Anisotropic Magnetic Response in the Superconducting Mixed State of UPt_3

K. Tenya,[1] M. Ikeda,[1] T. Tayama,[1] T. Sakakibara,[1] E. Yamamoto,[2] K. Maezawa,[3]
N. Kimura,[4] R. Settai,[4] and Y. Ōnuki[2,4]
[1]*Department of Physics, Faculty of Science, Hokkaido University, Sapporo 060, Japan*
[2]*Advanced Science Research Center, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-11, Japan*
[3]*Faculty of Engineering, Toyama Prefectural University, Toyama 939-03, Japan*
[4]*Department of Physics, Faculty of Science, Osaka University, Toyonaka 560, Japan*
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Equilibrium magnetization $M_{\rm eq}$ of the superconducting mixed state of UPt_3 has been measured as a function of field. At low temperatures, the discontinuity of $dM_{\rm eq}/dH$ at the upper critical field H_{c2} exhibits marked anisotropy between the two principal directions of the hexagonal crystal, being indiscernibly small for $H \perp c$, where the normal state paramagnetic susceptibility is largest. The results are not simply explained by the effective mass anisotropy nor by the ordinary paramagnetic effect of a spin-singlet pairing; they are rather in favor of an odd-parity pairing with an appreciable anisotropy in the pair-spin correlation. [S0031-9007(96)01311-7]

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Superconductivity in heavy electron systems has been attracting much interest because experiments suggest that the pairings are mostly of an unconventional type. Among heavy fermion superconductors known to date, UPt_3 is a unique compound where a realization of unconventional order parameters is evident from its complex field-temperature (H-T) phase diagram with three different vortex states (A, B, and C phases) [1]. In addition, a possibility of an odd-parity pairing is inferred from some experimental facts such as (i) the absence of a change in the NMR Knight shift below T_c [2,3] and (ii) crossover in the anisotropy ratio $H_{c2}^{\perp}/H_{c2}^{\parallel}$ [4,5]. Several theoretical models have been proposed so far to explain the superconductivity of UPt_3 [5–8], though no consensus has yet been reached on the pairing symmetry.

In further elucidating the pairing in UPt_3, it is of interest to examine the equilibrium magnetization $M_{\rm eq}$ in the superconducting mixed state. In general, there is a contribution to $M_{\rm eq}$ from a paramagnetic polarization of the system, in addition to the diamagnetic orbital currents around the vortices. As is well known, the normal state paramagnetic susceptibility χ_n of UPt_3 is large and anisotropic [9], with the easy direction being $H \perp c$. Since a substantial part of χ_n comes from the pseudospin Pauli paramagnetism [2,3,10], the behavior of $M_{\rm eq}$ near H_{c2} may depend strongly on the pairing symmetry. In the case of an even-parity pairing, for example, the spin polarization should be suppressed below H_{c2} for *all* directions [11]. This would lead to a sizable discontinuity in $dM_{\rm eq}/dH$ at H_{c2}, especially for $H \perp c$. If this anomaly, the paramagnetic effect, is absent, it would then be a strong implication of the odd-parity states.

This approach is indeed complementary to the NMR Knight shift experiment. It should be noticed, however, that the above NMR results (i) might not be fully compatible with the interpretation of the anisotropy crossover in H_{c2} and (ii); the latter assumes $H_{c2}^{\parallel}$ to be *paramagnetically limited* at low T [5]. It is thus highly worthwhile to inspect the bulk magnetization of UPt_3 near H_{c2}. In this Letter, we have examined $M_{\rm eq}(H)$ of UPt_3 by means of high-resolution dc magnetization $[M(H)]$ measurements on high-quality single crystals, focusing on the magnetic response of the high field state (C phase).

Two single crystals of UPt_3, sample 3-S and sample 4, were grown by the Czochralski pulling method in a tetra-arc furnace [12]. A clear double superconducting transition was observed in a specific heat measurement. The upper critical temperature T_c was 523 mK (sample 3-S) and 510 mK (sample 4). The resistivity ratio $\rho(300\ \mathrm{K})/\rho(T)$, extrapolated to $T = 0$ from above T_c, was in excess of 500 for both samples, indicating the excellent quality of the crystals. The crystals were shaped to $2.5 \times 2.5 \times 3\ \mathrm{mm}^3$ (sample 3-S) and $1 \times 1 \times 3\ \mathrm{mm}^3$ (sample 4), with the longest axes oriented to the c axis. $M(H)$ curves at temperatures ranging from 50 mK to above T_c were obtained by a Faraday force magnetometer installed in a dilution refrigerator [13], in a field gradient of 500–800 Oe/cm. By use of a high-sensitivity capacitive force-sensing device, the overall displacement of the sample was limited to less than 1 μm; there was virtually *no* fluctuation in the magnetic field experienced by the sample. This point is very important in measuring true hysteretic magnetization of the vortex states. Each measurement was carried out after zero-field cooling the sample from above T_c to the desired temperatures. Considering the flux line relaxation, the sweep rate of H was fixed constant (5 Oe/sec) throughout the measurements.

