Crystal field in metallic actinide compounds

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Abstract. Experimental evidence is presented for localized crystal-field states in metallic actinide compounds. By means of neutron inelastic scattering crystal-field transitions in UPd_4 and UAs are observed at 5.1 ± 0.4 meV and 6.4 ± 0.5 meV, respectively.

1. Introduction

The nature of the 5f electrons is of considerable interest for an understanding of actinide systems. The actinide 5f electrons are generally less localized than the 4f electrons of the rare earths but less itinerant than the transition metal 3d electrons. Information about the spatial extent of the 5f electrons may be obtained from the magnetic form factor by means of neutron diffraction. Information about the energy localization of the 5f electrons may result from measurements of the crystal-field levels by spectroscopic methods. In particular, the thermal neutron scattering technique has proven to be a useful tool in the exploration of crystal-field splittings in rare earth metallic compounds. Because of the spatially extended nature of the 5f electrons, however, the crystal-field energies in the actinides are expected to be about an order of magnitude larger than in the corresponding lanthanides and do not satisfactorily match the energy of thermal neutrons. As a consequence neutron spectroscopy gave no evidence for well defined crystal-field transitions in any actinide compound so far [1]: the magnetic scattering in the experiments performed to date is either absent or spread over a wide range of energy transfer.

We present in this paper the first direct measurements of crystal-field transitions in metallic actinide compounds. By means of neutron inelastic scattering we studied the systems UPd_4 and UAs, for which low-energy crystal-field transitions may be expected. UPd_4 crystallizes in the cubic $AuCu_3$ structure. Below 30 K it has antiferromagnetic ordering of $(\pi\pi 0)$ type [2]. Zero-field magnetization [3] and susceptibility data [2] suggest that the U ions have the $5f^2$ configuration with the Γ_5 triplet. the Γ_4 triplet, and the Γ_1 singlet at around 6 meV, 80 meV, and 200 meV above the Γ_3 doublet ground state, respectively. UAs has the NaCl-type structure and orders

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antiferromagnetically at 127 K with type I structure [4]. Neutron diffraction results [5] indicated that the magnetic structure changes from type I to type Ia at 64 K. The analysis of magnetic susceptibility measurements [6] shows that the U ions adopt the $5f^3$ electronic configuration with the Γ_6 doublet and the $\Gamma_8^{(2)}$ quartet at around 6 meV and 220 meV above the $\Gamma_8^{(1)}$ quartet ground state, respectively.

2. Experimental

The samples have been prepared by melting the stoichiometric compositions in an argon arc furnace. A final analysis by X-ray and neutron diffraction did not
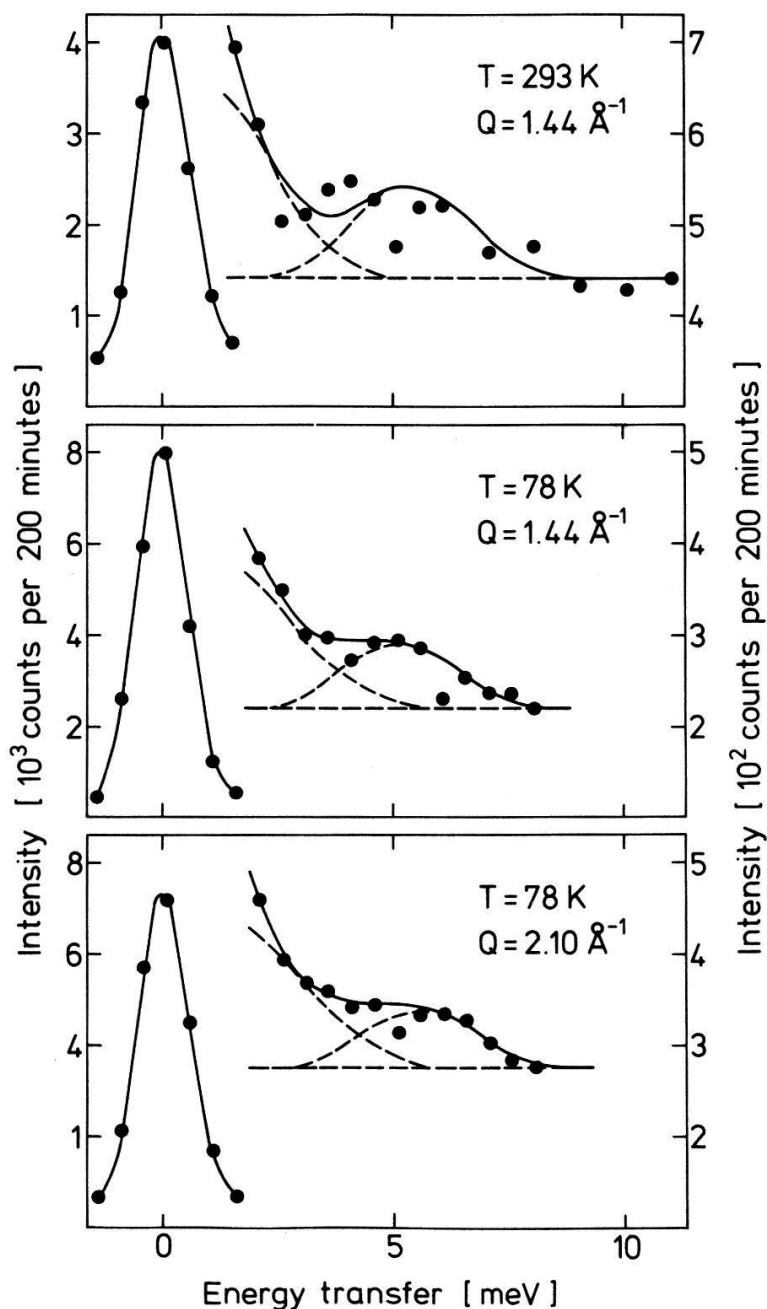

