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Interesting normal state and superconducting properties of the intermediate valence compound $CeRu_2$

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Abstract. Superconductivity in $CeRu_2$ was discovered 40 years ago, and was extensively studied because alloying with magnetic elements showed the coexistence of superconductivity and magnetic order. The normal state of $CeRu_2$ has been of interest because of its intermediate valence character. The superconducting state has been studied extensively because of its paramagnetic nature and anomalous pinning properties. This review presents the present status of knowledge, and discusses the puzzling features of $CeRu_2$.

Keywords. $CeRu_2$; intermediate valence; normal and superconducting state; peak effect.

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1. Introduction

The C15-Laves phase compound $CeRu_2$ came into prominence 40 years ago [1] as a system where on alloying with magnetic rare-earth elements there was a possibility of coexistence of superconductivity and magnetism. Ce in $CeRu_2$ was traditionally believed to be tetravalent, especially since it was possible to dissolve substantial amount of magnetic rare-earth elements at the Ce-cite before destroying the superconductivity. However, with the discovery of the phenomenon of intermediate valence in early 1970s, $CeRu_2$ together with various other Ce and Yb-based intermetallic compounds came under fresh scrutiny. Rare earth based systems in general have a magnetic ground state with an integral number of $4f$-electrons being localized at each rare earth site. The $4f$-electron states have negligible hybridization with those of conduction electrons. However certain special rare earth based systems, especially those based on Ce, Sm, Eu, Tm and Yb are non-magnetic in their ground states. This behaviour is anomalous since the negligible overlap between $4f$-orbitals of neighbouring sites suggests that these compounds should be strongly magnetic. Instead their ground state is either that of a small-moment magnet or a paramagnet and sometimes even a superconductor. It implies that the degree of delocalization or itenerancy of $4f$-electrons in these systems arises from the hybridization with s, p or d states on a neighbouring ion [2]. This '$4f$-ligand' hybridization can give rise to a wide range of interesting physical phenomena, some of which are listed below.

1. The problem of the coupling between the local moment of an isolated rare earth impurity and the conduction electrons that leads to anomalous thermodynamic and transport properties i.e. the Kondo effect [3].
2. The Kondo lattice problem where such rare earth atoms with local moments and associated (conduction electron) polarization clouds are arranged in a regular fashion on a subset of lattice sites, the other sites are occupied by non $4f$-atoms [4]. This arrangement is generally referred as 'Kondo lattice' and sometimes leads to the development of a unique highly correlated electronic ground state at low temperatures, known as 'heavy fermion' state [5–8].
3. The 'intermediate-valence(IV) state' where the atoms carrying $4f$-electrons in various compounds exhibit properties that reflect a time average between two $4f$-configurations that differ by one $4f$-electron. It is to be noted here that apart from such IV systems which are considered as a result of quantum mechanical hybridization, and where each ion has the same non-integer valence, there exists also systems with a static mixture of different integral valences [9]. These latter kind of systems are often termed as 'static mixed valence' or simply 'mixed valence' systems.
4. The coupling of the local $4f$-moments via the polarization they induce in the conduction electrons i.e. the Ruderman–Kittel–Kasuya–Yoshida (RKKY) interaction [10,11].
5. Competition between RKKY and Kondo interaction and long-range magnetic ordering with reduced moment [8].
6. The inherent tendency of the heavy-Fermi liquid state to become unstable (due to residual interactions between the heavy quasiparticles) leading to either a heavy fermion band magnetism and/or superconductivity [8].
7. The long-standing problem of whether alternatives to phonon-mediated interactions can couple electrons to yield superconductivity, and whether the electrons so coupled must always have opposite spins i.e. form Bardeen–Cooper–Schrieffer (BCS) singlet pairs; in other words, the possibility of unconventional superconductivity [6–8].

The C15 compound $CeRu_2$ has now turned out to be an interesting example of intermediate valence [12], but inspite of much activity of the last forty years, both the superconductivity and the normal state properties of this compound $CeRu_2$ are far from being understood completely. In this review we shall discuss, (i) various interesting properties of $CeRu_2$, (ii) the present day understanding of these properties and (iii) various puzzles which are yet to be solved. This review, however, will not be a totally exhaustive one and will be somewhat biased by the authors' interest in this area.

2. Normal state properties of $CeRu_2$

2.1 *Structural and metallurgical aspects*

Laves phase compounds have a chemical formula AB_2 and belong to three different structural types, namely $MgCu_2$ (C15 structure), $MgZn_2$ (C14 structure) and $MgNi_2$ (C36-structure). The C15 structure has a cubic symmetry and belongs to space group

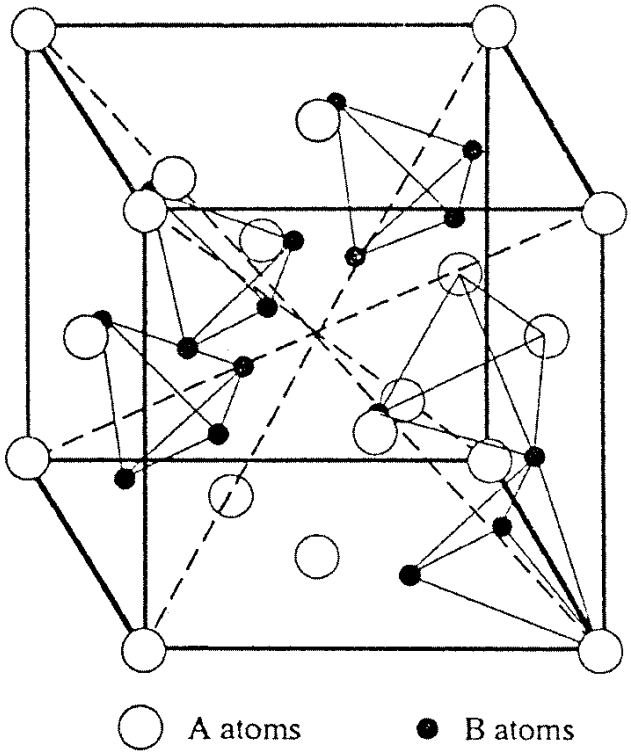

Figure 1. Crystal structure of C15 Laves phase.

Fd3m. The C14 and C36 compounds form an hexagonal structure and belong to the space group $p6_3/mmc$. The structural types have one common element: tetrahedra of B atoms forming a spatial skeleton in whose voids A atoms are located. $CeRu_2$ forms in the C15 structure and figure 1 shows such a structure. However, recent neutron study on single crystal sample of $CeRu_2$ has revealed that the structure of $CeRu_2$ is slightly different from that of an ideal C15-Laves phase [13]. The nature of the deviation does not directly affect the overall FCC symmetry, and the atoms are only slightly displaced from the ideal C15-Laves phase position.

$CeRu_2$ forms peritectically, and in the as-cast sample one finds three different phases: undissolved pure Ru, $CeRu_2$ and a Ce-rich phase [14]. This last phase may occur as β-Ce or β-Ce-Ru solid solution. After heat treatment at 950°C for a week, the quality of the samples improves but the three-phase structure does not totally disappear [15].

In recent years various groups have grown good quality samples (both polycrystals and single crystals) of $CeRu_2$ [16–18].

Laves phase structures are quite suitable for hydrogen storage. In C15 structure hydrogen resides in the available tetrahedral sites. Hydrogenation process causes the suppression of the long-range crystalline order in $CeRu_2$ [19].

2.2 *Thermodynamic properties: Magnetization and specific heat*

It is now well known that the normal state of $CeRu_2$ possesses enhanced paramagnetic character [18]. This paramagnetism, although not quite Curie–Weiss like, shows substantial temperature variation [20]. We have performed high resolution magnetization measurements on polycrystalline samples obtained from different sources (Imperial College, London, University of Kentucky and Los Alamos National Laboratory) as well as on a good quality single crystal sample (obtained from CNRS, Grenoble). A discernable temperature dependence of magnetization has been observed in all these samples. A typical example of such a behaviour is shown in figure 2 in the form of a magnetization versus temperature plot of a single crystal sample, obtained with an applied field of 5 kOe. Although the temperature dependence observed in the normal state susceptibility is often attributed to Ce^{3+} impurities [21], the possibility that such a magnetic response might be intrinsic in nature cannot be ruled out entirely; this is especially so in the light of the fairly recent suggestion of dual character of $4f$-electrons in $CeRu_2$ [22]. Also, in a recent polarized neutron study of $CeRu_2$, Huxley *et al* [13] suggested the existence of defect sites which could give rise to Ce-ions with locally different environments. Huxley *et al* [13] suggested an interesting possibility that such Ce-ions distributed randomly might be the source of weak static magnetization at low temperatures. Then there remains the question of a weak moment magnetic ordering of spin-density-wave (SDW) type as is observed in heavy fermion system UPt_3 [23]. In our magnetization measurements, in some samples of $CeRu_2$ (including the single crystal one), we have observed a structure around 45–50 K when the applied field is less than 500 Oe (see figure 3). This structure is accompanied by