Figure 1 shows the $M(H)$ curves of sample 4, measured at 50 mK. The lower critical field H_{c1} (~10 Oe) was not well resolved in this experiment. The strong irreversibility appearing at low field is due to the ordinary flux pinning effect. The hysteresis rapidly decreases as H increases, and $M(H)$ becomes almost reversible at $H \sim 17$ kOe. Similar $M(H)$ curves were obtained for sample 3-S, except

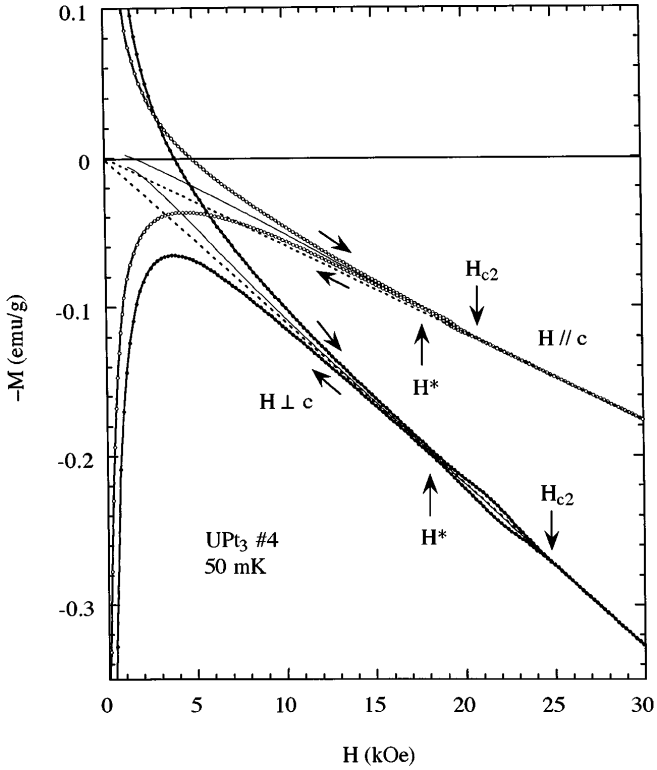

FIG. 1. Magnetization curves of the single crystal of UPt_3 (sample 4) at 50 mK. The thin solid lines are the equilibrium magnetization obtained by averaging the hysteresis. H^* denotes the onset field of the peak effect.

for a magnitude of the hysteresis that linearly depends on the sample dimension and was therefore larger in sample 3-S. The linear magnetization above H_{c2} is due to the normal state paramagnetism, from which we obtain $\chi_n^{\parallel} = 5.8 \times 10^{-6}$ emu/g and $\chi_n^{\perp} = 1.1 \times 10^{-5}$ emu/g. In both samples and for both field directions, we observed that the irreversibility in $M(H)$ increases again in a narrow region just below H_{c2} [14]. This is a so-called "peak effect," occasionally observed in type-II superconductors [15]. Hereafter, we define H_{c2} as the field above which the irreversibility vanishes completely. We show the resulting H_{c2} vs T plots in Fig. 2, which are in good agreement with those previously obtained by other experimental methods [1,4]. The onset field of the peak effect H^* is also shown in the figure.

When the magnetization hysteresis is small, the equilibrium magnetization M_{eq} of the vortex state can be well approximated by the average of the increasing- and decreasing-field data [15]. The results for M_{eq} are shown in Fig. 1 by thin solid lines. Also shown by the dotted lines are the extrapolated normal state magnetization $M_n^{(\parallel,\perp)} = \chi_n^{(\parallel,\perp)}H$. Evidently, the paramagnetic contribution to M_{eq} is quite large for both directions. Note that the difference between $M_{\text{eq}}^{\perp}$ and $M_n^{\perp}$ is surprisingly small near H_{c2}, whereas $M_{\text{eq}}^{\parallel}$ shows a small but distinct deviation from $M_n^{\parallel}$ below H_{c2}.

