample of BSCCO (Bi-2212) ($T_C \approx 89$ K) (obtained from the University of Warwick) and a 1% Fe-doped Nb polycrystalline sample ($T_C \approx 7$ K) (obtained from Imperial College).

The magnetization measurements were performed using a SQUID magnetometer (Quantum Design MPMS5). To minimize the sample movement in the inhomogeneous magnetic field of the superconducting magnet, we used a single scan of 2 cm length in the 'fixed-range' mode. In the 'auto-range' mode the sample goes through multiple movements while the system software searches for the most sensitive gain useful for the signal level detected. We carried out a separate preliminary run using the auto-range mode to identify the appropriate gain for the given experimental conditions and then performed a final run in the 'fixed-range' mode. In the case of a 2 cm scan length, the field inhomogeneity in an applied field of 20 kOe is ≈2 Oe. We checked the SQUID profile and regression value regularly and, except for the small field interval of the diamagnetic–paramagnetic crossover regime, the SQUID profile was always dipolar with a regression value more than 0.92. We have come to the conclusion that in an isothermal-field scan of a hard type-II superconductor, as long as the field for full penetration at a particular applied field is substantially greater than the field inhomogeneity encountered during the sample measurement, the error in the results will be negligible. This, however, may not be strictly true for temperature excursions in a fixed field, and we shall elaborate on this later in this paper.

3. Results and discussion

3.1. Comparative study of minor hysteresis loops in $CeRu_2$*, Bi-2212 and 1% Fe–Nb*

We have shown earlier [35] that at the onset of the anomalous (H, T) regime of $CeRu_2$, the behaviour of the minor hysteresis loops (MHLs) does not conform with the critical-state models (CSM). In order to make the present work self contained, we summarize these results



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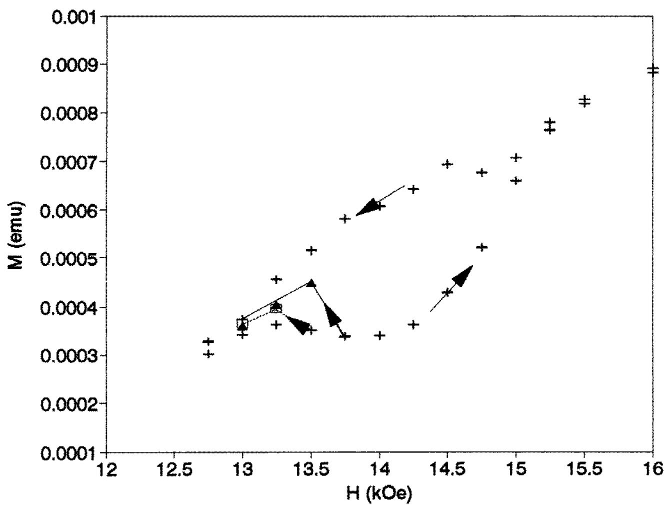


(b)

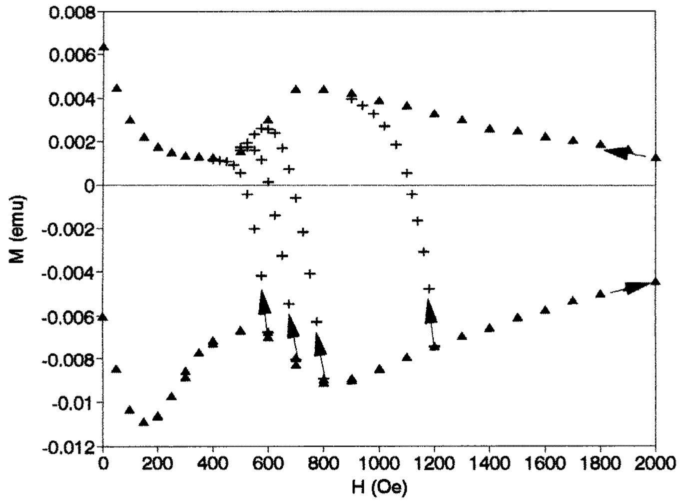
Figure 1. (a) The forward legs of the minor hysteresis loops (MHL) at $T = 4.8$ K, starting at $H = 13.5$ (+), 13.75 (∗) and 14.5 (□) kOe for the $CeRu_2$ sample obtained from Los Alamos. All of these minor loops are initiated from the ascending-field envelope cycle. The triangles represent the envelope curve. Note that the MHLs initiated at $H = 13.5$ kOe and 13.75 kOe saturated without reaching the descending-field envelope curve. (b) In this figure the MHLs (at $H = 13.5$ (□) and $H = 13.75$ (▲) and the envelope curves (+) were obtained with the same field sweep rate.