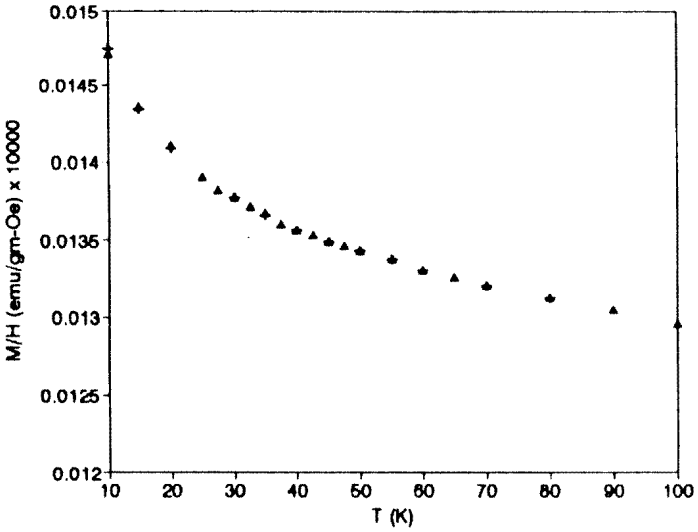

Figure 2. Magnetic susceptibility (M/H) vs temperature (T) plot of $CeRu_2$ single crystal sample, with external field (H) being kept constant at 5 kOe. ▲ stands for zero field cooled and + for field cooled susceptibility [20].

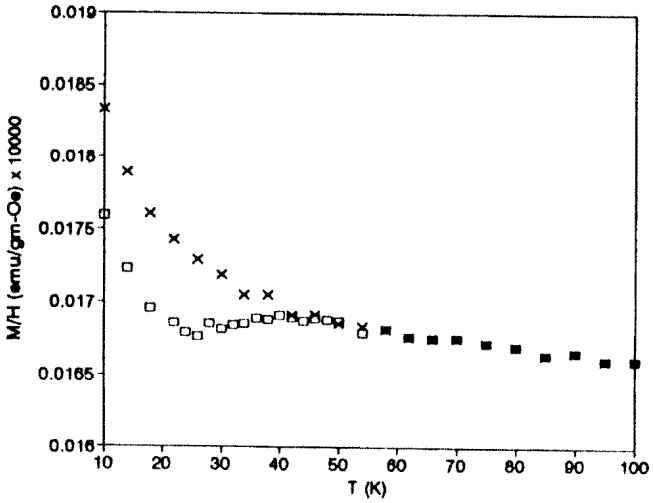

Figure 3. Magnetic susceptibility (M/H) vs temperature (T) plot of $CeRu_2$ single crystal sample, with external field (H) being kept constant at 500 Oe. □ stands for zero field cooled and X for field cooled susceptibility [20].

a distinct thermomagnetic irreversibility which also lends support to a possible magnetic origin of the observed behaviour. A subtle structure around 50 K in $CeRu_2$ has also been reported by Nakama *et al* in high field dc magnetization and ac susceptibility study [24]. In that study the suggestion that this structure is probably due to a magnetic ordering is further reinforced by results of magnetotransport and thermopower measurements [24].

We must point out that this structure in magnetization around 50 K is sample dependent and not observed in quite a few $CeRu_2$ samples we have studied [20]. We tend to believe that apart from the possibility that this magnetic structure is intrinsic to $CeRu_2$, this may also arise from either of these two sources: (1) disorder induced magnetism as is observed in many Ce-based systems [25] or (2) oxygen often leaks into the measuring apparatus in small quantity and solidifies around 50 K. Solid oxygen being antiferromagnetic in nature can contribute to the magnetic response [26]. To check the possible effect of any adsorbed oxygen on the surface of the sample, we have studied two $CeRu_2$ samples in detail after subjecting them to annealing at elevated temperatures ($T \geq 150$ K) [20]. We have observed that the subtle magnetic structure around 50 K gets diffused on annealing and can be totally erased on prolonged annealing and subsequent flushing with inert gas. This result definitely point out the possible role of adsorbed oxygen in the low temperature normal state magnetic properties of $CeRu_2$.

The specific heat measurement in $CeRu_2$ has been performed by Joseph *et al* [27] and they obtained from a least square fit of the heat-capacity data above 6 K, an electronic specific heat coefficient γ of $\approx 22.6 \pm 0.5$ mJ/g atom K^2 and a Debye temperature $\Theta_D = 179 \pm 1$ K.

In recent years specific heat measurement has been performed at low temperatures under different applied fields [18,28]. In fields higher than 55 kOe the sample remains normal down to temperatures well below the zero field superconducting transition temperature

($T_C \approx 6.1$ K). The specific heat in the normal state follows a relation $C/T = \gamma + \beta T^2 + A/T^3$ below $T \approx \Theta_D/50$, namely the specific heat at low temperatures consists of the electronic, phonon and nuclear contributions [28]. It is clear that there is a significant decrease in C/T measured under applied field from that obtained by linearly extrapolation of zero-field data from above T_C. Huxley *et al* suggested that such observation could be indicative of structure in the electronic density of states close to the Fermi level or of structure in the low-energy phonon density of states [18]. Within this approach Huxley obtained a γ value of 29 mJ/mol-K^2 and $\Theta_D = 140$ K. These are quite comparable to the values of $\gamma = 27$ mJ/mol-K^2 and $\Theta_D = 120$ K obtained by Hedo *et al* [28]. All these results suggest a moderate enhancement of electronic mass in $CeRu_2$. The A/T^3 term ($A = 2 \times 10^{-2}$ mJ/mol-K^4) which represents an upturn in the specific heat below 0.3 K, is most likely due to Ru-nuclear contribution.

2.3 *Transport properties: Resistivity and thermopower*

The normal state resistivity of $CeRu_2$ as well as $(Ce_{1-x}R_x)Ru_2$, where $R =$ Nd, La, Lu, U and Th show a marked deviation from the standard Bloch–Gruneissen form (see figure 4) [15,29]. The low temperature resistivity follows a T^n law where n varies from 1.5 to 3 in various samples [15]. Kuwai *et al* [30] reported a quadratic temperature dependence of resistivity of $CeRu_2$ below 25 K and down to T_C. The high temperature resistivity deviates appreciably from a linear temperature dependence and a marked tendency towards saturation is observed above about 80 K [15,29,30]. A correlation between the resistivity–temperature curve and the superconducting transition temperature of $(Ce, La)Ru_2$ alloys has been suggested by Lawson *et al* [29]. This sort of behaviour in the temperature dependence of resistivity has also been observed in $Ce(Ru_{1-x}Rh_x)_2$ pseudobinary systems [31]. Such a behaviour in resistivity is often referred to as resistivity saturation and has

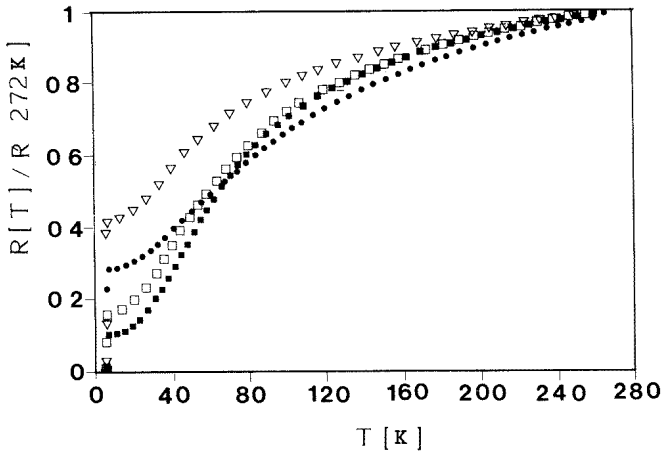

Figure 4. The normalized resistivity $\rho(T)/\rho(280\,\text{K})$ as a function of temperature of $CeRu_2$ (□), $(Ce_{0.95}Lu_{0.05})Ru_2$ (•), $(Ce_{0.95}U_{0.05})Ru_2$ (▽) and $(Ce_{0.9}Th_{0.1})Ru_2$ (□) [15].

been associated with A15 superconductors [32]. It is not clear, however, whether the same mechanism is responsible for the resistivity saturation in these two different classes of compounds. Difference resistivity between $CeRu_2$ and $LaRu_2$ i.e. $\rho(CeRu_2)-\rho(LaRu_2)$ shows a maximum around 100 K and is proportional to $-\ln T$ for temperature above that [24]. Magnetoresistance in $CeRu_2$ shows a maximum around 100 K and a change in sign from negative to positive at about 50 K with decreasing temperature [24].