Figure 1
Energy spectra of neutrons scattered from polycrystalline UPd_4. The full and broken curves are the result of the least-squares fitting procedure as described in the text. The scales at the left and at the right hand side refer to the elastic and inelastic part of the spectra, respectively.

indicate any parasitic phases. The polycrystalline samples were sealed in cylindrical aluminium containers of 10 mm diameter and 40 mm length.

The neutron inelastic scattering experiments were performed on a triple-axis spectrometer at the reactor Diorit, Würenlingen, in the neutron energy gain configuration with the monochromator energy kept fixed at 14.96 meV. A pyrolytic graphite filter was used to reduce higher-order contamination. The experiments were performed at various temperatures and momentum transfers $\hbar Q$ in order to identify undesired phonon scattering. In particular, with increasing scattering vector Q, the phonon intensity increases rapidly with Q^2, whereas the crystal-field intensity decreases slowly according to $f^2(Q)$ where $f(Q)$ is the magnetic form factor. As to the temperature variation of the intensities, the phonons obey Bose statistics, whereas the population of crystal-field levels is governed by Boltzmann statistics.

Energy spectra of neutrons scattered from UPd_4 are shown in Figure 1. The spectra can be qualitatively characterized as follows. There is an intense peak at zero energy transfer due to incoherent elastic scattering. Its full width at half maximum (FWHM) is 1.2 meV corresponding to the instrumental resolution. A second peak arises at zero energy transfer which can be attributed to quasielastic scattering. Since its width is much larger than the resolution width, it can easily be distinguished
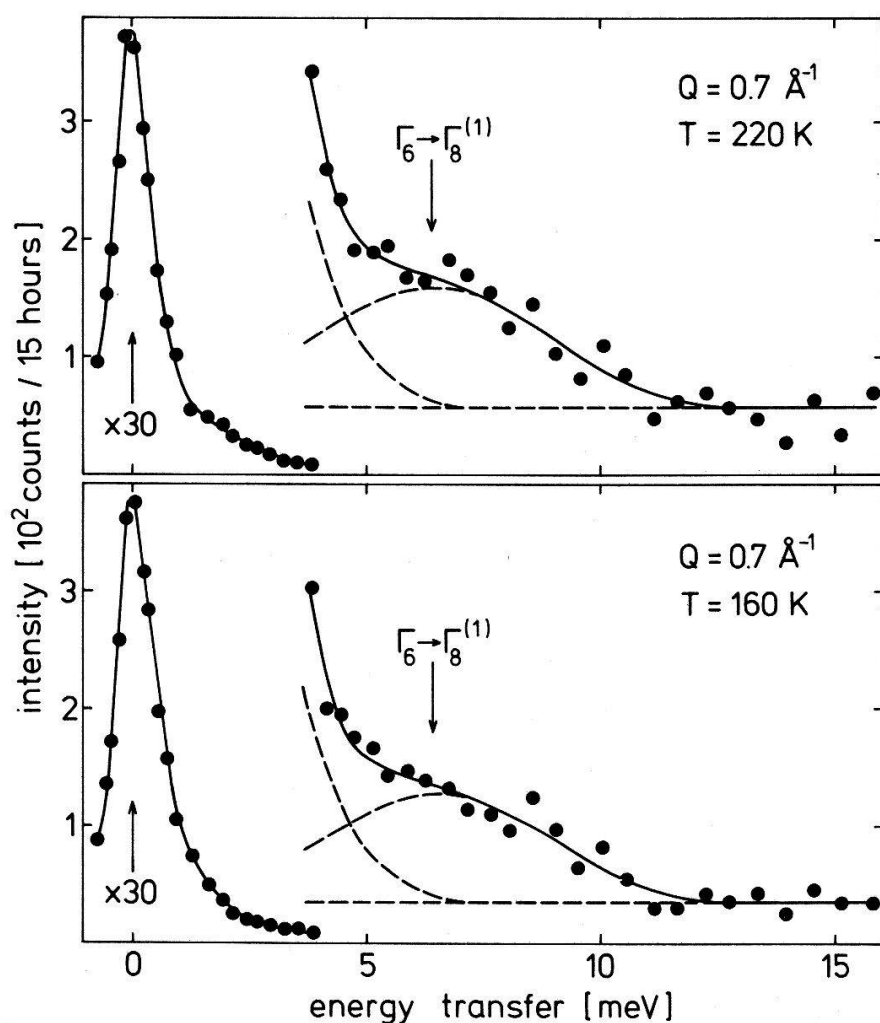

