Resonant Magnetic X-Ray Scattering Study of Phase Transitions in UPd_2Al_3

B. D. Gaulin,[1] D. Gibbs,[2] E. D. Isaacs,[3] J. G. Lussier,[1] J. N. Reimers,[1,*] A. Schröder,[1] L. Taillefer,[4,†] and P. Zschack[5]

[1]*Department of Physics and Astronomy, McMaster University, Hamilton, Ontario L8S 4M1, Canada*
[2]*Physics Department, Brookhaven National Laboratory, Upton, New York 11973*
[3]*AT&T Bell Laboratories, Murray Hill, New Jersey 07973*
[4]*Laboratoire Louis-Neél, Centre Nationale de la Recherche Scientifique, Grenoble, France*
[5]*Oak Ridge Institute for Science and Education, Brookhaven National Laboratory, Upton, New York 11973*

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Resonant magnetic x-ray scattering measurements were performed on a single microcrystallite at the surface of a polycrystalline boule of the antiferromagnetic, heavy fermion superconductor UPd_2Al_3. These measurements show a strong anomaly in the order parameter at 11.8 K, below $T_N \sim 14.5$ K, indicating at least two antiferromagnetically ordered phases which share a common periodicity. Measurements performed near and below $T_c = 2.0$ K show the antiferromagnetic order parameter to be unaffected on passing into the superconducting phase, to $\pm 2\%$.

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The fascinating low temperature transport, thermal, and magnetic properties displayed by heavy fermion materials have kept them at the forefront of metals physics research for more than a decade [1]. The interesting physics in the problem is believed to arise from the interplay between the relatively localized f electrons of these predominantly uranium and cerium based materials, and their metallic band states. Many properties can be described by the presence of a very large density of quasiparticle states at the Fermi level, hence large effective electron masses and their name; however, a full understanding remains elusive.

The electronic ground state of these materials is varied. The magnetic phenomena which they display ranges from long-range antiferromagnetic order with static moments of differing sizes to fluctuating short-range magnetic correlations. The most interesting phenomena which a subset of these materials display is the apparent microscopic coexistence of antiferromagnetic order and superconductivity at low temperatures. There are now four known compounds which display this extremely interesting ground state: UPt_3 [2], URu_2Si_2 [3], UPd_2Al_3 [4], and UNi_2Al_3 [5]. Of these UPd_2Al_3 and UNi_2Al_3 were discovered only recently, and their magnetic properties are not well established. However, the antiferromagnetism exhibited by UPt_3 [6] and URu_2Si_2 [7,8] is known to be highly unusual. The ordered moments present at saturation are extremely small ($\sim 0.02\mu_B$ for UPt_3 and $\sim 0.04\mu_B$ for URu_2Si_2), while the temperature dependence of the magnetic Bragg peak intensity is linear, consistent with mean field behavior, over an anomalously wide temperature regime. Also, in the UPt_3 and URu_2Si_2 crystals studied to date, the magnetic Bragg peaks are *not* resolution limited [6,8], indicating finite, antiferromagnetically ordered regions below T_N.

The magnetic properties of the two new heavy fermion superconductors (HFS) are currently the subject of intense study. Both of these new materials exhibit simple hexagonal crystal structures. Preliminary neutron measurements on UPd_3Al_3 [9] indicated that it orders in an incommensurate magnetic structure below ~ 21 K, and then transforms to a simple antiferromagnetic structure below ~ 15 K with a low temperature ordered moment of $\sim 0.85\mu_B$, which is huge by the standards of the other superconducting heavy fermions. It is superconducting below ~ 2 K, which is the highest T_c displayed by this group of HFS. Very recently, a neutron scattering study using single crystals has reported [10] a remarkable 10% dip in the integrated intensity of the $(0, 0, \frac{1}{2})$ superlattice Bragg peak near $T_c \sim 2$ K. This anomalous behavior is reported to be accompanied by an increase in the width of the Bragg peak. If correct, these results [10] would indicate an extremely strong coupling between the antiferromagnetic and superconducting order parameters in UPd_2Al_3, much more pronounced than any such possible effects in either UPt_3 [6,11] or URu_2Si_2 [12].

