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Magnetic excitations and the search for crystal-field transitions in the heavy-fermion superconductor UPd_2Al_3

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Abstract. We have performed inelastic neutron scattering (INS) experiments to study the spin dynamics and search for crystalline-electric-field (CEF) excitations in the antiferromagnetic heavy-fermion superconductor UPd_2Al_3. The low-energy-transfer spectra are predominantly characterized by a quasielastic Lorentzian (weighted by the detailed balance factor) with a residual line width of approximately 5 meV. For uranium-based intermetallics, this is an unusually small line width and UPd_2Al_3 is one of the rare examples of 5f-electron systems whose residual line width corresponds to the macroscopically estimated Kondo lattice temperature. However, significant deviations from this fit suggest additional inelastic contributions that persist up to $T = 150$ K, i.e. $10T_N$. This additional scattering may be attributed to the presence of CEF excitations or intersite magnetic correlations. A survey of the scattering within the whole accessible momentum–energy space provides further evidence for the existence of these inelastic magnetic intensities. We find a surprisingly good agreement between the excitation energies of our neutron scattering spectra and a CEF-level scheme proposed on the basis of magnetic susceptibility and specific heat measurements.

1. Introduction

UPd_2Al_3 belongs to the class of heavy-fermion superconductors. Among these materials it exhibits the highest transition temperature of $T_c = 2$ K [1] and the largest ordered magnetic moment of $\mu = 0.85\mu_B$ [2] known so far. Below its Néel temperature, $T_N = 14.4$ K, it shows a complex magnetic phase diagram [14]. In zero magnetic field, neutron diffraction revealed a simple antiferromagnetic structure consisting of ferromagnetic sheets within the basal plane, coupled antiferromagnetically along the c-axis [2, 3]. The magnetic ground-state properties—explicitly the magnetic structure, the value of the ordered magnetic moment and the magnetic anisotropy as well as recent results of de Haas–van Alphen measurements [4]—could be reproduced by band-structure calculations [5]. The remarkable agreement between theory and experiment had been obtained employing self-consistent density functional calculations treating all valence states, particularly the 5f states of uranium, as band electrons, i.e. evoking an itinerant-electron picture. On the other hand, macroscopic measurements of the specific heat and the magnetic susceptibility provided experimental evidence for the presence of crystalline-electric-field (CEF) excitations [4]. From these experimental data, an induced-moment system with two low-lying singlets has been proposed. It is well known that the 5f electrons of uranium-based intermetallics, due to their greater radial extent compared to that of rare-earth compounds, usually exhibit a behaviour between that of local moments and that of band-like states. Based on the results

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of heat capacity [6] and muon spin rotation experiments [7] it has been speculated that two different electronic subsystems, namely well localized 5f states responsible for the magnetic properties and delocalized states responsible for the superconducting properties, may coexist in UPd_2Al_3 [8]. One further problem is the valence state of uranium; it is often impossible to distinguish between a U^{3+} and a U^{4+} configuration. This holds true as well for UPd_2Al_3, based on the results of magnetic susceptibility [12] and a polarized neutron diffraction study [9]. Due to the lack of anisotropy of the neutron magnetic form factor, an analysis in terms of CEF wavefunctions could not be performed. Within the dipole approximation, both configurations U^{3+} and U^{4+} were compatible with the data. Evidently, in such a case of an ill defined electronic configuration as regards the valence state, the radial electronic extent, the possible intermultiplet mixing and the spin–orbit coupling, the description usually adopted within a CEF model will fail. In particular, there is up to now only one uranium intermetallic alloy, namely UPd_3, known to show well defined CEF excitations [11]. Note that UPd_3 is not a heavy-fermion system and has a rather special band structure. Bearing in mind the experimental evidence of well localized magnetic moments in UPd_2Al_3, possibly due to a separation into different electronic subsystems [6, 7, 8], we have performed an INS study on polycrystalline material to investigate the magnetic excitation spectrum and to search for CEF excitations in UPd_2Al_3.