in figure 1(a), presenting the MHLs obtained in the anomalous regime of $CeRu_2$ at 4.8 K. The envelope curves are obtained by cycling the applied field between $\pm H_{C2}$ (≈17.5 kOe at 4.8 K). Within the CSM, the magnetization in a MHL can only reach saturation by reaching the envelope curves and that happens when the excursion field is greater than the field for full penetration (H_{II}). The MHL initiated well inside the anomalous bubble at $H = 14.5$ kOe on the ascending-field envelope curve is in accord with the CSM, and touches the descending-field envelope curve at an estimated value of $H_{II} \approx 50$ Oe. At the onset of the anomalous region, a marked deviation from such a behaviour is observed. The MHLs initiated at 13.5 kOe and 13.75 kOe on the ascending-field envelope curve saturate without touching the descending-field envelope curve. Note that in figure 1(a) the field sweep rate for the envelope curve (obtained mainly in 250 Oe steps) is different from those for the MHLs (obtained in 50 Oe steps). To check whether the anomalous behaviour of the MHLs is due to the different field sweep rates, we have also obtained the MHLs at $H = 13.5$ kOe and 13.75 kOe with the same sweep rate (250 Oe steps) as was used to obtain the envelope curves. The results shown in figure 1(b) clearly show that the observed anomalous behaviour of the MHLs is independent of the field sweep rate. From our study it is clear that in the field regime 13 kOe $\leqslant H \leqslant$ 14 kOe the saturation magnetization hysteresis (ΔM_S) of the MHLs depends on the starting field (H) and increases with H. This interesting effect, in which the critical current (J_C) inferred from the saturation hysteresis ΔM_S is dependent on the starting field, does not occur when the MHL is initiated from above 14 kOe. Since ΔM_S is also proportional to the size D of the sample exhibiting pinning, a natural conclusion is that between 13 and 14 kOe the anomalous phase is not fully nucleated and the size D of the nuclei or domains depends on the starting field. ΔM_S at 14.5 kOe does not depend on whether one sweeps the field up to 15 kOe or all the way to above H_{C2} ($\approx$17.5 kOe) and this is consistent with the full development of the anomalous phase having occurred by the time 14.5 kOe is reached. The domains supercool on field reduction, retaining the size that they had at the starting field. The results discussed above are representative of the anomalous behaviour of $CeRu_2$ and similar results are available over a wide temperature regime for this particular sample as well as other samples of $CeRu_2$.

To check whether the observed anomalous behaviour of the MHLs is intrinsic to $CeRu_2$ only, we have studied MHLs in the peak effect regime for two different classes of hard type-II superconductors, namely a single crystal of Bi-2212 and a polycrystalline sample of 1% Fe-doped Nb. For the single-crystal samples of Bi-2212, the peak effect arises due to a crossover of pinning properties [37]. For pure Nb, the existence of a peak effect has also been reported earlier [38]. We failed to detect any peak effect in our magnetization study of pure Nb ($T_C \approx 9.25$ K) at least down to 2 K. On the other hand, for a 1% Fe-doped Nb sample ($T_C \approx 7$ K) we have detected a distinct peak effect below 4.5 K. We have measured MHLs for both of these samples in the (H, T) regime showing the peak effect (see figure 2). In clear contrast to the MHLs of $CeRu_2$, the MHLs in the peak effect regime of Bi-2212 and 1% Fe-doped Nb saturate only after reaching the envelope curve. This latter behaviour is of course consistent with the CSM and the picture of a dynamic crossover of the flux-pinning properties.

3.2. Can a dynamic crossover explain the anomalous MHLs for $CeRu_2$?

Before seeking any other explanation, we shall first put some effort into trying to explain the anomalous behaviour of the MHLs for $CeRu_2$ in terms of a dynamic crossover of the pinning properties. Such a model would indicate that J_C (obtained from the saturation hysteresis ΔM_S) is history dependent in the anomalous (H, T) regime. A history-dependent J_C (obtained from the transport measurement) has indeed been observed for amorphous Nb_3Ge films [39] in the peak effect regime. It is argued there that the flux lattice dislocations are created with the increase in field in that regime, enhancing the flux-pinning properties. In the descending-field cycle the dislocations persist and this results in an enhanced pinning, and hence a larger J_C than in the ascending-field cycle. These dislocations are annealed out only when the field is decreased below the peak effect regime. For $CeRu_2$, we find that if



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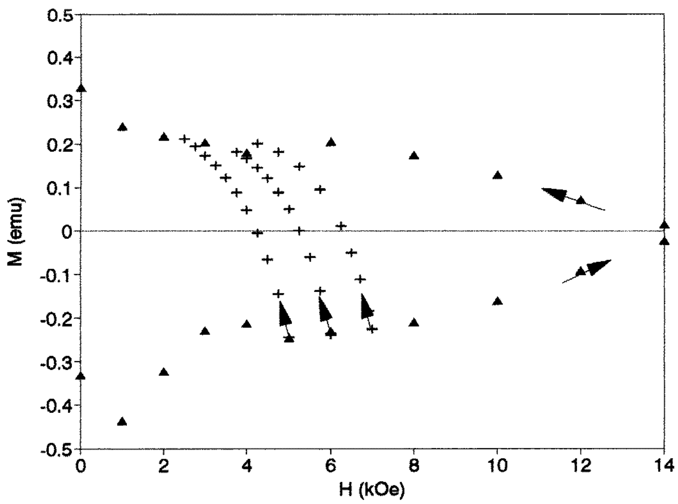