Thermoelectric power (TEP) for pure $CeRu_2$ has revealed a positive TEP in the temperature range $T_C < T < 300$ K with a pronounced peak at about 80 K [30]. TEP decreased approximately linearly above the peak. There also appears to be a subtle structure in TEP around 50 K [24,30].

2.4 *Elastic properties*

Elastic properties of $CeRu_2$ have been studied by Wolf *et al* [33] and Suzuki *et al* [34] from room temperature down to 1 K. The elastic modulus $(C_{11}-C_{12})/2$ continues to decrease with decreasing temperature down to 18.2 K, reaches a minimum and finally approaches a small constant value at low temperatures. Between 300 K and low temperatures the decrease in lattice stiffness for this mode is about 55%. C_{44} exhibits a similar temperature variation to that of $(C_{11}-C_{12})/2$, although the softening of C_{44} from 300 K to $\approx$20 K is only about 12%. In contrast the bulk modulus C_B shows a normal temperature dependence without softening. These results suggest the existence of marked structural fluctuations in $CeRu_2$ which persists down to low temperatures, but without an actual structural transition. Suzuki *et al* [34] attributed the observed behaviour to the existence of narrow electronic bands with relatively high density of states at E_F.

2.5 *Spectroscopic studies*

Core-level X-ray photoemission studies [12], as well as resonant photoemission [35] and L_3 absorption edge studies [36] strongly suggested that $CeRu_2$ was in intermediate valence state with f-electron count near one. Estimated Ce-valence from the spectroscopic studies seems to have an upper limit 3.3 which is lower than all bulk property estimates. In a recent high resolution photoemission spectroscopy study in $CeRu_2$ it was found that the photoemission spectrum near E_F has two well-resolved peaks at and about 270 meV below E_F [22]. The E_F and low energy peaks are attributed to the Kondo peak ($4f^1_{5/2}$ final state) and spin-orbit satellite ($4f^1_{7/2}$) respectively. However, non-crossing approximation (NCA) calculation based on the single-ion Kondo model for $CeRu_2$ using parameter estimated from the Kondo temperature ($\approx$ 1000 K) could not reproduce the spectrum quantitatively. This indicates a dual character (itinerant and localized) of the $4f$-electrons in $CeRu_2$ and suggests that the many-body correlation effect is necessary for understanding the electronic structure near the Fermi level E_F. It should be mentioned here that a fairly recent study of the elastic properties of $CeRu_2$ showed that the bulk modulus and the Poisson ratio had normal temperature dependence which in turn implied absence of any mixed valency effects [33].

It should also be mentioned here that there exists a study of X-ray absorption spectroscopy in hydrogenated samples of $CeRu_2$ which advocates the key role played by the

hybridization of the Ce-4f states with other extended states, namely Ce(5d) and Ru(4d) in determining the physical properties of $CeRu_2$ [19].

2.6 *μSR and neutron diffraction studies*

A recent μSR study on a single crystal sample of $CeRu_2$ has suggested the existence of a magnetic ordering around 45 K [37].

Polarized neutron experiments have been performed on single crystal samples of $CeRu_2$ in presence of applied magnetic fields [13]. The main results of that study suggest that the field induced magnetization density is located equally at the Ce and Ru sites. The distribution of the induced magnetization about the Ce site is found to be extended to larger distances than actually predicted for Ce^{3+} ions with well localized f-electrons. Magnetization density persisted even in the superconducting state. These neutron measurements also revealed that the crystal structure of $CeRu_2$ is probably slightly different from that of an ideal C15-Laves phase . The nature of deviation, however, is subtle, and it does not directly affect the overall FCC symmetry [13]. Presence of diffuse scattering was observed in this new structure which could be related to metallurgical defects. These defect sites can be the source of Ce-ions with locally different environments. Huxley *et al* suggest that such Ce-ions distributed randomly, might be the source of small magnetic anomaly in the 40 K regime [37]. These possible sources of weak average static fields might have some implication in the phenomenology of the superconducting mixed-state of $CeRu_2$.

2.7 *Theoretical studies of the electronic structure*

Yanase [38] has calculated the energy band structures of $CeRu_2$ using self-consistent augmented plane wave (APW) method in a local-density approximation (LDA). In that calculation, the 4f electrons were assumed to be itinerant and a scalar relativistic approximation was adopted, but the spin-orbit interaction was not taken into account. Based on his calculation, Yanase [38] proposed a Fermi surface for $CeRu_2$ which consisted of two kinds of hole sheets and two kinds of electron sheets. Subsequently Higuchi and Hasegawa [39] improved the LDA energy band structure calculation by using a fully relativistic linear APW method in which the spin-orbit interaction as well as the relativistic energy shifts is taken into account self consistently. While this newer calculation confirms the general predictions of Yanase [38] regarding the Fermi surface of $CeRu_2$, some modifications were found due to the introduction of spin-orbit interaction. The Fermi surface was found to consist of a set of six small hole pockets, a large multiply-connected hole sheet, a set of three complex electron sheets, and a set of three small electron pockets. Higuchi and Hasegawa [39] also investigated the possible nesting property of the Fermi surface of $CeRu_2$. Although there exists finite possibility of nesting in some portions of the Fermi surface, more detailed calculations are required before reaching a firm conclusion. It should be mentioned here that the existence of the nesting property might have some important implications on the superconducting mixed state properties of $CeRu_2$. In a recent preprint Agterberg, Barzykin and Gorkov have argued that exotic non-s-wave superconducting states may arise from the usual BCS mechanism in $CeRu_2$, $CeCo_2$, etc. due to their Fermi surface topologies.

2.8 *Experimental studies of the Fermi surface*

de Haas-van Alphen (dHvA) effect has been measured both in the normal and superconducting mixed state of $CeRu_2$ by Hedo *et al* [40]. The results for the dHvA effect are explained reasonably well in terms of the large hole sheet and the small electron pockets (described above) except for the cyclotron effective mass (m_C^*). $CeRu_2$ has a fairly large electronic specific heat coefficient ($\gamma \approx 30$ mJ/mol-K^2), which is comparable with the electronic specific heat coefficient of $CeCo_2$. In contrast m_C^* of about ten times free electron mass (m_0) has been observed in $CeCo_2$ [39], while in $CeRu_2$ maximum value measured for m_C^* is less than $3m_0$. Higuchi and Hasegawa [39] suggest that this inconsistency between the experimental results for m_C^* and γ in $CeRu_2$ implies that some dHvA frequency branches with much heavier effective masses might have been missed in the measurement by Hedo *et al* [40].

3. The superconducting state of $CeRu_2$

3.1 *$CeRu_2$: A paramagnetic superconductor*

$CeRu_2$ has a superconducting transition temperature T_C of $\approx$ 6.1 K, the highest value among the known superconducting intermetallic compounds of Ce [15–18]. This T_C is identified as the temperature where the diamagnetic response is first observed. However, it is now well known that the normal state of $CeRu_2$ possess enhanced paramagnetic character [18]. This paramagnetism, although not quite Curie–Weiss like, shows substantial temperature variation [20]. The competition between this paramagnetism and diamagnetism (at the onset of superconductivity) in $CeRu_2$ leads to a peak in magnetization (in the paramagnetic side) at a temperature distinctly higher than 6.1 K. We believe that this peak indicates the onset of superconductivity and the actual onset temperature of superconductivity is around 6.3−6.4 K.

The normal state enhanced paramagnetism of $CeRu_2$ also plays an influential role in the phenomenology of the superconducting mixed state of $CeRu_2$. Above a certain critical field $H_P(T)$ (where $H_P(T) < H_{C2}(T)$), the enhanced paramagnetic contribution from the normal cores of the flux-lines in the superconducting mixed state overwhelms the standard diamagnetic response of the system, and the superconducting mixed state becomes paramagnetic although the system still remains a superconductor [15,41]. Similar influence of the paramagnetism on the superconducting mixed state has been studied with magnetic and calorimetric measurements in the case of high-field superconductors, such as Ti–V, Ti–Nb alloys [43–46]. During the last couple of years a few other compounds like the sister C-15 compound $CeCo_2$ [46] and UPd_2Al_3 [21,47] are reported to be showing similar paramagnetic mixed state behaviour.