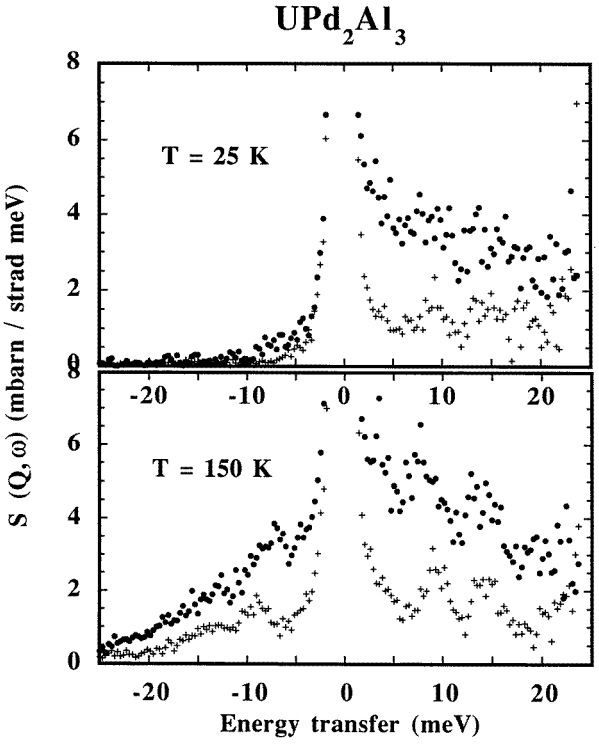

Figure 1. Uncorrected TOF spectra of UPd_2Al_3 (●) and $ThPd_2Al_3$ (+) converted to an energy-transfer scale. Upper frame: results at $T = 25$ K; lower frame: results at $T = 150$ K.

2. Experimental details

The experiments were performed on the time-of-flight (TOF) spectrometer HET at ISIS. A carefully powdered high-quality polycrystalline sample of UPd_2Al_3 of approximately 25 g was mounted in a thin-walled aluminium container and cooled in a closed-cycle refrigerator. Additionally, measurements were made for the isostructural, but nonmagnetic reference compound $ThPd_2Al_3$ to account for the phonon part of the scattering and for a vanadium standard to correct for detector efficiency. The susceptibility and specific heat data of [12] indicated the first excited CEF state 2.8 meV above the ground state and an overall CEF splitting of 50 meV. Therefore by varying the frequency and phases of the choppers, a neutron beam with thermal energy of either $E_i = 25$ meV or $E_i = 50$ meV was chosen, respectively. The detectors of HET covered an angular range from 4° to 29°. Due to the low intensities, the spectra were summed over all detectors. Because of the low incident energies, only small momentum transfers $\boldsymbol{Q}$ were accessible. Compared with recent polarized neutron scattering experiments [9], the neutron magnetic form factor was for all $\boldsymbol{Q}$-values well above 0.9. Hence, the summation of the detectors should not be critical. In any INS experiment employing the TOF technique and polycrystalline material, the crucial point for obtaining the magnetic excitation spectra is the proper correction of the phonon part of the scattering. To illustrate the difficulties arising in the present case, figure 1 shows the raw data of the TOF spectra (converted to an energy-transfer scale) for UPd_2Al_3 and $ThPd_2Al_3$ at $T = 25$ K and $T = 150$ K. Here, the incident-neutron energy was 25 meV and the corresponding instrumental resolution was 0.75 meV. As is evident, at $T = 25$ K (figure 1, upper part) $ThPd_2Al_3$ exhibits (at least) two well defined phonons at energy transfers of approximately $\hbar\omega$ = 9 meV and $\hbar\omega$ = 14 meV, respectively. It should be noted that the remaining phononic intensity at high energy transfers on the neutron energy-loss side is a clear indication for multiple scattering. To a first approximation, the multiple scattering should be uniformly distributed over the $\boldsymbol{Q}$, ω-space and equal in strength for both UPd_2Al_3 and $ThPd_2Al_3$, respectively. Three different techniques have been used to achieve accurate subtractions of the single-phonon and multiphonon contributions to the scattering: first the subtraction from the nonmagnetic reference compound $ThPd_2Al_3$ within the so-called mean-scattering-length approximation; secondly using the nonmagnetic sample for calculating a ratio of the scattering in the high-angle bank to that with the forward-scattering bank, and using that ratio to scale for the magnetic scattering between the high-angle and forward-scattering banks (Murani–Osborn method); and finally use of the DISCUS Monte Carlo simulation program. All three techniques were mutually consistent.