Figure 2

Energy spectra of neutrons scattered from polycrystalline UAs at $Q = 0.7$ Å^{-1}. The curves are the result of the least-squares fitting procedure as described in the text.

from the elastic line. A partly resolved inelastic line arises at an energy transfer of about 5 meV, which can be identified as a crystal-field transition.

For the experiments on UAs the triple-axis spectrometer was operating in the MARC configuration, i.e. with a large analyzer crystal and a position-sensitive detector. Figures 2 and 3 show observed energy spectra which are transformed to a linear energy scale and corrected for analyzer and detector sensitivity. There is again an intense elastic peak (FWHM = 0.8 meV) and a broad quasielastic line. For small momentum transfers the inelastic part of the energy spectra consists of an unresolved shoulder (Fig. 2). With increasing momentum transfer the overall inelastic intensity is increasing, and for $Q > 2.5$ Å^{-1} a resolved line appears at 8 meV (Fig. 3) which is hardly of magnetic origin. Thus phonon contributions will be important in the interpretation of the UAs spectra.
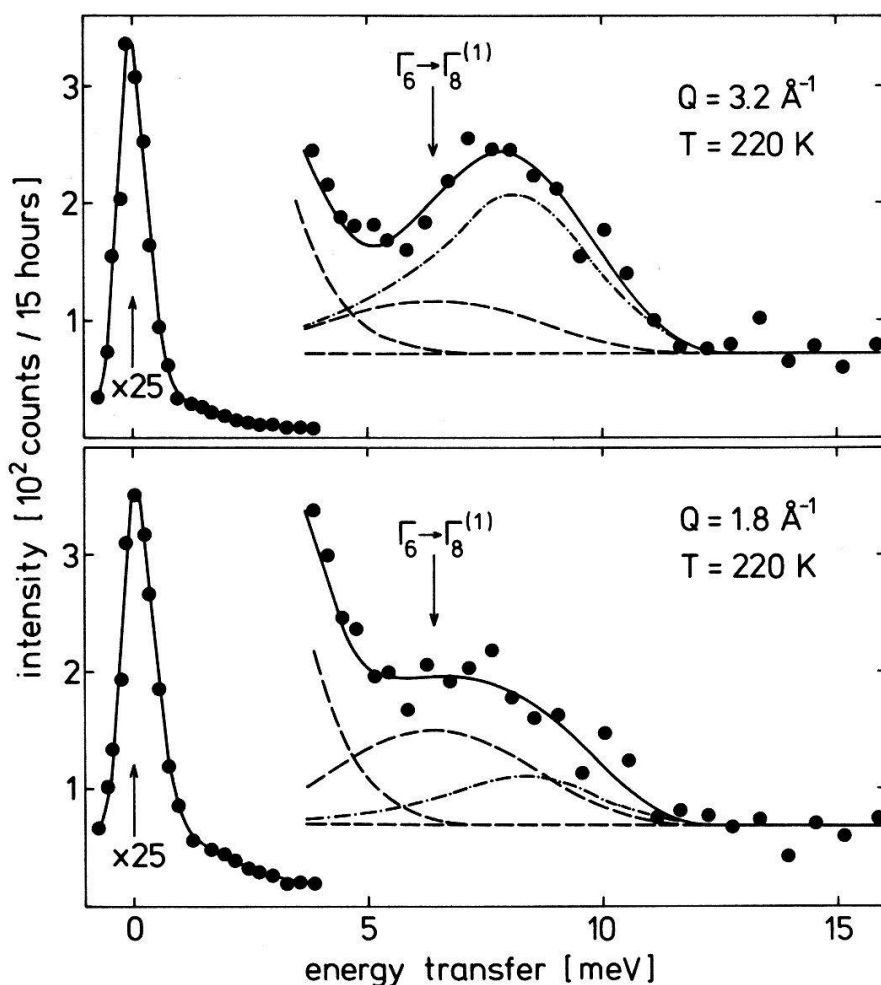