The effects of paramagnetic energy terms in the temperature dependence of the upper critical field in a type-II superconductor has been studied theoretically in early sixties by Chandrasekhar [48] and Clogston [49]. The results of their study culminated into the idea of the 'Pauli paramagnetic limitation' of the upper critical field H_{C2}, where H_{C2} is lowered by the Zeeman interaction of the magnetic field and the magnetic moments of the conduction electrons. For a BCS superconductor, paramagnetic critical field H_P is given by the Chandrasekhar–Clogston limit $H_{P0} = 1.84\, T_C$ Tesla/K. (This value of H_P changes

substantially in the presence of impurity spin-orbit scattering [50].) While it is still a matter of debate whether the H_{C2} in $CeRu_2$ is Pauli limited or not [21,51–53], it certainly remains one of the first ordered intermetallic compounds to show paramagnetic mixed state.

3.2 *Effects of doping on the superconductivity of CeRu* $_2$

The superconducting transition temperature and its pressure dependence have been studied for the series of $(Ce_{1-x}La_x)Ru_2$ alloys [54,55]. Superconductivity was observed for all compositions with a maximum around $x = 0.1$ followed by a minimum in T_C vs x around $x = 0.5$. The pressure-dependence of T_C, dT_C/dP shows a positive value for $0 \leq x \leq 0.4$ and negative value for $x \leq 0.5$. The more recent study, however, has revealed that in pure $CeRu_2$, T_C decreases linearly with increasing pressure in the small pressure region up to 0.5 GPa and then increases up to 1 GPa [55]. It is conjectured that a new phase is induced by pressure around 0.5 GPa. A recent study of elastic properties of $CeRu_2$ has also suggested that $CeRu_2$ is close to a cubic-tetragonal structural phase transition [33]. In $(Ce_{1-x}La_x)Ru_2$ the phase with a negative pressure derivative of T_C (as in pure $CeRu_2$) is retained for $x \leq 0.15$.

The effects of alloying with magnetic elements on superconductivity in $CeRu_2$ do not follow Abrikosov–Gorkov theory and it depends on the sites (Ce or Ru) where the substitutions are made. A systematic study in this regard has been performed by Wilhelm and Hillenbrand [14]. In consonance with the initial study of Matthias *et al* [1] it was found that a large amount of magnetic rare earth elements can be dissolved at the Ce site of $CeRu_2$ before destroying the superconductivity, and in some cases even an initial increase in T_C was observed on alloying [14,15,56].

Detailed studies have also been carried out by various groups to investigate the possible co-existence of magnetic order and superconductivity in various rare-earth doped $CeRu_2$ pseudobinary systems. Specific heat measurements below the superconducting transition temperatures on $(Ce_{1-x}Gd_x)Ru_2$ and $(Ce_{1-x}Tb_x)Ru_2$ systems showed contributions attributed to magnetic ordering of the rare-earth ions [57,58]. Using a spin-echo NMR technique in $(Ce_{1-x}Gd_x)Ru_2$ for $0.09 < x < 0.13$. Kumagai *et al* [59] argued for a coexistence of superconductivity and ferromagnetism. Matsumara *et al* [60] measured the temperature dependence of spin-lattice relaxation time T_1 for the zero-field NMR signal as a test for the coexistence of superconductivity and ferromagnetism in $(Ce_{1-x}Gd_x)Ru_2$. The reported exponential increase of T_1 as a function of temperature was interpreted as evidence of an energy gap. It appears that the magnetic correlation length in these systems is much shorter than the superconducting coherence length, hence the superconducting state is not overly sensitive to the magnetically ordered state. Mössbauer study on $Ce_{0.73}Ho_{0.27}Ru_2$ suggested co-existence of superconductivity with some type of short-range ferromagnetism [61]. The question of nature of the magnetic order in the co-existent state finally got settled with some careful neutron scattering measurements on (Ce,Tb)Ru_2 and (Ce,Ho)Ru_2 systems [62,63]. It was shown that the nature of magnetic order was of short-range ferromagnetic or spin-glass type.

The substitutions on the Ru site, on the other hand, depress T_C linearly and at a relatively faster rate [14]. Joseph *et al* [27], pointed out from their specific heat measurements that $CeRu_2$ and its pseudobinaries $Ce(Ru_{1-x}Pt_x)_2$ deviate from standard BCS type behaviour. They obtained a value of $(\Delta C/\gamma T_C)$=1.33 for $CeRu_2$ which was smaller than the BCS

prediction of 1.43. A GaAs probe tunneling experiment indicates BCS type behaviour by revealing a superconducting gap [64], however the gap thus obtained was found to be larger than the value expected from the transition temperature. A fairly recent ^{101}Ru NQR study in $CeRu_2$ revealed that the nuclear spin-lattice relaxation rate had the Hebel–Slichter coherence peak just below T_C which is followed by the exponential decrease at low temperature with measured energy gap of $2\Delta \approx 4.0 k_B T_C$ [65]. This seems to suggest that $CeRu_2$ is an s-wave strong coupling superconductor [65]. Sereni *et al* [66], on the other hand, suggested from specific heat measurements the possibility of an axial superconducting state.

Based on the results of superconductivity study in $CeRu_2$ narrated above, it has been traditionally assumed that Ce is tetravalent in $CeRu_2$, i.e. $4f^0$, and that the superconductivity is associated only with Ru sublattice and d electrons. The discovery of the phenomena of intermediate valence in early seventies, however, started questioning this wisdom and with many other Ce-based compounds $CeRu_2$ also became the subject of fresh scrutiny. Using a scheme which involves study of the superconductivity of the isostructural compounds $LaRu_2$ and $ThRu_2$ and the pseudobinary systems (Ce,Th)Ru_2 and (Ce,La)Ru_2, Hakimi and Huber [67] estimated the valence of Ce in $CeRu_2$ to be 3.9. (Such an approach had a prior assumption that the superconductivity in $CeRu_2$ was due to the Ru $4d$-electrons.) There exist other such estimates using bulk properties studies e.g. room temperature lattice parameter measurements [68] and high temperature susceptibility measurements [69]. While the former technique yielded a value of 3.42 for the valence of Ce in $CeRu_2$, the latter one gave an upper limit of 3.7.

The support for an important role of $4f$ character in $CeRu_2$ has been obtained on the theoretical front as well [38]. Using the self-consistent APW method, Yanase [38] has shown the existence of $4f$ bands of appreciable width in $CeRu_2$, the number of f-electrons being close to one. Yanase also found a non-uniform $4f$-contribution over the Fermi surface and suggested a contribution of $4f$ electrons to the superconductivity of $CeRu_2$. If the theoretical picture of the closeness of the Ce-$4f$ level to the Fermi surface and its contribution to superconductivity is relevant, then small substitutions by rare earth elements (with well localized $4f$ level) or Lu (with completely filled $4f$ level) or La and Th (with no f-electron) should not perturb the superconductivity of $CeRu_2$ very much. On the other hand, the $5f$ states of U, which are quite extended in nature and substantially hybridize with the conduction band, should affect the superconducting properties in a more drastic manner and that has been actually observed experimentally [56]. This picture, of course, cannot provide a simple explanation of the initial rise in T_C, due to small substitutions of Nd, Tb, Gd, La and Lu.

3.3 *Anomalous superconducting mixed state and possible vortex-matter phase transitions*

Apart from the paramagnetic mixed state, isothermal magnetization measurements have also revealed the existence of peak-effect in the superconducting mixed state of $CeRu_2$ [15,16,18,17,21,41,47,51]. The 'peak-effect' (PE) actually is a generic term used to describe a maximum which usually occurs in a field regime below H_{C2} in the critical current J_C or hysteretic magnetization (ΔM) versus applied magnetic field (H) plots for many hard type-II superconductors [70]. This phenomenon is of interest because it goes against the general wisdom that the vortex pinning and critical currents should decrease with in-

creasing field and acquire a small value around H_{C2} before finally reaching zero. PE has also been observed in the high temperature oxide superconductors, and there it is known more popularly as fish-tail effect.

Figures 5 and 6 show magnetization versus field plots of a polycrystalline and single crystal sample of $CeRu_2$ at $T = 4.5$ K. The PE near H_{C2} is highlighted in the inset of figures 5 and 6. The well characterized polycrystalline sample originates from Los Alamos National Laboratory and has been used in the past in important neutron measurements as a control sample [63]. The single crystal sample has been obtained from CENG-Grenoble and originates from the same batch samples which have been used in various measurements including neutron scattering [17,52]. The present magnetization results are obtained using a commercial SQUID magnetometer (Quantum Design MPMS-5). The experimental protocols and cross-checks are discussed in detail in references [72-74].

The PE in $CeRu_2$ is quite robust in nature and has been observed in single-crystals [17,21,47,51] polycrystalline samples of various purity [16,20,75] and substitutional alloys [41,71,72,75,76]. However the following characteristic features of PE in $CeRu_2$ distinguish it from various other hard type-II superconductors showing PE :

1. In the M–H plot, the PE appears in a temperature regime distinctly below T^*, where $T^* < T_C$ [18,21,47,51,71,75].
2. There is a fairly large field regime showing reversible or almost reversible magnetization before the onset of the PE [18,21,47,51,71,75–77].