The magnetic spectra of UPd_2Al_3 are predominantly characterized by a broad quasielastic contribution. However, they cannot be described satisfactorily by a single Lorentzian. The magnetic signal of UPd_2Al_3 at $T = 25$ K with an incident-neutron energy of $E_i = 50$ meV is plotted in figure 2. The best fit was achieved by fitting two Lorentzians convoluted with the instrumental resolution and weighted by the detailed balance factor. The second peak indicates a damped (FWHM = 8.8 meV) excitation at $\hbar\omega = 23.4$ meV. The magnetic spectra of UPd_2Al_3 collected with an incident-neutron energy of $E_i = 25$ meV are shown in figure 3. Well defined inelastic intensities develop at $T = 150$ K which, however, do not coincide in full detail with the phonon spectrum of $ThPd_2Al_3$. To be specific, peaks develop at 3 meV, 7 meV and 14 meV. The former two are not accounted for by the phonon spectrum of the isostructural thorium compound. This shift is definitely beyond what is expected on the basis of the differences concerning mass or scattering length ($m = 531.77$ au, $b = 30.584$ fm for UPd_2Al_3 and $m = 525.78$ au, $b = 32.007$ fm for $ThPd_2Al_3$ respectively). As can be seen from figure 3, the statistics of the data is

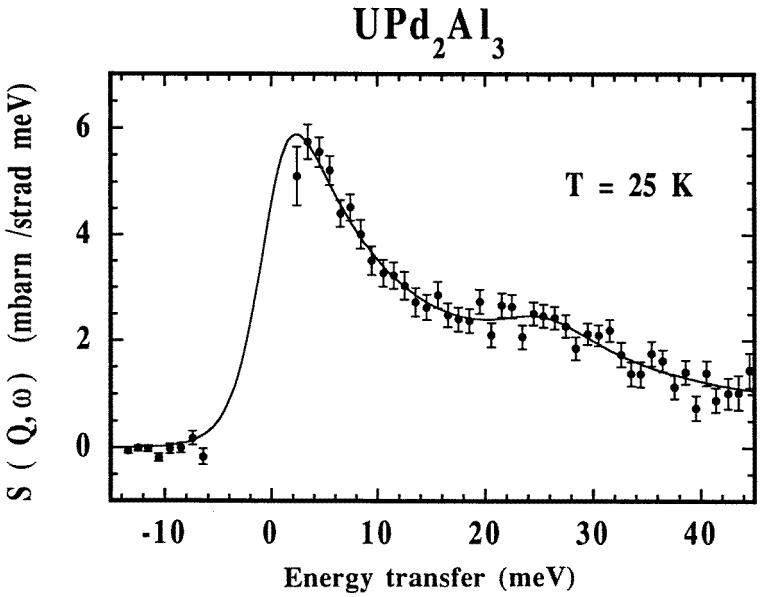

Figure 2. The magnetic excitation spectrum of UPd_2Al_3 at $T = 25$ K with an incident-neutron energy of $E_i = 50$ meV. The full line is a fit to the data with two Lorentzians convoluted with the instrumental resolution and weighted for the detailed balance factor; see the text.