More recent susceptibility, resistivity, and magnetostriction measurements [13] show indications that the magnetic behavior of this compound is complicated. Anisotropy between basal-plane and c-axis susceptibility indicates that the magnetic moments in this compound lie within the basal plane. This study showed three magnetically ordered states present on application of a basal-plane magnetic field, while only one is present on application of a field along the c direction. No evidence of the incommensurate phase above ~ 15 K is reported. In addition, a new study has reported evidence of substantial magnetic anisotropy within the basal plane [14].

We have carried out a resonant magnetic x-ray scattering study of a single crystal sample of UPd_2Al_3. This technique [15] involves tuning the energy of the incident x-ray beam through an appropriate absorption edge of the magnetic atom, in this case, the M_{IV} edge of uranium. For elastic scattering, a core electron is promoted to a partially filled magnetic level, where it exists briefly in an excitonlike state, before falling back to its original level, with the emission of a photon of the same energy. The M_{IV} edge corresponds to a $3d_{3/2}$ to $5f_{5/2}$ transition.

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Both the excitation of the core electron and its subsequent decay occur via strong electron-dipole transitions. The process [16] is sensitive to the local magnetization by virtue of the Pauli principle and polarization selection rules. Very large enhancements [17] of the magnetic scattering cross section have previously been observed in a growing list [18] of lanthanide and actinide based magnets. This process must occur coherently over the resolution volume, and thus the scattering satisfies the Bragg condition for the antiferromagnetic state under study.

A remarkable feature of the present work is that it was actually carried out on a polycrystalline ingot sample. This ingot was roughly cylindrical in shape, with a length of ~ 20 mm, and a diameter of ~ 5 mm. However, several single crystal grains of area ~ 1 mm^2 were clearly visible on its surface. The faces of these grains were found to be perpendicular to the c axis. They did not propagate very far into the ingot, as they could not be identified optically on examination of a broken surface. We estimate that the grains were well below 1 mm in thickness, and likely not thicker than a few microns. These single crystal measurements were therefore performed on a sample which was too small for single crystal neutron diffraction work, by a factor of between 2 and 4 orders of magnitude in volume.

The sample was prepared at the Laboratoire Louis-Néel (CNRS) in Grenoble, France. High-purity starting materials, U, Pd, and Al, were melted together in stoichiometric amounts, using RF induction and a water-cooled crucible in an ultrahigh vacuum. The boule was quenched shortly after being homogeneously molten in order to minimize evaporation. The resulting polycrystalline ingot was annealed for 3 d at 900°C in ultrahigh vacuum. A small piece of the annealed ingot was used for characterization, yielding a residual resistivity $r_0 = 2.2$ $\mu\Omega$ cm, and a superconducting transition temperature at $T_c = 2.0$ K with a width of 0.04 K. X-ray powder diffraction measurements show no phase other than the $PrNi_2Al_3$ structure. The residual resistivity, the superconducting T_c, as well as the width in T_c are often taken as figures of merit to describe the crystalline quality of HFS materials. The results from the sample under study here show this material to be of very high quality. In particular, the residual resistivity of this sample is lower than that displayed by other HFS samples, with the exception of the best UPt_3 samples [19].

Our x-ray measurements were performed on beam lines X22C and X14 at the National Synchrotron Light Source of Brookhaven National Laboratory. We first discuss the measurements at X22C. The sample was mounted inside a beryllium can with a helium exchange gas present. This sample can was then attached to the cold finger of a two-stage closed cycle refrigerator which allowed us to change the sample temperature continuously from 4 to 300 K. The temperature was stable to 0.01 K over the temperature range of interest in this Letter ($T \leq 30$ K).