Figure 3

Energy spectra of neutrons scattered from polycrystalline UAs at $T = 220$ K. The curves are the result of the least-squares fitting procedure as described in the text.

3. Analysis of results and discussion

A least-squares fitting procedure has been applied to the observed energy spectra of UPd$_4$ in Figure 1. The background has been assumed to be constant, and the elastic, quasielastic and inelastic lines have been approximated by Gaussians. Account has been taken of both the analyzer reflectivity and correction factors resulting from

the neutron cross-section formula and resolution effects. The results of the least-squares fitting procedure are partly listed in Table I and shown as full curves in Figure 1, whereas the broken curves show the background level and the subdivision into individual peaks. The crystal-field origin of the inelastic line is confirmed by its intensity variation as a function of temperature and momentum transfer as shown in Table I. The form factor of U^{4+} was calculated on the basis of the radial integrals $\langle j_i \rangle$ ($i = 0, 2$) tabulated by Freeman et al. [7]. Thus our experiments on UPd_4 give evidence for localized crystal-field states: the line width of the $\Gamma_5 \to \Gamma_3$ transition is about 3 meV and almost independent of temperature.

Table I

Energies Δ and observed and calculated intensities I of the crystal-field transition line in UPd_4. The intensities are normalized to the value 1.0 for the transition at $T = 78$ K and $Q = 1.44$ Å^{-1}.

T(K)	Q(Å^{-1})	Δ(meV)	I_{obs}	I_{cal}
78	2.10	5.2 ± 0.5	0.8 ± 0.2	0.8
78	1.44	5.0 ± 0.4	1.0 ± 0.2	1.0
293	1.44	5.1 ± 0.6	1.5 ± 0.3	1.4

The energy spectra of UAs for $Q = 0.7$ Å^{-1} (Fig. 2) have been analyzed in a similar way as the UPd_4 data, since for small momentum transfers $\hbar Q$ phonon contributions can be neglected. This is confirmed by the temperature variation of the inelastic intensity which is roughly constant from 160 K to 220 K in agreement with Boltzmann statistics, whereas an increase of 50% is expected from Bose statistics. The results of the least-squares fitting procedure are indicated in Figure 2. The position of the inelastic line is 6.4 ± 0.5 meV. In the analysis of the energy spectra shown in Figure 3 phonon contributions have to be taken into account. The phonon contribution was determined self-consistently assuming that it is Q dependent through the factor Q^2. The crystal-field contribution was determined from the magnetic intensity observed at $Q = 0.7$ Å^{-1} (Fig. 2) assuming that it is Q dependent through the factor $f^2(Q)$. For $f(Q)$ we used the values for U^{3+} as tabulated by Freeman et al. [7]. The results of this fitting procedure are shown as full curves in Figure 3, whereas the phonon contribution is indicated as a dashed-dotted line. The broken curves show the crystal-field intensity and the background level. Thus our experiments demonstrate that for UAs the crystal-field levels are localized: the line-width of the $\Gamma_6 \to \Gamma_8^{(1)}$ transition is approximately 5 meV.

The presence of localized crystal-field states in actinide systems depends to a large extent on the degree of hybridization between the 5f electrons and the 6d-7s conduction electrons, in close analogy to the cerium compounds in the rare-earth series. The analogy, however, is rather complex. The present experiments give evidence for a localized crystal-field transition in UPd_4, whereas in the corresponding compound $CePd_3$ no crystal-field transitions have been observed [8]. On the other hand, a well defined crystal-field splitting has been found in CeSb [9], whereas for USb no magnetic intensity has been detected [10]. Finally, both CeAs [11] and UAs exhibit localized crystal-field transitions. Thus further neutron scattering studies in the energy range up to a few hundred meV are highly desirable for understanding crystal-field effects in metallic actinide compounds.

Acknowledgement

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