High-energy-neutron spectroscopy of crystal-field excitations in NpO_2

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Neutron spectroscopy has been applied to study the crystal-field potential in NpO_2. The inelastic-scattering cross section shows a broad magnetic peak that is split into two components and is centered at about 55 meV. A quasielastic magnetic signal extending up to about 30 meV is also observed at temperatures below the phase transition at 25 K. The origin of the inelastic peak is attributed to excitations between the $\Gamma_8^{(2)}$ and $\Gamma_8^{(1)}$ crystal-field quartets. A mechanism that could be responsible for the observed splitting is proposed.

In this paper, we present a study of the crystal-field (CF) excitations in neptunium dioxide. According to bulk property measurements such as specific heat and magnetic susceptibility, this compound exhibits a phase transition at $T_c=25$ K.[1] However, the origin of this transition remains unexplained since microscopic measurements such as Mössbauer spectroscopy[2] and neutron diffraction[3] have failed to find any evidence of either magnetic ordering or lattice distortion. A determination of the crystal-field potential is therefore necessary to give an insight into the nature of the paramagnetic ground state and the possible mechanisms that are responsible for the phase transition.[4] An earlier attempt to observe the CF excitations in NpO_2 by neutron scattering[5] was inconclusive because of the scale of multiple-phonon scattering. We have now repeated the experiment using a much smaller sample; this reduces both the nuclear-scattering background and self-heating problems generated by ^{237}Np α activity.

NpO_2 has the CaF_2 type structure with a lattice parameter $a_0=5.431$ Å at room temperature. The free Np^{4+} ion has a $5f^3$ configuration and a $^4I_{9/2}$ ground state in the Russell-Saunders (RS) coupling scheme. The tenfold degeneracy of this lowest manifold is lifted by the cubic CF potential into a $|\Gamma_6\rangle$ doublet and two quartets, $|\Gamma_8^{(2)}\rangle$ and $|\Gamma_8^{(1)}\rangle$.

Dipolar transitions between crystal-field levels give rise to peaks in the neutron spectra, whose energies and intensities provide information on the eigenvalues and eigenfunctions of the CF Hamiltonian.[6] The momentum transfer or Q dependence of the cross section is dominated by the square of the magnetic form factor $f^2(Q)$, which is a rapidly decreasing function of Q. This allows an easy distinction between magnetic and vibrational contributions, since the latter increases in intensity with Q. The present experiment was performed using the direct-geometry chopper spectrometer HET at the ISIS spallation neutron source, Rutherford Appleton Laboratory, U.K. Scattered neutrons are detected by three arrays of ^3He detectors, covering scattering angles from $\phi=3°$ to 136°. Normalization of the spectra recorded at different angles was obtained by measurements on a vanadium standard. Incident energies of 120, 180, 600, and 1100 meV were used to study the scattering at different

sample temperatures ranging from 5 to 50 K. The experiment was complicated by the presence of strong absorption resonances in Np at about 500 meV and above 1300 meV, which prevented us from using an incident energy higher than ~1200 meV and caused a forbidden window between about 400 and 600 meV. Consequently, magnetic excitations could only be observed up to a maximum energy transfer of $\hbar\omega = 350$ meV.

The sample consisted of 32 g of NpO_2 powder doubly encapsulated in a special Al holder. It was prepared at the Centre d'Etudes Nucléaires de Cadarache by firing Np metal in oxygen atmosphere. A sample of the isostructural nonmagnetic compound ThO_2, encapsulated in an identical container, was also measured in order to perform a detailed subtraction of the phonon contributions. The neutron-inelastic-scattering cross section for ThO_2 is expected to be very similar to the vibronic component in the NpO_2 spectra.

The neutron-scattering spectra $S(\phi,\omega)$ from NpO_2 and ThO_2 measured at an angle $\phi = 136°$ and $T = 5$ K, with an incident energy of 180 meV, are shown in Fig. 1(a). It is seen that the two spectra are nearly identical. At this angle Q varies between about 14 and 17 $Å^{-1}$ across the spectrum, and $f^2(Q)$ for the Np^{4+} ions is of the order of 10^{-7}. Figure 1(b) shows the neutron spectra obtained for NpO_2 and ThO_2 with $E_i = 180$ meV at an average angle of 5° ($1 < Q < 3$ $Å^{-1}$) and $T = 5$ K. No sharp excitations