The energy dependence of the integrated intensity due to charge scattering at (0,0,1) and of that due to magnetic scattering at $(0, 0, \frac{3}{2})$ are shown in Fig. 1 for temperatures well below $T_N \sim 14.5$ K. The scattering at $(0, 0, \frac{3}{2})$ is well described by a Lorentzian centered at the M_{IV} edge energy, 3.728 keV, and is clearly distinct from the line shape of the (0,0,1) charge Bragg peak, which is typical of anomalous charge scattering near an absorption edge [20]. This energy dependence identifies the $(0, 0, \frac{3}{2})$ Bragg peak as being magnetic in origin [18]. A similar energy dependence is observed at $(0, 0, \frac{1}{2})$.

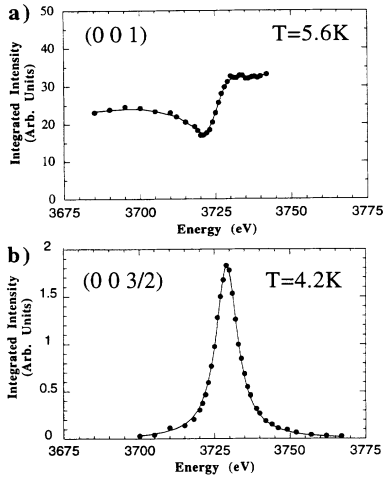

FIG. 1. The energy dependence of the (0,0,1) Bragg peak due to charge scattering in UPd_2Al_3 is shown in panel (a) at 5.6 K. Panel (b) shows the energy dependence of the $(0, 0, \frac{3}{2})$ Bragg peak at 4.2 K. This scattering is clearly distinct from that shown in panel (a) and is identified as being magnetic in origin. Solid lines are drawn only to guide the eye.

Figure 2 shows the wave-vector dependence of magnetic scattering at $(0, 0, \frac{3}{2})$, as well as that for the charge scattering at (0,0,1). These data were taken at several temperatures below $T_N \sim 14.5$ K. The results of longitudinal scans are shown. Transverse scans were also performed at these wave vectors, but are not displayed. The full width of the scattering in the transverse direction (θ) at the $(0, 0, \frac{3}{2})$ position was $\sim 0.1°$, demonstrating the single crystal nature of the grain under study. The inset of this figure shows the longitudinal scans at (0,0,1) and $(0, 0, \frac{3}{2})$, scaled so that their peak intensities coincide. Clearly the magnetic peak at $(0, 0, \frac{3}{2})$ is comparable in width to the charge scattering peak at (0,0,1). This measurement demonstrates the long magnetic correlation length within the antiferromagnetic state. Resolution considerations show that this is ~ 1500 Å. Very interestingly, this result contrasts a similar comparison of x-ray magnetic to charge scattering from URu_2Si_2 [8], in which a magnetic Bragg peak at larger wave vector was seen to be broader than a corresponding charge peak. In the case of URu_2Si_2 [8], this indicated finite magnetic domains with a temperature-independent extent of ~ 450 Å along its body-centered tetragonal c direction. The new results on UPd_2Al_3 also contrast with neutron scattering measurements on UPt_3 [6], which show that the antifer-