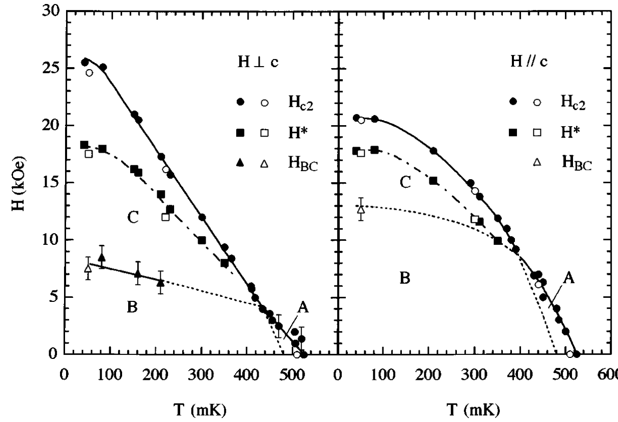

FIG. 2. H-T phase diagram of UPt_3 for sample 3-S (solid symbols) and sample 4 (open symbols). The phase boundaries indicated by dotted lines are not observed in the present measurements. The onset field of the peak effect H^* is also plotted as a reference.

The behavior of M_{eq} becomes more clear by plotting the magnetization difference $M_{\text{eq}}^0 = M_{\text{eq}} - M_n$ in an enlarged scale in Figs. 3(a) and 3(b), where the results for higher temperature are also shown for comparison. The small humps or dips seen in the curves for 50 mK near H_{c2} are probably due to the peak effect; the averaging procedure might not work well due to a nonlinear distribution of the vortex lines [15]. It is rather natural to assume a smooth variation of M_{eq}^0, as indicated by dot-dashed lines. We first note the feature in M_{eq}^0 that is associated with the B-C transition. Since this transition is of second order, we may expect a discontinuity in dM_{eq}^0/dH which can be estimated from the specific heat measurements [16] to be $\Delta(dM_{\text{eq}}^0/dH) \sim 5 \times 10^{-7}$ emu/g. We could ascertain a discontinuity of this order at low T, as shown in Fig. 3(c). The critical field H_{BC} thus obtained is also indicated in Fig. 2. The anomaly in M_{eq}^0 at H_{BC} was, however, smeared with increasing temperature, and could not be traced up to the tetracritical point. We also note that no appreciable change was observed in M_{eq}^0 across the A-B transition.

The salient feature of M_{eq}^0 at $T = 50$ mK is the marked anisotropy near H_{c2}. There is an order of magnitude difference in the slopes of $M_{\text{eq}(\parallel,\perp)}^0$ near H_{c2}. Moreover, the curvature of $|M_{\text{eq}}^0|$ in the C phase ($H_{BC} < H < H_{c2}$) distinctly changes with the field direction; downward (upward) for $H \parallel c$ ($H \perp c$). In general, M_{eq}^0 near H_{c2} can be expressed in terms of a Ginzburg-Landau parameter κ_2 as $M_{\text{eq}}^0 = (H - H_{c2})/4\pi\beta(2\kappa_2^2 - 1)$ [11], where β is a number of order unity that depends on the vortex lattice configuration. From the results in Fig. 3, we obtain highly anisotropic values of κ_2 at $T = 50$ mK, $\kappa_2^{\perp} \sim 140$, and $\kappa_2^{\parallel} \sim 40$; i.e., $\kappa_2^{\perp}/\kappa_2^{\parallel} \approx 3.5$. Here, the κ_2 values were determined from the average slope of M_{eq}^0 between H^* and H_{c2}. Thus, the actual value of $\kappa_2^{\perp}$ could be even larger, due to the upward curvature of $M_{\text{eq}\perp}^0$. In a conventional