rather poor and the assignment of the inelastic excitations has to be treated with caution. At $T = 150$ K, an excitation at $\hbar\omega = 7$ meV is clearly visible on both energy sides. An excitation at $\hbar\omega = 14$ meV is much less evident in the data. However, a significant increase of the inelastic intensity at $\hbar\omega = 12$ meV is visible on the neutron energy-loss side. Due to the detailed balance factor, this would be hard to see on the energy-gain side. Anyway, in this energy region, the data points clearly lie above the quasielastic Lorentzian. Furthermore, a hint of an excitation at around 3 meV is seen on the energy-loss side. By contrast, at $T = 150$ K and $\hbar\omega = 3$ meV, detailed balance dictates a corresponding peak at -3 meV almost equal in strength. This is not found, and this may be ascribed to either the phonon correction procedure or some spurious effect. But this may also lead to a suppression of some weak intensity on the energy-gain side. Hence, we assume the deviations of the Lorentzian line shape being originated by the inelastic transitions described above. If these extra intensities are of magnetic origin, the transitions must originate from excited states, or must be heavily overdamped with decreasing temperature. Otherwise, these excitations are expected to be much stronger at $T = 25$ K. First of all, we wanted to analyse the quasielastic line, naively assuming a simple Lorentzian response, only. But in a second step we tried to get insight into the inelastic intensities, which are likely to be of magnetic origin. The results with the two Lorentzians used to fit the 50 meV data are shown as solid line in figure 3. For this fit the position and half-width of the peak at 23.4 meV have been fixed, but the intensity was allowed to vary. The corresponding quasielastic line width is 4.9 meV at $T = 25$ K and 11.4 meV at $T = 150$ K. The low-temperature line width is in accord with an estimated Kondo lattice temperature of $T^* = 40$–70 K. On the other hand, this value of the relaxation rate is surprisingly small compared to those of other uranium-based intermetallics [10]. Spatially more extended 5f electrons should result in a stronger hybridization, which in turn gives rise to an increase of magnetic fluctuations and therefore

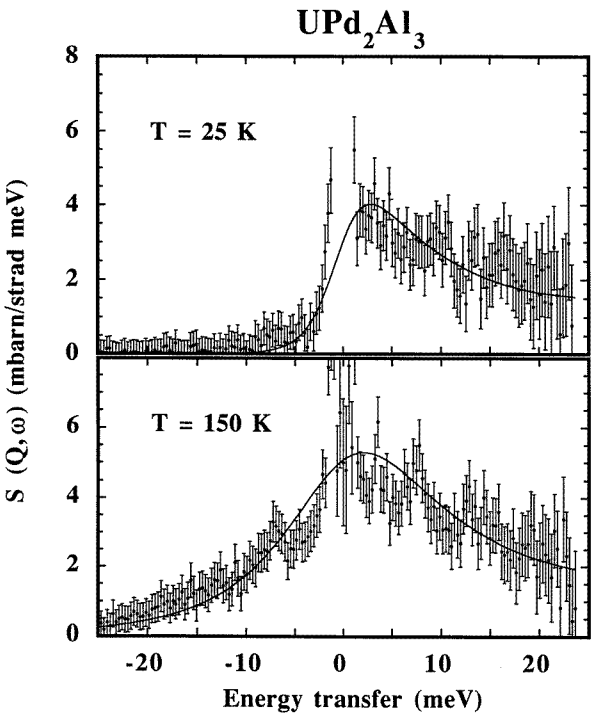

Figure 3. Corrected spectra of UPd_2Al_3 with an incident-neutron energy of $E_i = 25$ meV showing the magnetic intensity at $T = 25$ K and $T = 150$ K, respectively. The data are fitted by two Lorentzians, convoluted with the instrumental resolution and weighted by the detailed balance factor (full line).