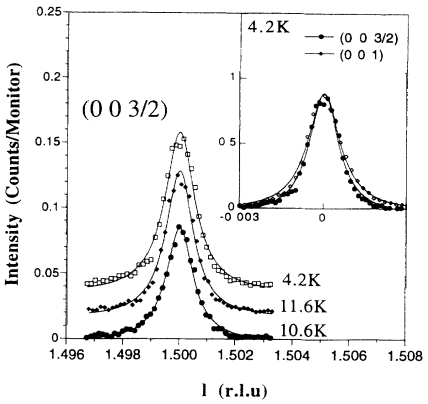

FIG. 2. Longitudinal scans along the (001) direction through $(0,0,\frac{3}{2})$ are shown for UPd_2Al_3 with the incident x-ray energy tuned to the M_{IV} edge (3.728 keV) at different temperatures below $T_N \sim 14.5$ K. The data have been offset in the vertical direction, for clarity. The inset shows the (0,0,1) charge peak and the $(0,0,\frac{3}{2})$ magnetic peak scaled to agree in peak intensity. All the solid lines in the figure are phenomenological fits to the data intended as guides to the eye. The magnetic Bragg peaks in UPd_2Al_3 show no anomalous width in wave vector, in contrast to other antiferromagnetic heavy fermion superconductors.

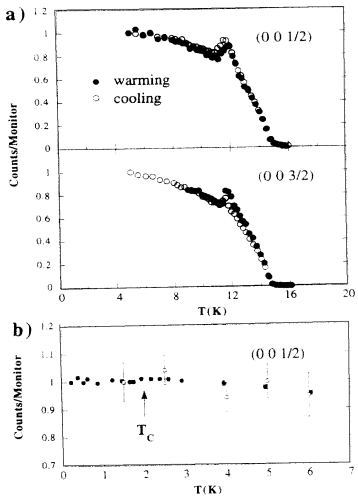

FIG. 3. (a) The temperature dependence of the resonant magnetic x-ray scattering at the $(0,0,\frac{3}{2})$ and the $(0,0,\frac{1}{2})$ Bragg peak positions in UPd_2Al_3 are shown for both warming and cooling runs. A large anomaly is present in these order parameter curves at $T_{N1} \sim 11.8$ K. (b) The temperature dependence of the resonant magnetic x-ray scattering (solid squares) at relatively low temperatures for the $(0,0,\frac{1}{2})$ Bragg peak in UPd_2Al_3 is shown, along with the same quantity measured by powder neutron diffraction (open squares). The intensity of the neutron data have been scaled to agree with the x-ray measurement at low temperature.

romagnetic ordered state, which it enters below ~ 5 K, is characterized by a temperature independent correlation length of ~ 250 Å.

The temperature dependence of the $(0,0,\frac{1}{2})$ and $(0,0,\frac{3}{2})$ magnetic Bragg peaks is shown for both warming and cooling in Fig. 3(a). The principal features of these curves reproduce for different sample histories from the same grain. The form of these curves is quite remarkable. The temperature dependence of the Bragg peaks displays a sharp onset at $T_N \sim 14.5$ K. At lower temperatures there is a large anomaly centered near $T_{N1} \sim 11.8$ K. This is evidence for the presence of at least two magnetically ordered phases below T_N, which exhibit a common periodicity as they share the same Bragg reflections. The transition at $T_N \sim 14.5$ K appears continuous as there is no evidence for hysteresis. The large anomaly at T_{N1} displays weak hysteresis, suggesting a discontinuous transition between two magnetically ordered phases.

Several such grains on the surface of the polycrystalline boule were investigated. The c axis of all of these grains were normal to the surface, but the basal-phase orientation was random. In all cases the order parameter turned on sharply with the same $T_N \sim 14.5$ K, and all grains displayed the same c-axis lattice parameter, to within the resolution of the instrument. However, the relative magnitude of the strong anomaly at T_{N1}, compared with the low temperature Bragg intensity, was variable.

The form of the amplitude for coherent elastic x-ray scattering within the dipole approximation [16] produces a magnetic polarization sensitivity very different from that obtained in magnetic neutron scattering [21] in which one is sensitive to the components of moment in a plane perpendicular to $\mathbf{Q}$. For the conditions relevant to the present measurements, the magnetic x-ray scattering cross section is proportional to the projection of the moment onto the scattered x-ray wave vector. Consequently, the strong anomaly at T_{N1} observed in the resonant x-ray measurement is consistent with at least one phase transition characterized by a spin reorientation within the basal plane.