(b)

Figure 2. (a) The M–H hysteresis curve (▲) of Bi-2212 single crystal taken at $T = 25$ K with $H \parallel c$-axis. We show the forward legs of the MHLs (+) initiated at 600, 700, 800 and 1200 Oe on the ascending-field envelope curve. Note that all of these merge with the descending-field envelope curve. (b) The M–H hysteresis curve (▲) of the 1% Fe–Nb sample taken at $T = 2$ K. We show the forward legs of the MHLs (+) initiated at 5, 6 and 7 kOe on the ascending-field envelope curve. Note that all of these merge with the descending-field envelope curve.

we increase the field at say $H = 13.25$ or 13.5 kOe in the descending-field envelope curve by 100 Oe, the MHL will reach the ascending-field envelope curve. However, on decreasing the field back by 100 Oe, we fail to reach the descending-field envelope curve and a small field excursion well within the anomalous region would have reduced the large J_C (see figure 3). In fact, this return leg of the MHL fails to reach the descending-field envelope curve until we cross the anomalous field regime. This suggests that a small field excursion starting from the descending-field envelope curve will also anneal out dislocations or any

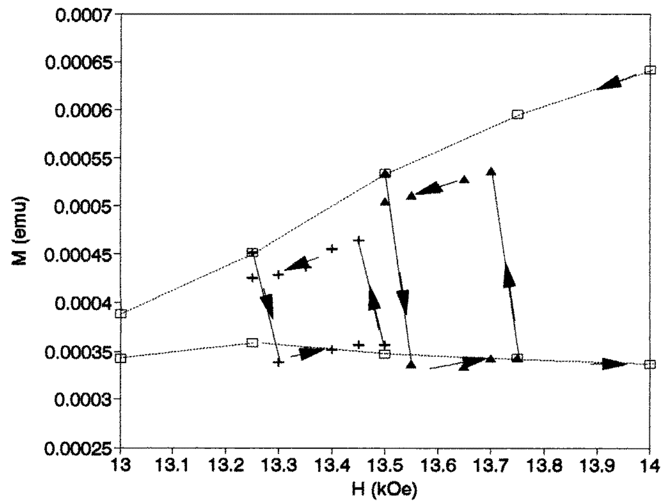


Figure 3. Complete MHLs initiated at $H = 13.25$ kOe (+) and 13.5 kOe (▲) on the descending-field envelope curve with maximum field variation $\Delta H = 250$ Oe. Squares represent the envelope curves. Note that, while the forward leg of the MHL in both cases merged with the envelope curve, the return leg saturated without reaching the envelope curve. In fact, on completion of the MHL, the $M(H)$ value did not return to the starting point.

other source of enhanced pinning. And this contradicts the conjecture [39] that annealing occurs only when the field is reduced below the peak effect regime. Thus the picture of [39] cannot explain our data.

3.3. Field dependence of the flux-pinning force (F_P) in $CeRu_2$

To address further the difficulties of using the picture of 'a dynamic crossover of the pinning properties' in explaining the anomalous superconducting behaviour of $CeRu_2$, we shall discuss the results for the field dependence of the flux-pinning force in $CeRu_2$. We recognize that the fundamental measure of the flux pinning is the pinning force per unit volume, F_P, rather than the hysteretic magnetization (or critical current density). When F_P is plotted against the reduced field $h = H/H_{C2}$, a peak is observed for much wider varieties of conditions [40]. In a pioneering paper, Kramer [41] proposed that the peak in F_P corresponds to a changeover in the mechanism of flux motion from depinning to synchronous shear of the flux-line lattice about pins too strong to be broken. Within this picture, a peak effect in the hysteretic magnetization $\Delta M(H)$ or critical current $J_C(H)$ gives rise to a narrow peak in F_P usually at high 'h', whereas a monotonic behaviour of $\Delta M(H)$ or $J_C(H)$ gives rise to a broad peak in $F_P(H)$. This has been observed experimentally for a variety of hard type-II superconductors [40, 41]. Our study of F_P in Bi-2212 and 1% Fe-doped Nb is in qualitative agreement with such a picture [42]. Marked deviation from such a behaviour is observed for $CeRu_2$. A distinct two-peak structure is observed for the F_P versus h plot (see figure 4). (F_P is estimated from the M–H data as $F_P = J_C \mu H \propto \Delta M\, H$, where ΔM stands for the difference between the descending and ascending legs of the M–H curve.) This two-peak structure has also been observed for a single-crystal sample of $CeRu_2$ [27]. The higher-field structure, which is clearly associated with the anomalous behaviour, does not scale with temperature [42]. A detailed quantitative analysis of the