to a line broadening in energy. However, at present it is still an open question whether or not the quasielastic line width in uranium compounds can be taken as a direct measure of the hybridization strength and correspondingly of the Kondo temperature. Figure 3 reveals that the fit using a quasielastic Lorentzian and a Lorentzian at $\hbar\omega = 23.4$ meV (weighted by the detailed balance factor) is not satisfactory. The data rather suggest that some additional inelastic intensities are superimposed on a dominant quasielastic contribution. Despite the poor statistics, inelastic transitions may be seen at energy transfers of $\hbar\omega = 3$ meV, 7 meV and around 14 meV. The additional intensities may be ascribed to either intersite correlations or to CEF excitations. Taking into account that the intensities persist up to $T = 150$ K, i.e. $10T_N$, the explanation in terms of CEF excitations seems to be more likely. Comparing these transition energies of our neutron scattering study with the result of the CEF analysis of the magnetic susceptibility and specific heat of UPd_2Al_3 (2.8, 9.4, 14.4, 25 and 48.6 meV [12]), we find surprising coincidence for all four levels accessible with the incident-neutron energies used in the present experiment. As can be seen in figure 3, the peak-like intensities are more pronounced at $T = 150$ K than at $T = 25$ K. This temperature dependence then leads to the conclusion that the transitions as seen in our neutron scattering spectra cannot be due to excitations out of the ground state but rather stem from excited levels. Due to the poor statistics, a detailed analysis of the Q-dependence of the scattering was not possible. However, by binning the detectors into three or four groups, it can be seen that the inelastic intensities are almost vanishing with increasing momentum transfer (not shown). This

supports our conclusion that the inelastic intensities are of magnetic origin. No dispersion could be observed. On the other hand, a significant enhancement in intensity is observed for the lowest excitation as the scattering angle is increased to a corresponding momentum transfer of about 1 Å^{-1}, as shown in figure 4. This additional contribution to the scattering has been described by a Lorentzian at 2.24 meV with a width of FWHM = 0.751 meV. This effect is clearly visible on the contour plot of the region $S(\boldsymbol{Q}, \omega)$ accessed with the instrument in this configuration (figure 5, left-hand side). A well pronounced peak in the scattering centred at 0.9 Å^{-1} and 2 meV is apparent. These values are consistent with antiferromagnetic spin fluctuations occurring above the ordering temperature of T_N = 14.4 K. When the temperature was raised to 150 K (figure 5, right-hand side), there was no evidence of the sharp peak that we have attributed to spin fluctuations.

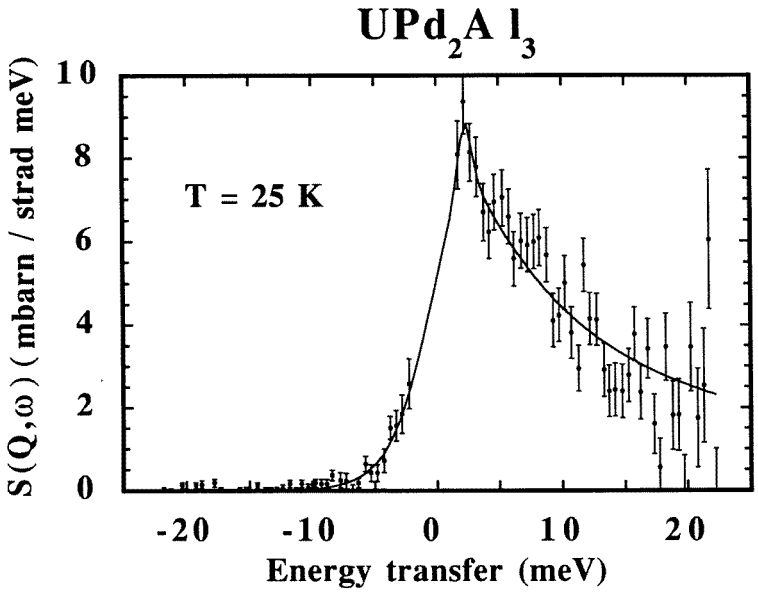

Figure 4. The magnetic excitation spectrum of UPd_2Al_3 at $Q = 0.9$ Å^{-1} for $T = 25$ K. The additional magnetic intensity at $\hbar\omega = 2$ meV can be attributed consistently to antiferromagnetic spin fluctuations above the ordering temperature.