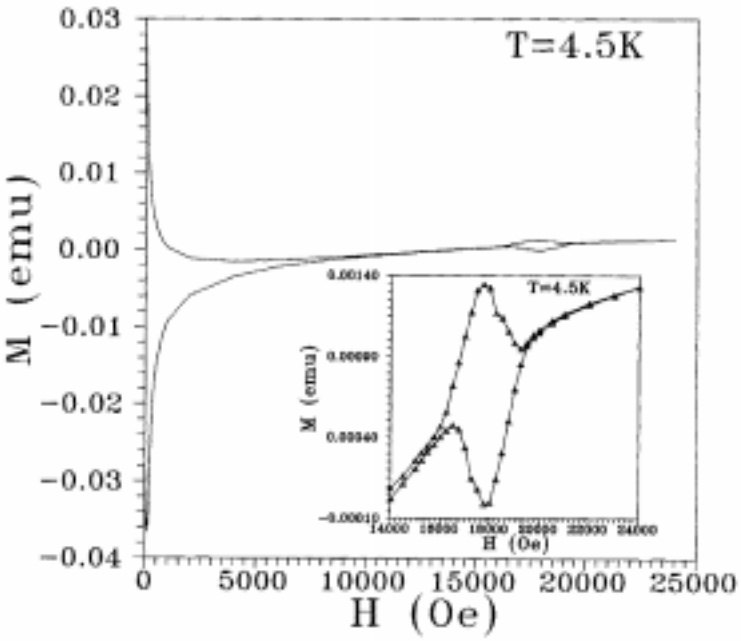

Figure 5. Magnetization (M) vs field (H) plot for a polycrystalline sample of $CeRu_2$ at $T = 4.5$ K. Inset shows enlarged M–H plot near H_{C2} to highlight the peak-effect.

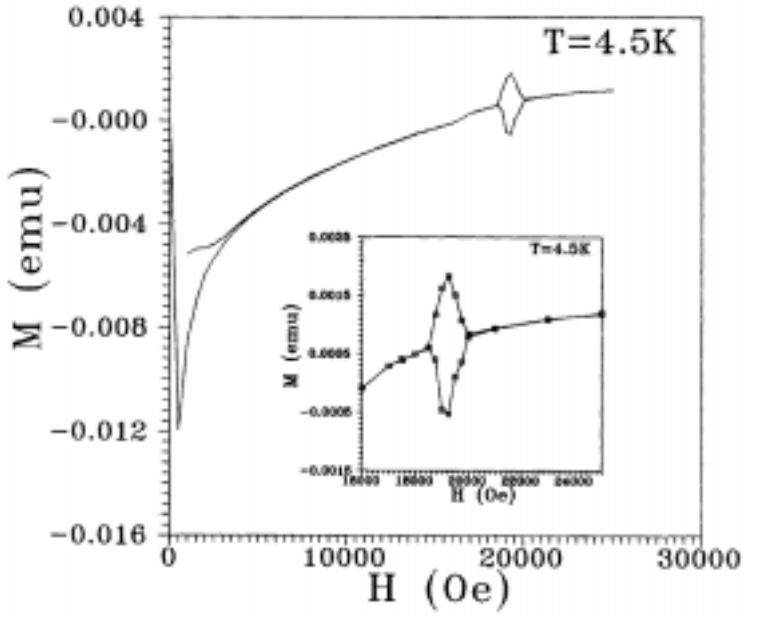

Figure 6. Magnetization (M) vs field (H) plot for a single crystal sample of $CeRu_2$ at $T = 4.5$ K. Inset shows enlarged M–H plot near H_{C2} to highlight the peak-effect.

3. The increase in the volume-pinning force in the PE regime is by more than one order of magnitude [21,51,76,77].

4. The estimated volume-pinning force, when plotted against the reduced field H/H_{C2} at various values of T, does not scale into a universal curve [21,51,77].

5. The onset field of the anomaly is distinctly different in the ascending- and descending-field cycles [21,47,51,73,74].

All these observations have led to the usage of the terminology 'anomalous peak-effect' [78] to describe the anomalous behaviour in $CeRu_2$.

From the field dependent study of the superconducting mixed state of $CeRu_2$ it is now apparent that there are two distinct regions of irreversible magnetization. From the M–H curve at $T = 4.5$ K (see figure 5) these two regions can be discerned as a low field region I (below 5 kOe) and a high-field region II (above 16 kOe) which includes the PE. Depending on the purity of the sample the regions I and II are separated by a reversible or almost reversible regime. We have argued recently that while the irreversibility and concomitant metastability in region I, like that of other hard type-II superconductors (including the high T_C superconductors), is akin to that of spin-glasses, the metastability in region II is akin to that of random field Ising systems [79]. The main characteristics underlying this differentiation are (i) field cooled magnetization ($M_{\rm FC}$) is greater than the equilibrium magnetization ($M_{\rm eq}$) i.e. $M_{\rm FC} > M_{\rm eq}$ in region I, while $M_{\rm FC} < M_{\rm eq}$ in region II; and (ii) the relaxation rate $\mathrm{d}M_{\rm FC}/\mathrm{d}t$ is negative in region I but positive in region II.

At this moment there are two distinct approaches to understand the existence of PE in $CeRu_2$. 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 [80] and is based on the argument that the shear modulus of the Abrikosov flux-line lattice (AFL) in the mixed state of a type-II superconductor falls to zero quadratically as a function of applied magnetic field near H_{C2}, whereas the pinning force density goes 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 critical current J_C. Softening of the AFL has also been predicted within a collective pinning model [81]. Such a picture of dynamical crossover in the pinning properties has been invoked by various groups [52,53] to understand the properties of $CeRu_2$. We must assert here that this explanation is indeed valid in the PE seen in many superconductors [71] but the anomalous characteristic features described above are not seen in those cases. In the second approach, the PE can actually arise due to an equilibrium phase transition within the AFL. This subject of various possible phases and associated phase transitions within the AFL or vortex-lattice is in fact a matter of current interest in an area now commonly known as 'vortex matter' [82]. The debate as to whether a PE can arise due to a thermodynamic phase transition in the vortex-matter has become particularly interesting with the suggestions of such phase transitions in the PE region of various HTSC samples like Bi-2212 [84], Y-123 [85] and Nd–Ce–Cu–O [86]. The PE in these materials is believed to be associated with a second order phase transition from an ordered (quasilattice or Bragg-glass) to a disordered vortex-lattice or vortex-glass [86]. Although it is not known yet whether similar phases of vortex-matter i.e. Bragg-glass and vortex-glass are also present in the superconducting mixed state of $CeRu_2$, there exists suggestion of a field induced first-order transition in $CeRu_2$ [21,47,87–89] to a superconducting state with a new superconducting order parameter. The idea of this high field-Fulde–Ferrel–Larkin–Ovchinnikov (FFLO)-superconducting state has some support from various experimental studies including magnetization [21,47], magnetostriction [21,47], magnetoelastic [87] and μSR measurements [89].

With the study of minor hysteresis loops (MHL), measured at closely spaced field intervals, one can ascertain whether the irreversibility in magnetization is consistent with Bean's critical state model (CSM) because the behaviour of MHLs therein is well documented [90]. One can also distinguish between surface effects and bulk irreversibility. The MHLs in Bi-2212 show a continuously varying initial slope, indicating the absence of surface-driven hysteresis [74].They also merge with the envelope hysteresis curve in all field regimes (including the PE or fish-tail regime), as predicted by the CSM [74]. Pradhan *et al* [91] have similarly reported MHLs in the PE regime of $NdBa_2Cu_3O_7$ consistent with CSM. Even in $CeRu_2$, MHLs are consistent with the CSM in region I [72]. In region II also, the MHLs are non-linear throughout, ruling out surface effects. However, the MHLs obtained at the onset of the region II of $CeRu_2$ are not consistent with the CSM and they show distinct field-temperature history dependence [72–74]. For example the MHLs initiated from the lower envelope curve just above the onset of the region II do not show the expected merger with the upper envelope curve. To highlight this behaviour we show in figure 7 the MHLs obtained at the onset of the region II for a 5% Nd-doped $CeRu_2$ sample. (We emphasise that this behaviour is a general feature of all $CeRu_2$ samples, including pure and Nd-doped polycrystalline samples [73,74] and single crystals [92].) As shown in figure 7(b), the saturated value of the MHL at say 26.5 kOe further depends on whether

the MHL was initiated from 27 kOe or from 29 kOe. We argue that this indicates the formation of a new vortex phase (say phase X) at the onset of region II via a first order phase transition [72–74].