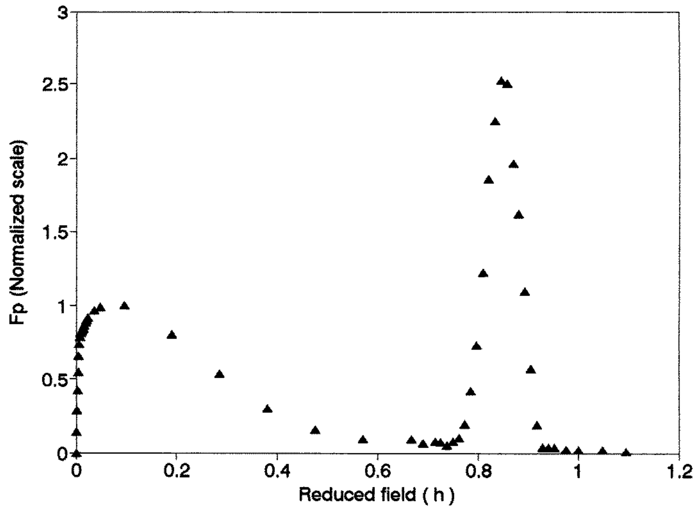


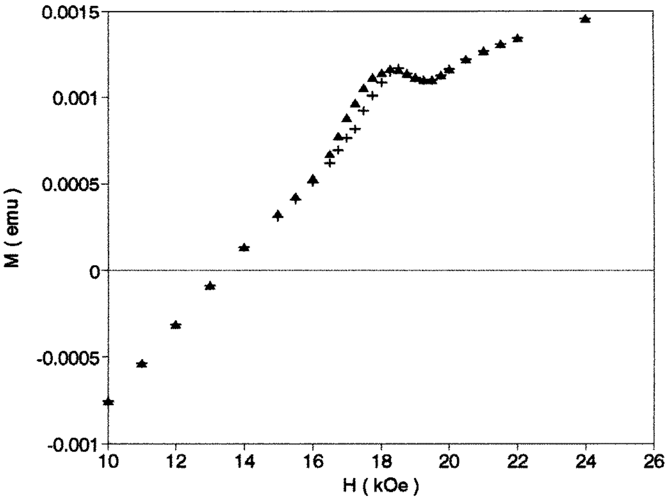
Figure 4. The pinning force (F_P) versus reduced field (h) plot for the $CeRu_2$ sample obtained from Los Alamos.

flux-pinning force over the entire (H, T) regime for various samples of $CeRu_2$ will be published elsewhere [42].

3.4. *Evidence of a first-order transition in* $CeRu_2$

It is apparent from the results and discussion given so far that the picture of a 'dynamic crossover of pinning properties' is not adequate to explain the anomalous superconducting properties of $CeRu_2$. We considered earlier an alternative picture in which a new superconducting state with enhanced flux-pinning properties is formed via a first-order transition in the anomalous (H, T) regime [35, 36] and we shall elaborate more on this subject now. This new superconducting state is nucleated in domains whose physical size grows on increasing the field, and which supercool on decreasing the field. The enhancement of the pinning properties of this anomalous phase is used to track the growth of the phase itself across the transition. We now recognize the argument of Zeldov *et al* [43], given in connection with the width of the vortex-melting transition in the single-crystal sample of Bi-2212, that in a cube-shaped sample the local field at various points inside the sample is not the same, even when the magnetization is reversible. Zeldov *et al* [43] confirmed this by showing that micro-Hall probes placed at different locations in the sample showed a melting transition at the same value of the local field, but at different values of the applied field. It is accordingly expected that the transition to the anomalous superconducting state will occur at different points in the sample over a range of applied fields. As the transition occurs at some points in the sample at an applied field H_a^*, we have domains of the anomalous superconducting state in the underlying Abrikosov flux lattice (AFL) state. As the applied field is raised, a greater fraction of the sample undergoes this transition, and the size of the domains increases. These domains have enhanced pinning and hence large values of J_C in comparison to that for the underlying AFL. The nucleation into the new phase is complete above a certain field, say H_P. If a field reduction is initiated from $H \geqslant H_P$, the domains will supercool and retain their size.

The results and the associated arguments presented above provide, at best, indirect



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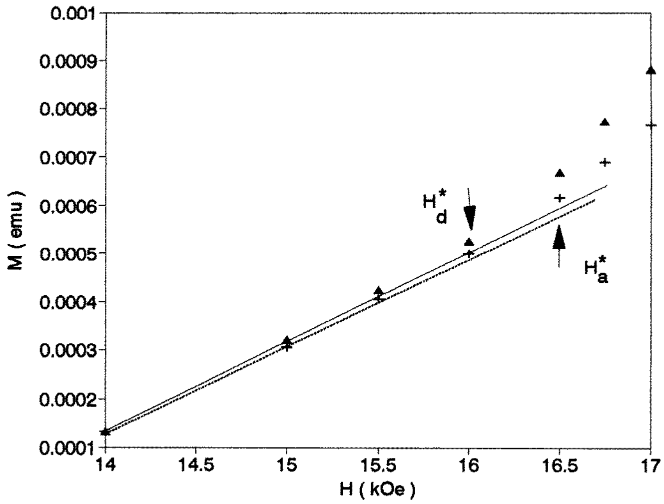