3. Discussion and conclusions

We have investigated the relaxational behaviour and the magnetic excitation spectrum of the heavy-fermion superconductor UPd_2Al_3 by means of INS. The data cannot be interpreted in a unique fashion, because it is impossible to extract the magnetic part of the scattering unambiguously and to discriminate between on-site and intersite magnetic interactions. A fit with a quasielastic Lorentzian yields a line width of less than 5 meV at $T = 25$ K, i.e. a factor of at least two smaller than what is usually found in uranium-based intermetallics [17]. The residual quasielastic line width for $T \rightarrow 0$ K will be even smaller, although it cannot be observed directly due to the onset of magnetic order. But the data suggest some inelastic intensities on top of the major quasielastic contribution. These additional intensities may be

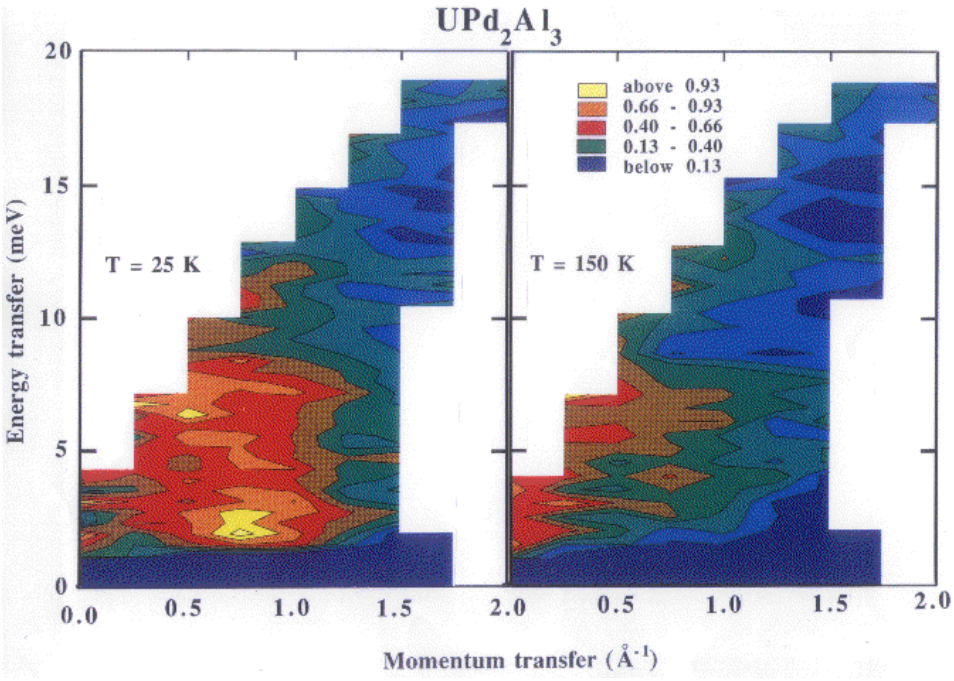

Figure 5. A survey of the magnetic intensity of UPd_2Al_3 over the whole accessible $\boldsymbol{Q}$, ω-space. An excitation at around $\hbar\omega = 2$ meV is visible at $T = 25$ K (left-hand side), confirming the Q-averaged spectrum. At $T = 150$ K (right-hand side), no similar peak can be observed, giving further support for the occurrence of antiferromagnetic spin fluctuations above the magnetic ordering temperature of $T_N = 14.4$ K.

ascribed to either CEF excitations or magnetic correlations. Bearing in mind the rather poor quality of the data, the corresponding transition energies are in amazingly good agreement with the results of a CEF analysis of the magnetic susceptibility and the specific heat. At the moment it is rather unclear how well defined CEF levels can coexist with a broad quasielastic Lorentzian line. We are aware that the extra inelastic intensities may be of a phononic origin that was not taken into account in subtracting the reference compound, or may be due to a coupling of phonons and magnetic excitations. However, we also want to point out that a CEF-level scheme with similar excitation energies has been proposed on the basis of magnetic susceptibility and specific heat data [12], and recent experiments [6, 7] point towards the existence of two independent electronic subsystems of 5f character. One was identified with the almost itinerant (strongly hybridized) heavy quasiparticles that are responsible for the superconductivity. In the present neutron scattering experiment, this component is represented by the Lorentzian quasielastic line with a characteristic width of 50 K, corresponding to the Kondo lattice temperature as estimated from bulk measurements. The other electronic subsystem represents the more localized 5f electrons and is responsible for the antiferromagnetic order. In these neutron scattering experiments the local 5f electrons give rise to the inelastic contributions. Antiferromagnetic spin fluctuations above the ordering temperature give rise to an enhanced intensity peaked at $Q = 0.9$ Å^{-1} and $\hbar\omega = 2$ meV. Low-energy excitations at around 1 Å^{-1} are in accord with the results of the INS study by Petersen *et al* [13] investigating the spin-wave properties of single-crystalline UPd_2Al_3 in the magnetically ordered state. Remarkably, they found a spin-wave