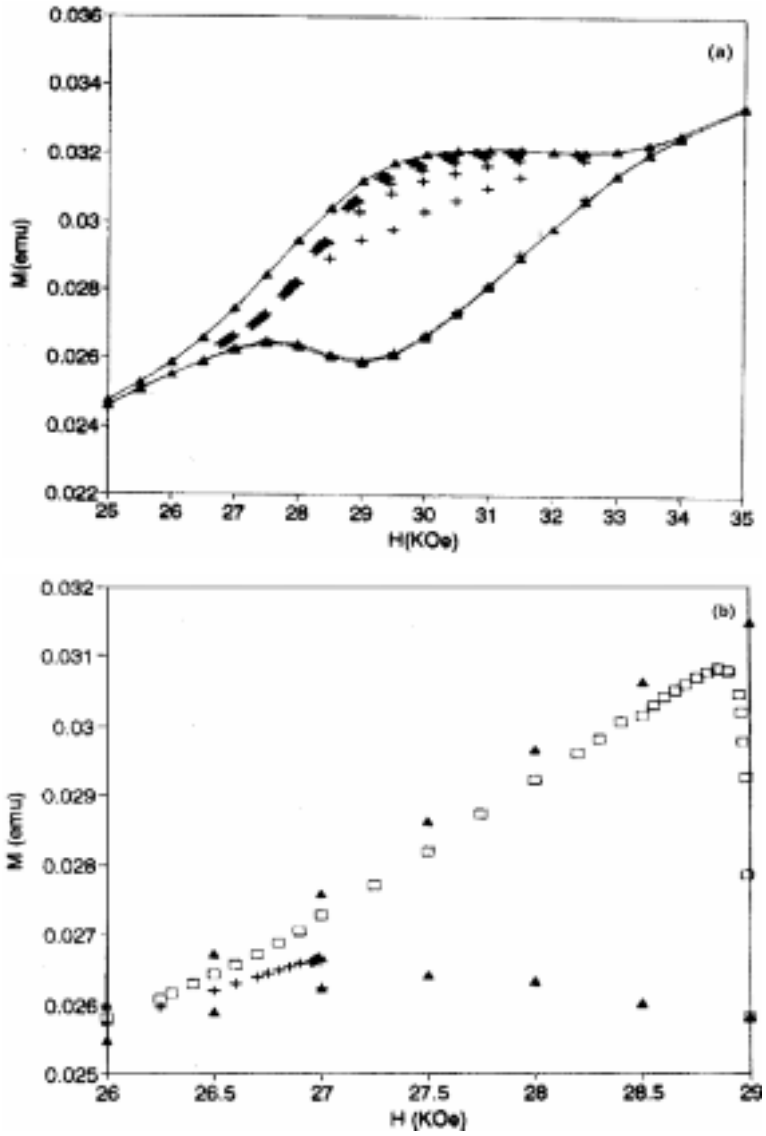

Figure 7. Forward legs of the minor hysteresis loops (MHL): (**a**) starting at $H = 27$, 27.5, 28, 28.5, 29, 29.5, 30, 30.5, 31, 31.5 and 32.5 kOe with the maximum change in field $(\Delta H)_{\max}$=250 Oe [(+) MHLs; (▲) envelope curve]; (**b**) starting at $H = 27$ kOe (+) and 29 kOe (▲) and reducing the field to 26 kOe. All these MHLs are initiated from the lower envelope curve [72].

We show in figure 8, a schematic phase diagram of superconducting mixed state of $CeRu_2$ in which H_a^* gives the onset of the peak effect or region II, and H_{pk} is the field value in region II where the magnetization hysteresis shows a peak [93]. The data presented in figure 7 clarifies that MHLs show multivaluedness of saturation magnetization M_S as the field is raised above H_a^* and before it reaches H_{pk}. The transition to phase X is thus initiated H_a^*. We have argued that the sample geometry may cause the transition to have a width of a few kOe [94]. We suggest that the multivaluedness of M_S results from supercooling of states in which different extents of the phase X is formed. Such a supercooling is not seen from a study of MHLs across the continuous phase transition, from vortex-glass to Bragg-glass phase, in Bi-2212 [74] and $Nd_2Ba_2Cu_3O_7$ [91].

Measurement of MHLs at closely spaced field intervals also allows one to estimate artifacts that may be introduced in data taken on a commercial SQUID-magnetometer because of the sample being moved through the inhomogeneous field of the superconducting magnet [72–74]. We have estimated that these artifacts are insignificant in our data [72–74]. Such an artifact is even more insignificant in data taken with a vibrating sample magnetometer, and we have confirmed the anomalous nature of MHLs in region II, in both pure and doped $CeRu_2$, through measurements using a VSM [95].

Various thermomagnetic histories had been reported by Steingart *et al* [96], while studying transport critical current (J_C) in strained Nb single crystal exhibiting PE. They observed that J_C measured in the PE region was highest on cooling in constant field, next when field was lowered isothermally from above H_{C2}, and lowest when field was raised isothermally from zero. While Steingart *et al* [96] did not consider a phase transition in the vortex state, we view the qualitative similarity between their isothermal transport data and our isothermal magnetization data as significant. While explaining the different values of J_C obtained under different field-temperature histories as due to synchronized pinning, Steingart *et al* [96] had argued that the readjustment of vortex spacing is least in field-cooled case. The energy change experienced by vortices is thus least in this case.

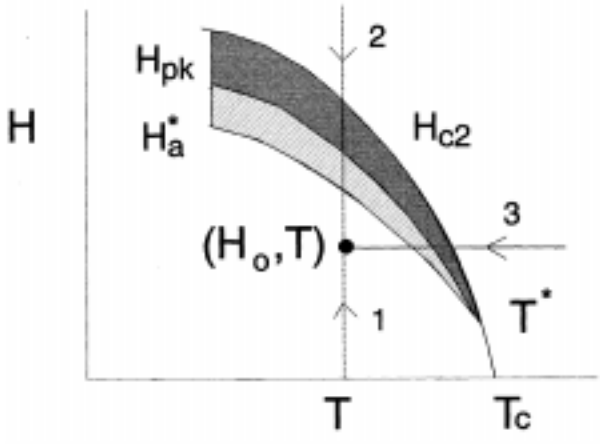

Figure 8. Schematic phase diagram of the superconducting mixed state of $CeRu_2$. Paths indicated by 2 and 3 corresponds to isothermal field reduction and field cooling through the high-entropy phase. A critical point is indicated at T^*, above which this phase does not exist [93].

Supercooling of phase X in $CeRu_2$ can also be expected to persist farthest when the energy change of vortices is least. The arguments of Steingart *et al* [96] thus prompted us to access region I from region II by cooling in constant field. As explained earlier, multivaluedness of saturation magnetization of MHLs in $CeRu_2$ is attributed to supercooling of phase X. While we have found no supercooling in Bi-2212 even on field-cooling, supercooling was indeed seen in $CeRu_2$ and found to persist to much lower fields [74,79]. Specifically, supercooling was not seen below 20 kOe at 5 K on isothermal field reduction in 5% Nd-doped $CeRu_2$, but persisted down to 13 kOe and 5 K on field-cooling [74]. Finally, field-cooling failed to show multivaluedness or supercooling above a critical temperature T^*, indicating a critical point in the schematic phase diagram (see figure 8).

We shall now discuss a true thermodynamic signature of the isothermal transition at H_a^*, being a first-order transition. Recently there has been quite some discussion on the observation of a first-order transition of the vortex lattice [97]. The equilibrium magnetization $M_{\rm eq}$ is a thermodynamic quantity whereas resistivity is not. In clean single crystals of HTSC, the melting transition shows a clear change in $M_{\rm eq}$ vs H since the M–H curve is reversible. In $CeRu_2$, we have to infer $M_{\rm eq}$ from a hysteretic M–H curve [98], which is further complicated by supercooling. We have accordingly used the MHLs to estimate $M_{\rm eq}$ [73,74].