(b)

Figure 5. (a) The equilibrium magnetization (M_{eq}) versus field (H) plot at $T = 4.5$ K for the $CeRu_2$ sample. Crosses represent the ascending-field cycle and triangles represent the upper bound on the descending-field cycle. (b) Note the distinct rise in magnetization which occurs at $H_a \approx 16.5$ kOe in the ascending-field cycle (+) and at $H_d \approx 16$ kOe in the descending-field cycle (▲).

support for a first-order phase transition, and one has to look for a thermodynamical signature of the isothermal transition at H^* being a first-order transition. We have argued [35] that for a first-order transition, the change in the equilibrium magnetization (ΔM_{eq}) has to satisfy the Clausius–Clapeyron relation

$$L = T\,\Delta S = -T\,\Delta M_{eq}(\mathrm{d}H^*/\mathrm{d}T). \tag{1}$$

Since the high-field phase is also the high-temperature phase, it has a higher entropy. Thus ΔS is positive, as H increases across H^*, and a negative $(\mathrm{d}H^*/\mathrm{d}T)$ requires that ΔM_{eq}

be positive, i.e. the equilibrium magnetization (M_{eq}) must rise as the field is raised through H^* at constant temperature. We then proposed obtaining $M_{eq}(H)$ for the ascending-field cycle by measuring MHLs from the ascending-H branch $M\uparrow(H+\delta)$ and lowering the field to below $H-\delta$ to obtain minor-loop magnetization $M_{ML}\downarrow(H-\delta)$. We shall keep $2\delta = H_{\rm II}$, where $H_{\rm II}$ is the field for full penetration such that $M_{ML}\downarrow$ reaches the envelope curve for the domain size prevailing on the ascending branch at $H+\delta$. We note that $\delta \leqslant 50$ Oe. Furthermore, $M_{ML}\downarrow(H-\delta)$ was smaller than $M\downarrow(H-\delta)$ because the domain in the descending-field envelope curve was a supercooled domain of larger size. Since the domain size was unchanged for the MHLs, and δ was small, we could estimate $M_{eq}(H)$ from

$$M_{eq}(H) = \tfrac{1}{2}[M\uparrow(H+\delta) + M_{ML}\downarrow(H-\delta)]. \qquad (2)$$

$M_{eq}(H)$ obtained using such a procedure in the ascending-field cycle for various samples of $CeRu_2$ and 5% Nd-doped $CeRu_2$ show a pronounced rise as H crosses H_a^* and enters the anomalous (H, T) regime [35]. For the sake of completeness of the present discussion, we reproduce in figure 5(a) the results obtained for the pure $CeRu_2$ sample from Los Alamos at $T = 4.5$ K. The dip in the magnetization in $M_{eq}(H)$ just below H_{C2} for the pure $CeRu_2$ is, however, not observed for the other two samples of $CeRu_2$ and the 5% Nd-doped $CeRu_2$ sample [35]. The possible origins of such a dip were discussed earlier [35] and this discussion will not be repeated here. In the descending-field cycle, the domains on the envelope curve in the field regime below H_P are the supercooled domains. (It is to be recalled here that H_P is the field in the ascending-field cycle, at which the nucleation of the anomalous superconducting phase was completed.) The sizes of these supercooled domains are larger than those of the corresponding fields on the ascending-field envelope curve. We cannot estimate the equilibrium magnetization of these supercooled domains using the MHLs, because the domains will shatter on increasing the field. We have actually demonstrated this effect for the pure $CeRu_2$ sample in figure 3 and for the 5% Nd-doped $CeRu_2$ sample in reference [36]. In figure 3 the return legs of the MHLs are seen to saturate before reaching the descending-field envelope curve. In fact, on completion of the MHL the $M(H)$ curve did not return to its starting point; a distinct difference between the initial and final values of $M(H)$ is quite apparent in figure 3. This we attribute to the shattering of the supercooled domains which existed on the descending-field envelope at the starting points of the FHLs. The arithmetic mean of $M\uparrow(H)$ and $M\downarrow(H)$ (where $M\uparrow(H)$ and $M\downarrow(H)$ correspond to saturation magnetization on the ascending- and descending-field envelope curves respectively) will give the upper limit of the equilibrium magnetization curves for the descending-field cycle. This result for $M_{eq}(H)$ for the descending-field cycle thus obtained for the pure $CeRu_2$ sample (obtained from Los Alamos) is shown in figure 5(a). Marked hysteresis in magnetization is observed below H_P ($\approx$18.25 kOe at $T = 4.5$ K) and the anomalous behaviour is completed at a field H_d^*, which is distinctly lower than H_a^* (see figures 5(a) and 5(b)). Such a behaviour has earlier been taken as a typical signature of a first-order transition in $CeRu_2$ [22, 23].