dispersion relation displaying no anisotropy gap. These excitations had not been referred to the in-plane or out-of-plane mode, respectively. Since one has to assume a magnetically multidomain crystal, the measured inelastic intensities would correspond to a mixture of the two modes. If the major part of the spectral weight were to correspond to the in-plane spin-wave mode, then no information concerning the out-of-plane anisotropy could be obtained on the basis of these measurements alone. The published data [13] do not seem to allow an extraction of intensities corresponding to the two different spin-wave modes. Anyway, the absence of a spin-wave gap implies some severe restrictions on the on-site anisotropy and, in consequence, on the possible CEF-level schemes. The level scheme proposed by Böhm *et al* [12] implies a negligible in-plane anisotropy, but the susceptibility data reveal that $\chi \perp c$ is enhanced by a factor of five compared to $\chi \| c$. A very small in-plane, but a large out-of-plane anisotropy had been established as well by high-field magnetization [15] and field-dependent neutron diffraction experiments [14]. We want to stress that the two main features of our present results, namely a small quasielastic line width and a low-energy excitation at around 1 Å^{-1}, are in agreement with the INS study by Petersen *et al* [13] performed for the magnetically ordered state. By contrast, the bulk measurements [12] as well as our INS study refer to the *paramagnetic* state. Due to the onset of magnetic order, the internal magnetic field will change the CEF-level scheme considerably. Based on the occurrence of the metamagnetic transition [15] an internal field of at least 20 T can be estimated. Unfortunately, up to now, there do not exist calculations of the CEF-level scheme within the magnetically ordered state. At this point it is interesting to note that similar observations, namely inelastic features on top of a broad quasielastic response, have been reported for the two intermediate-valence compounds $YbCu_2Si_2$ [16] and YbCuAl [17]. In the former compound an interpretation in terms of CEF transitions has been provided; in the latter, CEF transitions were explicitly excluded. Finally, we want to discuss the quasielastic line which is the dominant feature in UPd_2Al_3. The small residual line width is especially remarkable. Usually it is interpreted as a measure of the Kondo lattice temperature or the low-energy scale of the on-site interactions. This holds true for the electronically well localized rare-earth intermetallics, while for 5f systems an increasing amount of experimental evidence is contradicting this interpretation [3]. The results of neutron scattering studies of uranium-based heavy-fermion compounds in general give residual quasielastic line widths of more than 10 meV, thus pointing towards an almost intermediate-valence behaviour. On the other hand, macroscopic measurements usually estimate a Kondo lattice temperature of 30–80 K, i.e. the energy scale of the quasiparticle dynamics. A recent INS study of $UCu_{4+x}Al_{8-x}$ [3] drastically demonstrates the discrepancies between the Kondo lattice temperature and residual quasielastic line width in 5f heavy-fermion compounds. Therefore, the broad quasielastic line widths in 5f heavy-electron systems cannot be identified with a unique low-energy scale governing the quasiparticle dynamics within the single-channel Kondo model. In fact, there are some examples of uranium-based heavy-fermion compounds displaying non-Fermi-liquid behaviour and involving possibly a multichannel Kondo effect ($U(Pd, Cu)_5$ and $(Y, U)Pd_3$ [18, 19, 20]). UPd_2Al_3 is a rare example of a uranium-based heavy-fermion system, where the residual quasielastic line width is consistent with the estimated Kondo temperature of $T^* = 40$–70 K, based on the results of macroscopic measurements.

Acknowledgments

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