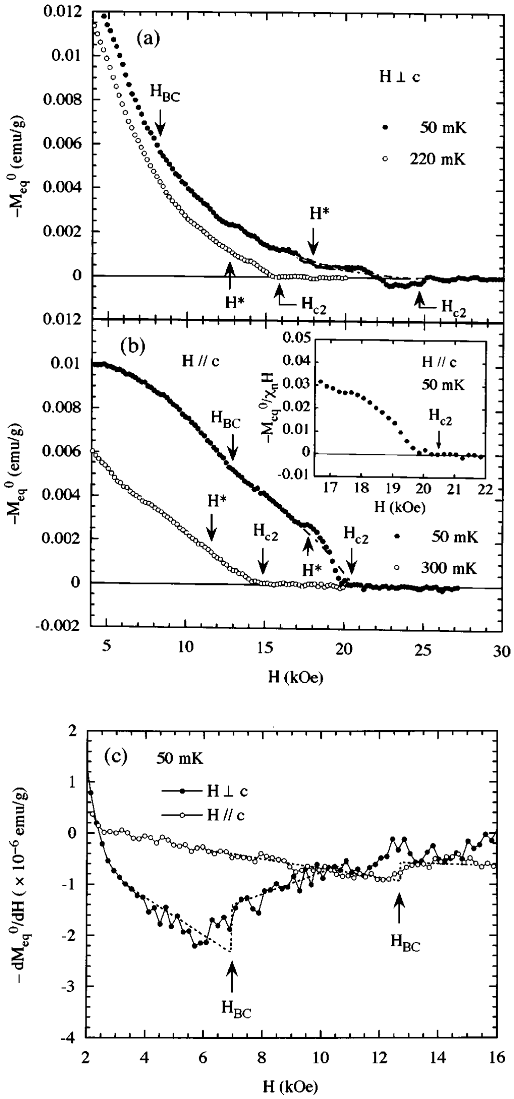

FIG. 3. Field variation of the magnetization difference M_{eq}^{0} in the superconducting mixed state of UPt_3 (sample 4) for (a) $H \perp c$ and (b) $H \parallel c$, and the differential susceptibility around H_{BC} at 50 mK (c). The dot-dashed lines in (a) and (b) indicate the expected smooth variation of M_{eq}^{0} in the region of the peak effect between H^* and H_{c2}. The inset shows the relative change in the susceptibility for $H \parallel c$ near H_{c2}.

superconductor, κ_2 could be direction dependent reflecting the effective mass anisotropy, which can be estimated by $\kappa_2^{\perp}/\kappa_2^{\parallel} \approx (H_{c2}^{\perp}/H_{c2}^{\parallel})_{T \sim T_c}$ [17]. For UPt_3, this results in a much smaller value $\kappa_2^{\perp}/\kappa_2^{\parallel} \sim 0.6$ [4]. Evidently, effective-mass anisotropy (anisotropic orbital current) is not the origin of the low-temperature anisotropy in M_{eq}^{0} [18].

The upward curvature of $|M_{eq\perp}^{0}|$ with a vanishingly small change of the slope at H_{c2} is specific to a clean superconductor *in the absence of* the paramagnetic effect [19]. This implies that the orbital current contribution is predominant in $M_{eq\perp}^{0}$. By contrast, the downward curvature of $|M_{eq\parallel}^{0}|$ with a sharp change of the slope at H_{c2} is the typical behavior of the ordinary paramagnetic effect [20]; suppression of the spin polarization due to pairing enhances $|M_{eq}^{0}|$ below H_{c2}. This strongly suggests that the spin susceptibility for $H \parallel c$ is somewhat reduced in the C phase of UPt_3. Note that these features in M_{eq}^{0} become weaker with increasing temperature, as expected [11].

It should be noticed that the anisotropy in M_{eq}^{0} changes at low field as can be seen for the curves at 50 mK in Fig. 3; $M_{eq\perp}^{0}$ becomes larger than $M_{eq\parallel}^{0}$ below $H \sim$ 6 kOe. This crossover is consistent with the thermodynamic constraint $H_c^2/8\pi = -\int_0^{H_{c2}} M_{eq(\parallel,\perp)}^{0}\,dH$, where H_c is *the direction independent* thermodynamic critical field. Extrapolating $M_{eq(\parallel,\perp)}^{0}$ to lower fields, we can obtain $H_c(T \sim 0) \approx 260$ Oe for both curves, in agreement with the value that can be estimated from the specific heat data [21]. These facts confirm that the observed anisotropy in M_{eq}^{0} is indeed closely related to that of H_{c2}. It is very important to point out that the paramagnetic energy $\chi_n H_{c2}^2/2$ significantly exceeds the condensation energy $H_c^2/8\pi$ by a factor of ~ 10 ($\parallel c$) and ~ 25 ($\perp c$); the paramagnetic polarization in the vortex state is essentially large for both directions.

Temperature variation of κ_2 evaluated from M_{eq}^{0} is summarized in Fig. 4, which further confirms the existence of the anisotropic paramagnetic effect. The anisotropy ratio of κ_2 at ~ 450 mK decreases to $\kappa_2^{\perp}/\kappa_2^{\parallel} \approx 0.8$, approaching the value ~ 0.6 expected from the mass anisotropy. Remarkably, $\kappa_2^{\perp}(T)$ continues to *increase* on cooling, without an indication of saturation. This is actually the behavior that is predicted for a clean superconductor *in the absence of* the paramagnetic effect [22], where $\kappa_2 \propto \sqrt{\ln(T_c/T)}$ as $T \rightarrow 0$ as shown by the dotted line. In contrast, $\kappa_2^{\parallel}$ continues to *decrease* on cooling; the typical behavior in

