CRYSTAL-FIELD SPECTROSCOPY OF UCl_4
BY NEUTRON INELASTIC SCATTERING

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Abstract

The crystal-field level scheme of uranium tetrachloride has been the subject of a number of investigations by both optical and magnetic measurements. Agreement does not exist. To attempt to resolve this problem we have performed experiments with the pulsed neutron source at ANL which allows electronic spectroscopy to be extended to $\sim 2000 \text{ cm}^{-1}$.

Initially using incident energies of 400 cm^{-1} we examined the Γ_4 (ground state) to Γ_5 (excited state) level with the sample at 10K. A very strong line is seen at $92 \pm 1 \text{ cm}^{-1}$ which is clearly the $\Gamma_4 \rightarrow \Gamma_5$ transition. This is in good agreement with a previous neutron study but in disagreement with the 110 to 120 cm^{-1} assignment by other techniques.

On warming to 50K the peak position shifts to lower energy by $\sim 4\%$, broadens, and decreases dramatically in magnitude to $\sim 1/3$ of its value at 10K. Boltzmann statistics would predict a decrease of only 20% on warming from 10 to 50K. We assume from this that a strong coupling occurs between the crystal-field and vibronic states.

We have also used an incident energy of 2000 cm^{-1} to search for the higher Γ_5' state. This was found at $1125 \pm 3 \text{ cm}^{-1}$, in good agreement with previous work. On warming the sample this $\Gamma_4 \rightarrow \Gamma_5'$ transition strength rapidly diminishes. Since the phonon spectrum does not extend beyond $\sim 300 \text{ cm}^{-1}$, this behaviour is most unusual. Because of this strong relaxational process, we have not been able to determine the positions of the other crystal-field levels.

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1. Introduction

A series of optical and magnetic susceptibility measurements have been performed on the tetravalent uranium compound UCl_4 over the last 30 years in order to establish the energy of the crystal-field (cf) levels. Despite these efforts there is little agreement. In the most recent study¹ Gamp et al. analyze the anisotropic magnetic susceptibility from a single crystal and deduce that the Γ_4 (ground state) to Γ_5 excited state is at 109 cm^{-1} with the Γ_1 singlet at 97 cm^{-1} . In a summary of previous studies they point out that assigned values for the excited Γ_5' doublet range from 1113 to 1878 cm^{-1} .

Our interest in UCl_4 stems from work² on dilute U^{4+} doped into $ThBr_4$, which is isostructural with UCl_4 , and the recent discovery of interesting bonding or covalency effects in this material with polarized neutrons.³ The advent of spallation neutron sources⁴ has given us, for the first time, an opportunity to perform neutron crystal-field spectroscopy up to $\sim 2000\text{ cm}^{-1}$ and thus cover the complete ground-state manifold in UCl_4 .

2. Experimental method

The experiments were performed on the high-resolution medium-energy chopper spectrometer (FRMECS) at the Intense Pulsed Neutron Source at Argonne. See Ref. 4 for details. Briefly, a monochromatic neutron beam is incident on the sample and the time-of-flight and angle of the scattered neutrons are measured. From these quantities t , and ϕ , respectively, and knowing the incident neutron energy we can determine the energy and momentum transfer, E and Q , of the scattering process. Since the magnetic moment of the neutron couples to the magnetic dipoles of the $5f$ electron we may determine transition energies between crystal-field (cf) levels provided that magnetic dipole matrix elements exist.⁵ The neutron also has an interaction with the nucleus so is sensitive to lattice vibrations. However, lattice vibrations as seen by neutrons increase

with momentum transfer Q (approximately as Q^2), whereas the magnetic interaction decreases with Q so that for $Q > 6 \text{ \AA}^{-1}$ the magnetic dipole transitions cannot be seen. This provides a method of separating the two contributions if coupling between them is weak. Multiphonon effects are also seen at higher Q values, but seldom give sharp peaks.

The experiment was performed on a ~ 150 g sample of polycrystalline UCl_4 prepared at Orsay. The material, which is very hygroscopic, was encapsulated in a Al container of dimensions $100 \times 75 \times 7 \text{ mm}^3$. The direction of the neutron beam was perpendicular to the thin dimension of the flat plate holder. The holder was then fixed to the cold plate of a variable temperature DISPLEX refrigerator.

3. Results

The initial experiments were performed at 10 K with an incident neutron energy of 50 meV (403 cm^{-1}). The result of scattering at one angle, $\phi = 11.4^\circ$, is shown in Fig. 1. A very strong peak is observed at $92 \pm 1 \text{ cm}^{-1}$ and a much smaller peak at $\sim 180 \text{ cm}^{-1}$. Examination of the ϕ -dependence of the latter peak shows that it arises from vibrational effects. Based on the matrix elements from the Γ_4 ground state $\langle \Gamma_4 || \Gamma_5 \rangle^2 = 42.5$, $\langle \Gamma_4 || \Gamma_3 \rangle^2 = 4$, and $\langle \Gamma_4 || \Gamma'_5 \rangle^2 = 21.5$, all others from the Γ_4 being zero, we unambiguously identify the 92 cm^{-1} transition as the $\Gamma_4 \rightarrow \Gamma_5$.

This result has been obtained before by Murasik et al.⁶ They correctly reported the Γ_5 excited state at $\sim 90 \text{ cm}^{-1}$, but incorrectly suggested that the 180 cm^{-1} line was also magnetic in origin.