While there are plenty of studies of the isothermal-field excursions available for the anomalous superconducting mixed state of $CeRu_2$ [14–16, 22, 23, 27–29], there have been very few attempts to investigate temperature excursions in fixed applied fields [22, 44]. We shall first highlight why iso-field temperature excursions can provide important information. It has been observed for various hard type-II superconductors that when the magnetization is due to pinning and is related to the temperature-dependent critical current $J_C(T)$, then lowering of the temperature does not result in an increase in the magnetization magnitude. This is because, although the pinning strength increases in those superconductors with the lowering of temperature, the field profile associated with pinning (or J_C) does not become sharper, since there is no change in the magnetic induction [45, 46]. This argument is a general one and does not depend on whether the temperature is lowered or raised; it states that an enhanced J_C does not show up and magnetization does not become larger if the temperature is varied in a constant field. No change in magnetization when a single-component superconductor is subjected to constant-field temperature variation in a temperature regime where the pinning strength increases can be explained by the change in this pinning property alone.

However, there are a few problems in measuring M versus T with a commercial SQUID magnetometer. (Quantum Design model MPMS2 and model MPMS5 have been used extensively to study the magnetic properties of $CeRu_2$.) First, the available temperature window (1.8 K $\leqslant T \leqslant$ 6.1 K) is relatively narrow and even in this narrow window it is not possible to change the temperature unidirectionally and at a constant rate through 4.2 K. Second, there is a problem related to the sample movement during the measurements using a commercial SQUID magnetometer. During the measurement process the sample moves through the slightly inhomogeneous field of the magnet. The sample experiences a field varying from $H - \Delta$ to H to $H - \Delta$ during its upward motion, and then a variation from $H - \Delta$ to H to $H - \Delta$ as it is returned to its initial position after the measurement. (Here Δ represents the field inhomogeneity, which depends on the scan length used in the measurement.) The important point is that in a supposedly iso-field M–T measurement, the sample experiences the field tracing out a minor loop between $H - \Delta$ and H at each temperature. (In a standard measurement procedure, this loop is traced out twice, but even in the recently proposed half-scan method [47], this loop is traced out once.) The measured magnetization at each temperature thus also includes the effect of shielding currents set up as this minor loop is traced out. Since the field inhomogeneity Δ reduces with the scan length L as L^4, this complication can be reduced by using a smaller scan length. This contribution can also be estimated by intentionally following a minor loop in appropriate steps.

We must emphasize that the second problem would not exist in a M versus T measurement with a vibrating-sample magnetometer (VSM). However, such measurements have not yet been reported.

Even if all of the problems mentioned above were avoided, we would still not get an ideal response from a SQUID magnetometer if and when the anomalous structure straddled the $M = 0$ line. From preliminary explorations we have found that, with an applied field of 3 T, T_C goes down to ≈4 K and there is a hint of an unusual structure (which is substantially separated from the $M = 0$ base-line) at around 3.5 K in the pure $CeRu_2$ sample. We have subsequently made magnetization measurements in the zero-field-cooled (ZFC), field-cooled cooling (FCC) and field-cooled warming (FCW) modes in this temperature window, 1.8 K $\leqslant T \leqslant$ 4.1 K, and with the applied field H kept fixed at 3 T, using a 2 cm scan length in the 'fixed-range' mode (see figure 6). Unlike the case for the isothermal-field excursion, the anomaly is not very distinct. There is a change in slope in the M versus T plot at 3.25 K both for M_{ZFC} and M_{FCW} and a small but distinct minimum for M_{FCC}. Retrospectively, we think that in our previous study [44] the use of a 4 cm scan length and the proximity of the anomalous structure to the $M = 0$ base-line probably conspired to make the anomalous structure more prominent than it actually is. However, in the present study, we find the overall temperature dependence of the magnetization to be highly non-ideal in the temperature regime 3.2 K $\leqslant T \leqslant$ 3.7 K. In this temperature regime, M_{ZFC} is found to be larger than both M_{FCC} and M_{FCW}. We have earlier observed similar behaviour in the magnetization study of 5% Nd-doped $CeRu_2$ as well [28]. Such a non-ideal

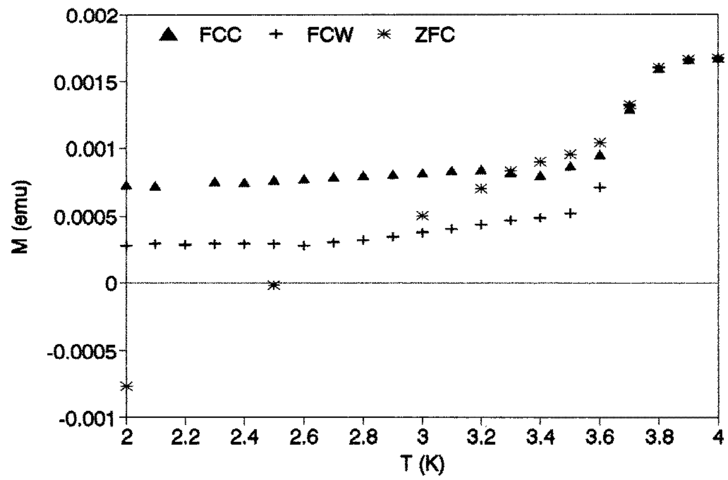

Figure 6. The magnetization (M) versus temperature (T) plot for the $CeRu_2$ with H kept fixed at 30 kOe in the ZFC ($*$), FCC (▲) and FCW ($+$) modes.