We first note that the field H_a^*, at which the transition sets in, rises as the temperature falls. Further the high field phase is also the high temperature phase and therefore has higher entropy. Now from the Clausius–Clapeyron relation $L = T\Delta S = -T\delta M_{\rm eq}({\rm d}H_a^*/{\rm d}T)$, the volume of the vortex state must fall or $M_{\rm eq}$ must rise as the field is increased isothermally across H_a^*. We have measured $M_{\rm eq}$ vs H as an essential failure test for the first-order transition hypothesis. We show in figure 9 the results of our measurement on a polycrystalline sample of pure $CeRu_2$ [73,74]. A perceptible rise in $M_{\rm eq}$ is seen at H_a^*. Same behaviour has been observed in other samples of pure as well as Nd-doped $CeRu_2$ [73,74]. We have made similar measurements at other temperatures [94]

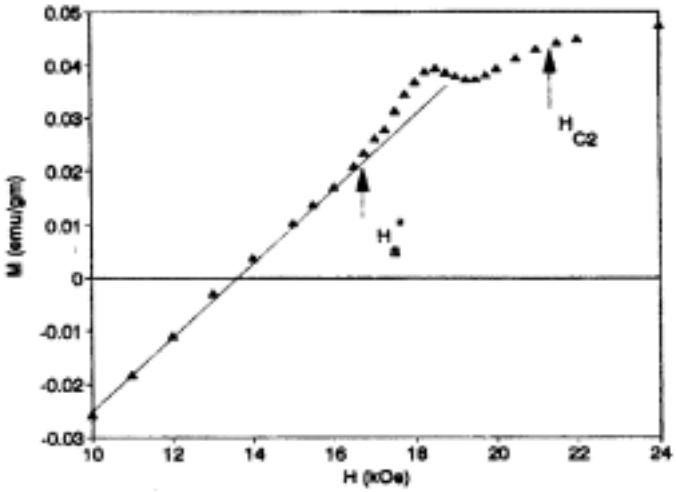

Figure 9. Equilibrium magnetization ($M_{\rm eq}$) versus field (H) plot at $T = 4.5$ K for a polycrystalline $CeRu_2$ sample [73].

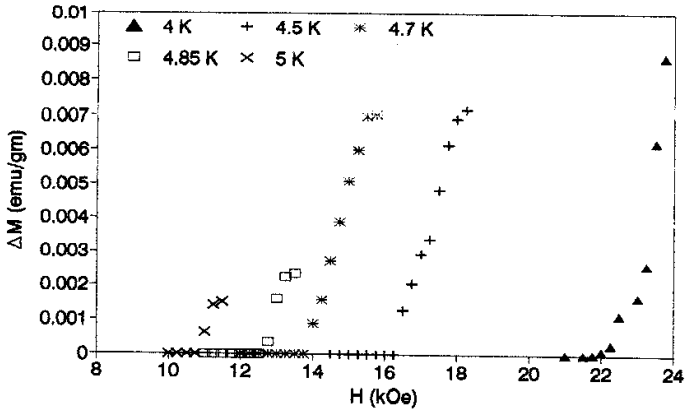

Figure 10. Field dependence of the rise in equilibrium magnetization for a polycrystalline $CeRu_2$ sample at various temperatures [94].

and we plot in figure 10 the field dependence of the rise in $M_{\rm eq}$ over the extrapolated value. We have found that the jump in $M_{\rm eq}$ drops to zero as T rises from 0.75 T_C to 0.9 T_C consistent with the existence of a critical point at T^*. The jumps shown in figure 10 have a width $\Delta/H_a^* \approx 0.1$, whereas one expects a sudden rise in a first order transition. In the evidence for flux lattice melting in $YBa_2Cu_3O_7$, presented by Welp *et al* [97], the rise in $M_{\rm eq}$ also occurs over about 2 kOe even though their M–H data is reversible. The results
of Zeldov *et al* [99] show that such a width in a first-order transition can be understood as a sample shape artifact in global magnetization measurements.

Summarizing the results we say that the DC magnetization data indicates a phase transition in the vortex state of $CeRu_2$, with the higher entropy phase exhibiting enhanced pinning. We have shown that the field dependence of $M_{\rm eq}$ is not inconsistent with a first-order transition of the vortex lattice. Our study, however, does not address to the question of the microscopic order parameter of this high-field higher entropy superconducting phase.

While FFLO state (defined below) has been considered as a possible explanation for the anomalous superconducting properties of the high field phase of not only $CeRu_2$ but also a few other type-II superconductors, namely UPd_2Al_3 [21,47], UPt_3 [100], $CeCo_2$ [46,101] etc, there also exists serious reservations regarding the applicability of such an idea to $CeRu_2$ [52,53]. In the light of such controversies it is worth discussing this subject in some more detail.

In 1964, Fulde and Ferrel [102] and independently Larkin and Ovchinnikov [103] 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 superconducting state to higher magnetic fields. In other words the destructive influence of Pauli paramagnetism on superconductivity can be (mitigated) by pairing spin-up and spin-down electrons with a non-zero total momentum whose value depends on the applied magnetic field. The order parameter of this new high-field superconducting state (or FFLO state) is spatially

modulated with planar nodes of the order parameter periodically aligned perpendicular to the AFL. The following characteristics of the FFLO state seem to be in consonance with the experimental findings for $CeRu_2$ and UPd_2Al_3 [21,47]:

1. The transition from the BCS state to this partially depaired FFLO state is a first-order one.
2. The existence of planar nodes in the order parameter of the FFLO state leads to the segmentation of the flux-lines in this field regime, and these quasi-2D flux-line segments can be pinned by the weak-pinning potential more easily (than the original flux-lines at lower fields), leading to a large irreversibility in the magnetization.

However there also exist several problems, which discourage one from straightforward adaptation of the FFLO state in explaining the anomalous superconducting mixed state properties of $CeRu_2$:

1. The FFLO state is supposed to occur only in strongly Pauli limited type-II superconductors. It is still a matter of debate whether $CeRu_2$ actually meets this condition. While $CeRu_2$ has been reported to be Pauli limited in some works [47,51], the opposite view is presented in other reports [75].
2. The rather stringent conditions for the existence of FFLO state have so far mainly been examined in spherical symmetric systems [104]. Recently it has been argued that, in contrast to the case for the ordinary BCS superconductivity, the band structure of electrons is important for the FFLO state [105]. It is expected that FFLO state will be enhanced if there is nesting in the Fermi surface [105]. The possibility of the nesting in the Fermi surface of $CeRu_2$ has been examined recently [39]. However, more works (both theoretical and experimental) are required before reaching any final conclusion.
3. The FFLO state was predicted to occur only at temperatures lower than $T^* \approx 0.56 T_{C0}$, where T_{C0} is the zero-field superconducting transition temperature [104,106]. This is in contradiction with the experimental findings in $CeRu_2$, where the anomalous magnetic response has been observed even at temperatures $\approx 0.9 T_{C0}$. This problem has been overcome by Tachiki *et al* [107] with the introduction of a generalized FFLO (GFFLO) state, which predicts that the inhomogeneous superconducting state can exist up to $T^* \approx 0.92\, T_{C0}$.
4. The FFLO or GFFLO state is expected to occur only in very clean superconductors with large ratio of electronic mean free path (l) and superconducting coherence length (ξ_C) i.e. $l/\xi_C >> 1$. In $CeRu_2$, however, the anomalous magnetic response has been found to be quite robust in nature and occurs, with all the characteristic features, for off-stoichiometric polycrystalline samples as well as Nd-, Rh-, and Co-doped pseudobinary alloys [41,71,75,76]. Although this insensitivity to disordering is contrary to the theoretical predictions regarding the existence of the FFLO or GFFLO state, on a closer look it is quite apparent that, for all of these polycrystalline and alloyed $CeRu_2$ samples, l is substantially larger than ξ_C [75]. It should also be pointed out here that while substitution of non-magnetic elements like La and Lu has a destructive influence on the PE in $CeRu_2$, the opposite is true for the substitution of a magnetic element like Nd [76]. Theoretically it has been predicted that the FFLO state could withstand a small amount of ferromagnetic impurities [108]. 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 [109]. It is of some interest to note that the FFLO state has been revisited recently in the question of superconductivity in ferromagnetic metals [110].

It should be mentioned here that the possibility of multiple superconducting phases, as in UPt_3, has also been considered for $CeRu_2$ in some works [16,24]. The PE in this scenario is associated with the phase transition between different superconducting phases. Such an approach draws some support from the observation of PE in ac-susceptibility measurements across the phase boundary of B and C phases in UPt_3 [111].