We also carried out a set of resonant magnetic x-ray measurements on the X14 beam line with the same UPd_2Al_3 sample in a dilution refrigerator which allowed us to access temperatures as low as 225 mK, well below the superconducting phase transition near 2 K. These measurements were carried out under conditions similar to those described for X22C. The sample was mounted in Cu-impregnated low temperature grease and sat on the cold finger in vacuum. The surface of the ingot sat just above the grease allowing restricted access to the $(0,0,\frac{1}{2})$ magnetic Bragg peak only.

The temperature dependence of the magnetic scattering at $(0,0,\frac{1}{2})$ as measured at X14 at low temperatures is shown in Fig. 3(b). As in the measurement at X22C described above, the intensity has an onset near 15 K. The measurements extend down to 225 mK and we can see that the resonant magnetic scattering intensity is temperature independent on passing through the superconducting transition near 2 K, at least to the accuracy of

the measurement, ±2%. This clearly contradicts the recent report of a strong coupling between the antiferromagnetic and superconducting order parameters near T_c [10]. Also, recent heat capacity measurements have observed evidence of an additional phase transition at 600 mK in a sample of $UPd_2Al_{3.03}$ [22]. We see no evidence for such a transition in our measurements, to within the accuracy quoted above.

Powder neutron diffraction measurements were performed on a sample taken from the same boule as that used in the x-ray study. These data were collected on the E3 triple axis spectrometer at the Chalk River Laboratories. The intensities of the $(0,0,\frac{1}{2})$ and $(1,0,\frac{1}{2})$ reflections were studied as a function of temperature. The position of the $(0,0,\frac{3}{2})$ reflection closely coincided with a reflection of nuclear origin, and was thus obscured. The powder neutron scattering results were qualitatively similar at these two wave vectors, and the temperature dependence of the neutron scattering from the powder at $(0,0,\frac{1}{2})$ is also displayed in Fig. 3(b). It is clear from Fig. 3(b) that the qualitative behavior of the powder neutron scattering at low temperatures is very similar to the resonant x-ray scattering at $(0,0,\frac{1}{2})$. The powder neutron scattering at $(0,0,\frac{1}{2})$ shows no anomaly near $T_{N1} \sim 11.8$ K, consistent with previous results [9,10].

A systematic search for additional magnetic Bragg scattering along the $(0,0,l)$ direction was carried out, with particular emphasis on the temperatures between 14 and 21 K. The purpose of these scans was to check for possible incommensurate magnetic structures above T_N, as previously suggested [9]. No such scattering was observed in either the resonant magnetic x-ray or powder neutron studies.

The present magnetic x-ray results show evidence for multiple antiferromagnetically ordered phases present in zero applied field. This is a different conclusion than that reached by a previous bulk study [13] in which three phases were only identified in the presence of a sizable ($\sim$ 0.4 T) magnetic field applied within the a-b plane. Our measurements imply that the magnitude of the anomalies in the bulk properties associated with these transitions become unmeasurably small in small applied fields or for fields applied along the c direction. In addition, this Letter demonstrates that magnetic single crystal diffraction measurements can be made on extremely small single crystal grains. These grains form from the melt very quickly at the surface of polycrystalline boules. Large single crystal growth often involves maintaining the constituents at least partially within the melt for long periods of time. Problems in stoichiometry may arise for such large crystals, as one constituent may evaporate preferentially. This is known to occur in several HFS materials: Si in URu_2Si_2, and Al in both UNi_2Al_3 and UPd_2Al_3. Consequently, studies of systems which are sensitive to low concentration of structural imperfections may well require small, high-purity samples of the type studied in this Letter.

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* Present address: Moli Energy (1990) Ltd., Maple Ridge, BC, Canada V2X 9E7.

† Present address: Physics Department, McGill University, Montreal, QC, Canada H3A 2T8.

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