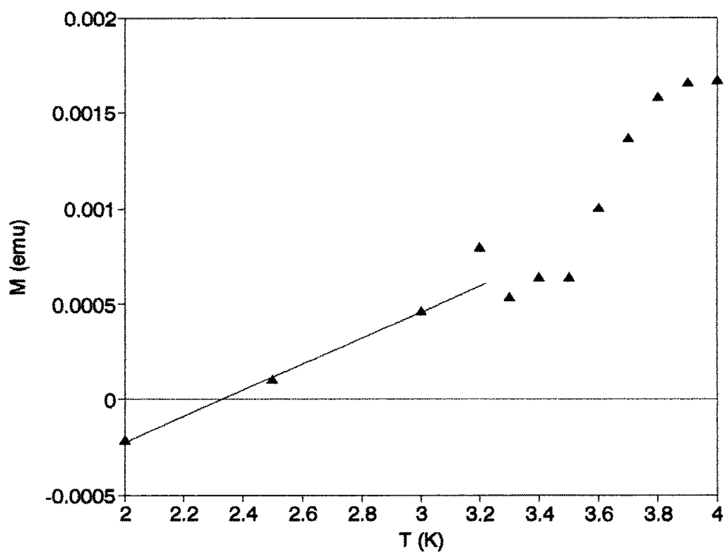

Figure 7. The equilibrium magnetization (M_{eq}) versus temperature (T) plot for the $CeRu_2$ sample in an external field of 30 kOe. See the text for details.

behaviour as regards the FC and ZFC state of $CeRu_2$ has also been observed in neutron [20] and magnetotransport measurements [17]. The distinct difference in M_{FCC} and M_{FCW} clearly indicates a substantial influence of pinning even in the field-cooling mode, and hence neither of these measurements can be treated as equilibrium measurements. In our attempt to extract the equilibrium magnetization, we propose the following protocol. We first reach each temperature in the ZFC mode, stabilize a field of 3 T and then draw a minor hysteresis loop (MHL) around 3 T by changing the field by ± 200 Oe. For all of the temperatures concerned, wherever we could draw a MHL, it became saturated during the field excursion of ± 200 Oe and the estimated values of the field for full penetration (H_{II}) lay in the range between 50 to 100 Oe. (This value of H_{II} is much larger than the field inhomogeneity $\Delta \approx 3.8$ Oe of the superconducting magnet at the applied field of 3 T.). We estimate the equilibrium magnetization M_{eq} at each temperatures as the arithmetic mean of the saturation magnetization values $M\uparrow$ and $M\downarrow$ on the corresponding MHLs. In figure 7 we plot M_{eq} thus estimated as a function of T. An upward change in slope of the magnetization is apparent at around $T = 3$ K, which is followed by a minimum in the temperature regime $3.5 \text{ K} \leqslant T \leqslant 3.75$ K. Although a distinct rise in magnetization at around 3 K would be an indication of a first-order transition, our data are not very conclusive on this point.

3.5. Theoretical models for a first-order transition in type-II superconductors

On the basis of detailed magnetization measurements (mainly for isothermal-field excursions) we have argued that there exists strong evidence of a thermodynamic first-order transition in the anomalous (H, T) regime of $CeRu_2$. To our knowledge, there exist three theoretical models which envisage such a first-order transition in the high-field regime of the superconducting mixed state of type-II superconductors.

(i) Formation of a Fulde–Ferrel–Larkin–Ovchinnikov (FFLO) state [48, 49].

(ii) First-order transition from a standard Abrikosov flux lattice to a super-softened flux lattice before the actual melting of the flux-line lattice occurs [50].

(iii) A scaling model of superconductivity which includes the possibility of a first-order transition in the (H, T) plane [51].

One of these three models, the FFLO state, has been considered by many groups as a possible explanation for the anomalous superconducting properties of not only $CeRu_2$ but also a few other superconductors, namely UPd_2Al_3 (reference [52]), UPt_3 (reference [53]), $CeCo_2$ (reference [54]) etc. In 1964, Fulde and Ferrel [48] and independently Larkin and Ovchinnikov [49] predicted the existence of a non-uniform superconducting state in the presence of a magnetic field acting on the electron spins. They argued that when the Zeeman energy between singlet-pairing electrons was sufficiently high, a modification of the singlet state was expected to be energetically favourable, which extended the stability of the superconductivity to higher magnetic fields. The order parameter of this new superconducting high-field state is spatially modulated with planar nodes of the order parameter periodically aligned perpendicular to the Abrikosov flux-line lattice. The following characteristics of the FFLO state seem to be in consonance with the experimental findings for $CeRu_2$ and UPd_2Al_3 [15, 22].

(i) The transition from the BCS state to this partially depaired FFLO state is a first-order one.