There is another interesting aspect of the anomalous response in the superconducting mixed state of $CeRu_2$, has so far been observed mainly in the polycrystalline samples near H_{C2} [15,16,24,41]. This feature consists of the paramagnetic magnetization in the reversible regime just below H_{C2} being significantly larger than that just above the H_{C2} in the normal state. This excess magnetization was also observed with 5% La substituted alloy but not with 5% Nd substituted alloy, although in the latter kind of substitution, the general anomalous structure was quite visible [41]. Similar behaviour has also been observed in $CeCo_2$ [101]. It should be noted here that a subtle minimum has been observed between the anomalous PE regime and H_{C2} in the isothermal magnetization scans, in the single crystal samples as well [21]. Neither 'peak effect' nor FFLO state can provide a suitable explanation of these features. One fascinating possibility that presents itself, however, is the modification of the magnetic character of the Ce ions from the Kondo-compensated non-magnetic state (which exists in the normal state), by the onset of superconductivity [15,41,101]. Ce moments would appear to give a large paramagnetic response to any magnetic field they see, if the establishing of the superconducting gap at the Fermi level leads to the removal of those very single particle states whose hybridization with the $4f$ states demagnetizes the latter. Under such circumstances, on increasing the field towards H_{C2}, the Ce atoms in the superconducting phase would yield a paramagnetic response greater than that just above H_{C2}, where they will be in the normal phase. The spatial variation of the magnetic character of the Ce atoms in a flux lattice may prove a difficult problem for proper calculation. The magnetic field seen by them will require the sort of considerations used by Baberschke *et al* [112] to discuss the behaviour of the ESR g value of Gd ions dissolved in $CeRu_2$ in the vortex state, and the anomalous increase in g shift they observe at the X band may be related to the effects we just discussed.

3.4 *Possible correlation between normal state properties and superconductivity in CeRu* $_2$

Is there any correlation between the normal state magnetic properties and the anomalous superconducting response in $CeRu_2$? Our study on eight samples of polycrystalline and alloyed samples of $CeRu_2$ and one single crystal sample of $CeRu_2$ has revealed that while the normal state spin-glass like magnetic properties are very much sample dependent and even absent in some cases, the anomalous PE in the superconducting mixed state is quite robust in nature; there is no apparent correlations between these two features [20]. There remains, however, the possibility that the paramagnetic impurities (as individual entities and not correlated objects) can influence the superconducting response. The source of such paramagnetic impurity can be up to 0.2 at% non-transformed Ce^{3+} ions [21] and/or

the randomly distributed Ce-ions with locally different environments [13]. Polarized neutron measurements has shown that the normal state spin-susceptibilty survives well inside the superconducting regime [13]. The presence of paramagnetic impurities can introduce a gap-less superconducting regime in the (H, T) phase diagram of a type-II superconductor [113]. It has been argued recently by Balatsky and Trugman, that any superconductor with magnetic impurities has gapless region due to a Lifshitz tail in the density of states extending to zero energy [114]. It was shown that the fluctuations in the impurity distribution produced regions of suppressed superconductivity [114]. This latter effect can produce additional pinning centres at high magnetic fields.

4. Various puzzles and scope for future works

Here we shall note down some particular aspects of both the superconducting and normal state of $CeRu_2$ which need further scrutiny.

1. There has been a recent interesting development in the field of heavy fermion and intermediate valence compounds. In a number systems like $CeSn_3$ and $CePd_2Si_2$, a pressure-induced heavy fermion ground state emerges from a magnetically ordered state [115]. Most interestingly, superconductivity is observed in the crossover regime from magnetically ordered local moment state to the moment compensated heavy fermion state. The T_C attains a maximum value as a function of pressure before the disappearence of superconductivity with further increase of pressure. It is conjectured that magnetism and superconductivity are different manifestations of the 'spin-density-wave' present in such systems [116]. In the crossover regime the spin density wave probably fails to propagate and instead acts as a glue that holds together the charge carriers in the superconducting state [115,116]. Fisk and Pine [116] mention that other members of the strongly correlated electron family are prime candidates for the presence of such 'failed' spin-or charge density waves. In this context there exists quite a few characteristic features of $CeRu_2$ which require further investigations. First, T_C of $CeRu_2$ shows a maximum on doping with La, Nd etc. [14,15,56,75]. It is interesting to note that lattice volume of $CeRu_2$ increases on doping with La and Nd [30]. Now, if one starts with an alloy $(Ce_{0.75}T_{0.25})Ru_2$ (where T = La or Nd) and approaches the parent compound $CeRu_2$ $CeRu_2$ by decreasing the concentration of T, it will be equivalent to applying positive pressure. Here lies the uncanny similarity with the recently studied heavy fermion systems that in $(Ce_{1-x}T_x)Ru_2$, T_C goes through a maximum as a function of x, equivalently as a function of pressure. A recent study on the actual pressure dependence of T_C in pure $CeRu_2$ has revealed that T_C decreases linearly with increasing pressure up to 0.5 GPa [117]. (After $P = 0.5$ GPa, T_C increases with the increase in pressure and this is attributed to a pressure induced transition at $P = 0.5$ GPa [117].) It will now be interesting to study the actual pressure dependence of T_C of $(Ce_{1-x}T_x)Ru_2$ alloys from the other side of T_C vs x maximum, and check whether T_C can actually be increased by applying pressure. Regarding the normal state magnetic properties of $CeRu_2$, it remains an open question whether there exists a spin density wave in $CeRu_2$ [37]. Careful experiments are now required involving $CeRu_2$ and its pseudobinaries to get a clear picture of the normal state properties of this interesting compound.

Even if this effort to draw an analogy to the recent developments in the field of heavy fermion physics turns out to be a mere speculation, the problem of substantial increase in T_C with both magnetic and non-magnetic doping still remains to be understood.

2. There is no clear consensus regarding the superconducting pairing mechanism in $CeRu_2$. Various suggestions starting from an axial superconducting state in which the superconducting gap vanishes on points at the Fermi surface [66] to conventional s-wave superconducting state with a large anisotropic energy gap [65,118], have been put forward. More experimental works are required to reach a definite conclusion in this regard.
3. The question, whether the upper critical field (H_{C2}) in $CeRu_2$ is Pauli limited or not, is yet to be answered properly. Applying the usual expression for the Pauli limiting field H_P = 1.84 T_C(K) (Tesla) and for the orbital critical field H_O^* = 0.72 (dH_{C2}/dT)T_C (Tesla), we find that the extrapolated values of $H_{C2}(0)$ for $CeRu_2$ (obtained from our own experimental works as well as from the literature) lie between H_O^* and H_P i.e. $H_O^* < H_{C2}(0) < H_P$ [119]. On the other hand, theoretically one expects the value of $H_{C2}(0)$ to be less than the smaller of the two limiting fields H_P and H_O^* [120]. To our knowledge there is no discussion so far in the literature regarding this unusual behaviour in $CeRu_2$. We have also found [119] that $H_{C2}(T)$ line in various samples of $CeRu_2$ (including good quality single crystal) deviate clearly from the theoretical predictions of WHH [50]. We believe that strong electron–electron correlation, the effect of which was not incorporated in the theory of WHH [50], is playing an important role in $CeRu_2$. More experimental as well as theoretical works are necessary for a proper understanding of the physics of H_{C2} in $CeRu_2$.
4. In the investigation of PE in $CeRu_2$, most of the effort, so far, is spent to understand the origin of this interesting phenomenon. Not much is known regarding the microscopic nature of this high field superconducting phase. Also it is now quite clear that there exists a distinct reversible regime between the PE regime and the $H_{C2}(T)$ line [20,121,122]. The questions regarding the nature of the transition from the PE regime to this reversible regime and the microscopic nature of this later regime are yet to be addressed.
5. The question of the existence of a tricritical point in the (H, T) phase diagram of the superconducting mixed state of $CeRu_2$ is yet to be solved. While magnetic measurements clearly indicate that PE is not observed beyond a point (T^*, H^*) in the phase diagram [17,18,21,51,71,121], transport studies suggest the presence of PE at temperatures almost up to the T_C [123]. It is not quite clear whether magnetic and transport property measurements are studying the same phenomenon in the temperature regime very near to T_C. Careful experiments, preferably involving microscopic techniques like scanning hall-probe method, are required to confirm the existence (or non-existence) of the tri-critical point.
6. There remains the question of interplay of magnetism and superconductivity leading to multiple superconducting phases (with different order parameters) in $CeRu_2$ as in the widely studied heavy fermion compound UPt_3. Some suggestions already exist in this regard [16,24]. We have mentioned earlier that PE has been observed in the ac-susceptibility measurements across the phase boundary of B and C (supercon-

ducting) phases in UPt_3 [111]. In this connection it is interesting to note that similar signature of PE has been observed in the ac-susceptibility measurements of $CeRu_2$ [24,51,124]. A detailed comparative study of the ac-suceptibility involving $CeRu_2$ and UPt_3 is likely to provide interesting information regarding the superconducting mixed state of $CeRu_2$.

5. Conclusion

It is to be noted that the earliest study of superconductivity in $CeRu_2$ [1] almost coincided with the arrival of BCS theory of superconductivity. However, even in those heydays of BCS theory, this cubic binary compound clearly indicated that there was still something to look beyond BCS model. Forty years have passed since then, and neither the normal state properties nor the superconductivity of $CeRu_2$ is completely understood. Today, $CeRu_2$ remains one of the simple and relatively accessible (both experimentally and metallurgically) systems to study the interesting physics of electron–electron correlation.

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