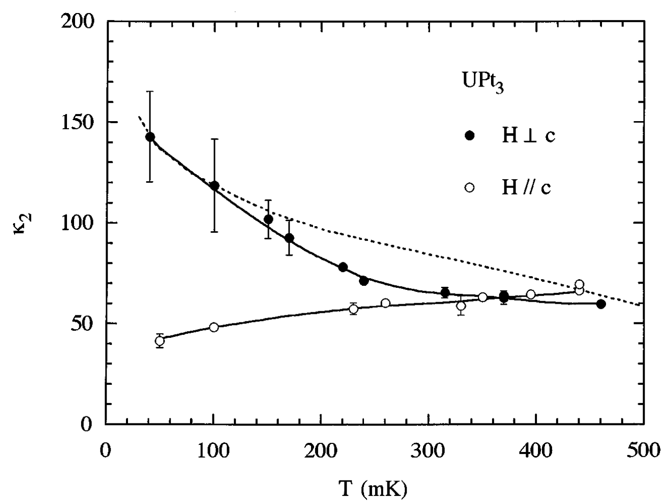

FIG. 4. Temperature variation of the Ginzburg-Landau parameter κ_2. The dotted line is the theoretical prediction for a clean superconductor without paramagnetic effect. The solid lines through the data points are guide to the eye.

the presence of the paramagnetic effect [11] where the pair breaking by the Zeeman energy becomes important at low temperatures. As a result, there is a crossover in the anisotropy ratio $\kappa_2^{\perp}/\kappa_2^{\parallel}$ at about $T \sim 0.7T_c$. Except for this crossover, the sign reversal in $d\kappa_2/dT$ between two directions is in agreement with the results inferred from the recent specific heat measurements [16].

The anisotropic paramagnetic effect itself is not unusual. For instance, in $ErRh_4B_4$, where ferromagnetic interactions between Er ions compete with the superconductivity of conduction electrons, a strong paramagnetic effect is observed in the magnetization for the spin-easy axis ($H \parallel a$), while the effect is weak for the hard axis ($H \parallel c$) [20]. The crucial point in UPt_3 is that the paramagnetic effect in M_{eq}^0 is apparently absent for the direction ($H \perp c$), *where the normal state paramagnetic susceptibility is largest*. This is the opposite of what is normally expected for a clean spin-singlet superconductor. It is important to note that the spin-orbit scattering mechanism is not relevant in this case. In the presence of strong spin-orbit scattering, spin paramagnetism might be recovered in the singlet pairing states [23]. This mechanism, however, would be essentially isotropic and therefore does not explain the slight but appreciable paramagnetic effect for $H \parallel c$. It should also be noticed that the present samples are in the clean limit; the mean free path of the carriers can be estimated from the residual resistivity ($\rho_{0\parallel} \approx 0.2\ \mu\Omega$ cm) to be over 2000 Å, much longer than the coherence length $\xi_0 \sim 120$ Å expected from the H_{c2} values.

Let us now turn to the implication of the unusual anisotropic paramagnetic effect. The probable scenario that emerges is the odd-parity pairing with anisotropic pair-spin orientation. The apparent lack of the paramagnetic effect in the basal plane would imply an equal-spin pairing in this direction, whereas the appreciable paramagnetic effect along the *c* direction would mean that the pair-spin orientation is somewhat confined in the *c* plane, implying a non-negligible spin-orbit coupling in the pairing channel [5]. This scenario relies largely on the results of the recent NMR Knight shift experiment on single crystals [3] which reports the spin susceptibility to be largest for $H \perp c$ [24]. Our results are consistent with theirs, except for the anisotropy along the *c* direction; no change is observed in the Knight shift for *two* principal directions. We stress, however, that the expected pair-spin anisotropy is not very strong. To show this somewhat quantitatively, we note that the orbital current contribution to $M_{\mathrm{eq}\parallel}^0$ would be small for $\sim 0.8H_{c2} \leq H \leq H_{c2}$, as expected from $M_{\mathrm{eq}\perp}^0$. Then $M_{\mathrm{eq}\parallel}^0$ near H_{c2} consist mostly of the spin susceptibility change $\Delta\chi_s^{\parallel}$ due to pairing, which can be estimated as $\Delta\chi_s^{\parallel}/\chi_n^{\parallel} \sim M_{\mathrm{eq}\parallel}^0/\chi_n^{\parallel}H$. The result is plotted in the inset of Fig. 3(b), which indicates $\Delta\chi_s^{\parallel}$ in the *C* phase to be, at most, a few percent of $\chi_n^{\parallel}$. This amount of change might not be detected in the Knight shift measurements [2,3] within the resolution of the experiment.

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