(ii) The existence of planar nodes in the order parameter of the FFLO state leads to the segmentation of vortices in this field regime, and these quasi-two-dimensional vortex segments can be pinned by the weak-pinning potential more easily (than the original vortices at lower fields), leading to a large irreversibility in magnetization.

However there are also several problems, which discourage us from using a straightforward adaptation of the FFLO state to explain the anomalous properties of $CeRu_2$.

(i) The FFLO state is supposed to occur only in strongly Pauli-limited type-II superconductors. It is not clear yet whether $CeRu_2$ actually meets this criterion. While $CeRu_2$ has been reported to be Pauli limited in references [15] and [23], the opposite view is presented in references [14] and [29]. It should be noted here that the FFLO state (and the stringent conditions for its existence) has so far been examined mainly in spherical symmetric systems [55]. It has been argued recently that, in contrast to the case for the ordinary BCS superconductivity, the band structure of electrons is important for the FFLO state [56]. It is expected that FFLO state will be enhanced if there is a flat portion in the Fermi surface [56].

(ii) In the theoretical work [55], the FFLO state was predicted to occur only at temperatures smaller than $T^* \approx 0.56T_{C0}$, where T_{C0} is the zero-field superconducting transition temperature. This is in contradiction with the experimental findings for $CeRu_2$, for which the anomalous magnetic response has been observed even at temperatures $\approx 0.9T_{C0}$. This problem has been overcome recently by Tachiki *et al* [57] with the introduction of a generalized FFLO (GFFLO) state, which allows the inhomogeneous superconducting state to exist up to $T^* \approx 0.92T_{C0}$.

(iii) The FFLO state is expected to occur only in very clean superconductors with large electronic mean free paths (l) and superconducting coherence length (ξ_C) ratios, i.e. $l/\xi_C \gg 1$. On the other hand, for $CeRu_2$ the anomalous magnetic response has been found to be quite robust in nature and occurs, with all of its characteristic features, for off-stoichiometric polycrystalline $CeRu_2$ samples as well as Nd-, Rh- and Co-doped pseudobinary alloys [24, 27–29]. Although this insensitivity to disordering is contrary to the theoretical expectation, on a closer inspection it is apparent that, for all of these polycrystalline and alloyed $CeRu_2$ samples, l is still substantially larger than ξ_C. We should also point out here that while substitution of non-magnetic elements like La and Lu has a destructive influence on the anomalous magnetic response for $CeRu_2$ [27], the same is not true of the substitution of a magnetic element like Nd. Theoretically, it was predicted earlier that the FFLO state can survive doping with a small amount of ferromagnetic impurity [58]. In the case of the heavy-fermion superconductor URu_2Si_2, it has been argued that the intrinsic antiferromagnetic ordering actually stabilizes the FFLO state in that compound [59].

From the discussion above, it is apparent that the question of whether the FFLO (or GFFLO) state can explain the anomalous experimental results for $CeRu_2$ or not still remains open. Although the results of a very recent μSR study of the anomalous (H, T) regime of $CeRu_2$ have been interpreted in terms of a FFLO state [60], a true microscopic study regarding the existence of a FFLO state in $CeRu_2$ is lacking.

3.6. The role of magnetism in the anomalous (H, T) regime

There is a feature common to $CeRu_2$ and the other compounds, namely UPd_2Al_3 (reference [52]), UPt_3 (reference [53]) and $Yb_3Rh_4Sn_{13}$ (reference [61]), which have also been reported recently as showing similar anomalous superconducting mixed-state properties. In the normal state, all of these compounds either possess a subtle kind of magnetic ordering or they show distinctly temperature-dependent paramagnetism. The possibility of a small-moment magnetism has been considered recently for $CeRu_2$ [62]. The influence of magnetism in the superconducting mixed state of these compounds needs to be investigated carefully. This is particularly so in view of the theoretical suggestions that the magnetic impurities can induce gapless superconductivity [63, 64]. It is not totally out of place to recall here that Fulde and Ferrel [48] actually argued that when a strong exchange field, such as that produced by magnetic impurities in metals, is strong enough to break many electron pairs, the self-consistent gap equation is modified and a new type of depaired superconducting ground state can occur.

4. Conclusions

Summarizing our results and the discussion of the dc magnetization measurements for $CeRu_2$, and making a comparative study with two other type-II superconductors, namely Bi-2212 and 1% Fe-doped Nb, we have come to the conclusion that the anomalous superconducting response of $CeRu_2$ is certainly not a case of a conventional peak effect. The various features associated with the anomalous behaviour do not find a ready explanation within the realm of the critical-state models. On the other hand, a phenomenological picture involving a first-order transition to a new superconducting state with enhanced pinning properties can explain all of the experimental results. Although there exist (to our knowledge) at least three theoretical models which envisage such a first-order transition (and among which the FFLO state has already found favour in certain quarters [15, 22]), on the basis of our present study alone it is not possible to reach any firm conclusion in favour of or against these models. For this, one would need true microscopic measurements which can probe the nature of the superconducting order parameter and the detailed structure of the superconducting mixed phase.

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