The detailed study of the $\Gamma_4 \rightarrow \Gamma_5$ transition as a function of temperature is shown in Fig. 2 at one angle corresponding $\phi = 10^\circ$, for 92 cm^{-1} , $Q = 1.0 \text{ \AA}^{-1}$. Measurements at other Q values confirm the results of Fig. 2.

The incident neutron energy was then changed to 250 meV (2016 cm^{-1}). The result of a run at 10 K was that a single peak at $1125 \pm 3 \text{ cm}^{-1}$ was found and this is shown in Fig. 3. The instrumental resolution is essentially a function of the incident energy so gives a peak width of $\sim 50 \text{ cm}^{-1}$ at this higher incident energy, as opposed to $\sim 10 \text{ cm}^{-1}$ at the lower. Peak positions can, of course, be determined to much better than this. This transition is therefore the $\Gamma_4 \rightarrow \Gamma_5'$, and is in surprisingly good agreement with the prediction of 1113 cm^{-1} of Ref. 1. At 160 K the $\Gamma_4 \rightarrow \Gamma_5'$ line cannot be observed.

4. Discussion

The temperature dependence of both the Γ_4 - Γ_5 transitions is unusual. Crystal-field levels are populated by Boltzmann statistics, so that using a level scheme similar to that of Ref. 1, we can calculate the level populations. We find that at 50 K the $\Gamma_4 \rightarrow \Gamma_5$ transition should decrease to $\sim 80\%$ of its strength at 10 K. Instead Fig. 2 shows that it has only $\sim 30\%$ of its strength left, has broadened, and softened in energy. Although it has not disappeared by 160 K (expected decrease should be to $\sim 40\%$ of its 10 K value), the most striking feature is that the frequency now appears at about 75 cm^{-1} , a drop of almost 20%. These results suggest a very strong coupling between the vibrational and electronic states. It is, however, unusual to find the higher Γ_5' level also decreasing rapidly with temperature, because the phonon spectrum in this material does not extend beyond $\sim 300 \text{ cm}^{-1}$. A detailed study of the phonons and coupling to the 92 cm^{-1} line will be undertaken shortly. New calculations of the susceptibility will be presumably have to await a more detailed theory of this coupling, although it is clear that calculations based on $\Gamma_4 \rightarrow \Gamma_5$ as 109 cm^{-1} (Ref. 1) are incorrect.

The neutron experiments clearly provide the most direct measurement of the cf levels. This is commonly accepted for metallic materials but appears to

also be true for ionic systems such as UCl_4 . By using high-energy neutrons we have been able to identify both Γ_5 levels unambiguously. Relaxational processes at higher temperatures prevent the observation of transitions from the populated Γ_5 state to other states, so that the whole crystal-field manifold cannot be determined.

References

1. E. Gamp, N. Edelstein, C. Khan Malek, S. Hubert, and M. Genet, J. Chem. Phys. 79, 2023 (1983).
2. P. Delamoye, J.C. Krupa, J.G. Conway, and N. Edelstein, Phys. Rev. B28, 4913 (1983); ibid B28, 4923 (1983) and references therein.
3. G.H. Lander, P.J. Brown, M.R. Spirlet, J. Rebizant, B. Kanellakopulos, and R. Klenze; see paper in this proceedings.
4. J.M. Carpenter, G.H. Lander, and C.G. Windsor, Rev. Sci. Instrum. 55, 1019 (1984); C.K. Loong, J. Appl. Physics 57, 3772 (1985).
5. The calculation of these within the $^3\text{H}_4$ manifold is straight forward. See, for example, "Theory of thermal neutron scattering", W. Marshall and S.W. Lovesey, Oxford University Press, Oxford, 1971, p. 169.
6. A. Murasik, J. Leciejewicz, and Z. Zolnierrek, Phys. Stat. Solidi 80b, K 137 (1977); A. Murasik in "Crystalline Electric Fields and Structural Effects in f-electron Systems", eds. J.E. Crow, R.P. Guertin and T. Mihalisin, Plenum Press, N.Y. (1980), p. 229.

Figure captions

Fig. 1 Scan of neutron energy loss spectrum (incident energy 50 meV) at $T = 10$ K of UCl_4 . The peak at 92 cm^{-1} arises from the $\Gamma_4 \rightarrow \Gamma_5$ transition, that at $\sim 180 \text{ cm}^{-1}$ from vibrational effects. The momentum transfer is $1 \text{ \AA}^{-1}$ at 92 cm^{-1} , $\phi = 11^\circ$. The vertical arrow marks the level position estimated in Ref. 1. The solid line is a fit to the one electronic transition.

Fig. 2 Scans of the inelastic peak from UCl_4 showing the temperature dependence of the $\Gamma_4 \rightarrow \Gamma_5$ transitions. Note that the vertical scale changes between 50 and 27 K. All scans are at $\phi = 10^\circ$. The rise in the intensity at low energy as a function of T is because of increases phonon scattering. The solid lines are Gaussian fits to the data.

Fig. 3 Scan of neutron energy loss spectrum (incident energy 250 meV) at $T = 10$ K. The peak is the $\Gamma_4 \rightarrow \Gamma_5'$ transition. The solid line is a Gaussian fit to the data points, the vertical arrow is the energy estimate of Ref. 1. The momentum transfer at $\phi = 10^\circ$ is $4.7 \text{ \AA}^{-1}$ for an energy transfer of 140 meV.

Fig 1

Fig. 2

Fig 3

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