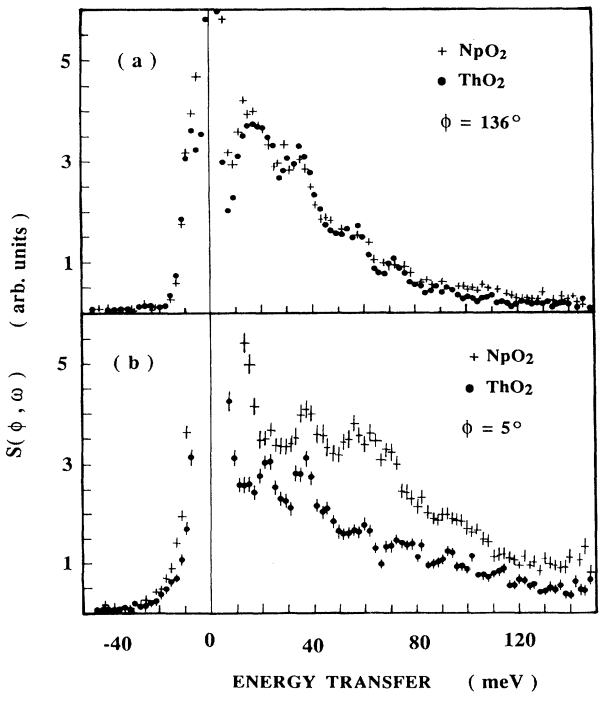

FIG. 1. Inelastic-neutron-scattering cross section of NpO_2 (+) and ThO_2 (●) measured at $T = 5$ K with an incident energy of 180 meV. (a): scattering angle $\phi = 136°$. Only vibronic contributions to the cross section are observed in these conditions. (b): scattering angle $\phi = 5°$. Extra intensity of magnetic origin is visible in the NpO_2 cross section.

are observed, but extra intensity of magnetic origin is clearly visible in the NpO_2 data.

In order to go beyond these qualitative observations, the phonon scattering at low angles has been estimated in the following way. The ratio of the 5° to 136° spectra of ThO_2 has been fitted by a continuous function $r(\hbar\omega)$. To obtain the magnetic scattering, we have multiplied the NpO_2 136° spectrum by $r(\hbar\omega)$ before subtracting it from the 5° spectrum. The results of this procedure, whose justification is discussed elsewhere,[7] are shown in Fig. 2 for four different temperatures, both above and below the phase transition at $T_c = 25$ K. A broad magnetic signal centered at about 55 meV, which appears to be split into two components, is positively identified, together with quasielastic scattering below 30 meV. Scans using higher incident energy did not reveal any other peak up to 350 meV.

The quasielastic intensity, integrated between 10 and 30 meV, decreases with Q, in good agreement with the behavior of $f^2(Q)$, and decreases abruptly as the temperature is raised through T_c. The profile of the inelastic signal changes only slightly with temperature and angle. It can be fitted by two Gaussian line shapes with the first peak centered at ~42 meV and the second more intense peak at ~67 meV.

The intensities of the two peaks at $T = 5$ K are shown as a function of Q in Fig. 3, where they are normalized separately to $f^2(Q)$ at the lowest Q. The total inelastic intensity shows a Q dependence similar to that of the second peak and remains, in contrast to the quasielastic contribution, almost constant with temperature. However, the ratio of the first to second peak intensity increases slightly as the temperature is raised through T_c. This is shown in the inset of Fig. 3 using the data measured at $\phi = 5°$.

The parameters defining the cubic crystal-field Hamiltonian in NpO_2 may be estimated from the values determined experimentally by neutron spectroscopy for UO_2, namely $V_4^U = -123$ meV and $V_6^U = 26.5$ meV.[8] Using relativistic calculations of the radial integrals,[9] $\langle r^4 \rangle = 6.5$ a.u. and $\langle r^6 \rangle = 37.8$ a.u., and neglecting the small difference in the metal-ligand distances in the two cases, one obtains $V_4^{Np} = -105$ meV and $V_6^{Np} = 21$ meV. These values, used in conjunction with the results of Ref. 5 for the eigenvalues of the system in the presence of J mixing effects, give an energy separation of ~50 meV between the ground $\Gamma_8^{(2)}$ and the excited $\Gamma_8^{(1)}$ quartets, with the Γ_6 doublet at ~220 meV. Alternatively, we can obtain the CF parameters W and x of the Lea, Leask, and Wolf Hamiltonian[10] by scaling those parameters that give a good fit to the UO_2 splittings, i.e., $W^U = 4.3$ meV and $x^U = 0.90$.[8] In the RS approximation, this gives $W^{Np} = -1.74$ meV and $x^{Np} = -0.75$ and a splitting of 50 meV between the two quartets. The x value is the same as that found using a similar scaling procedure by Solt and Erdös.[4]

If we now consider the transition probabilities from the ground to the excited states given in Ref. 11, it appears that for $x = -0.75$ the matrix element $|\langle \Gamma_6 | J_\alpha | \Gamma_8^{(2)} \rangle|^2$ is very small, compared to $|\langle \Gamma_8^{(1)} | J_\alpha | \Gamma_8^{(2)} \rangle|^2$. For this

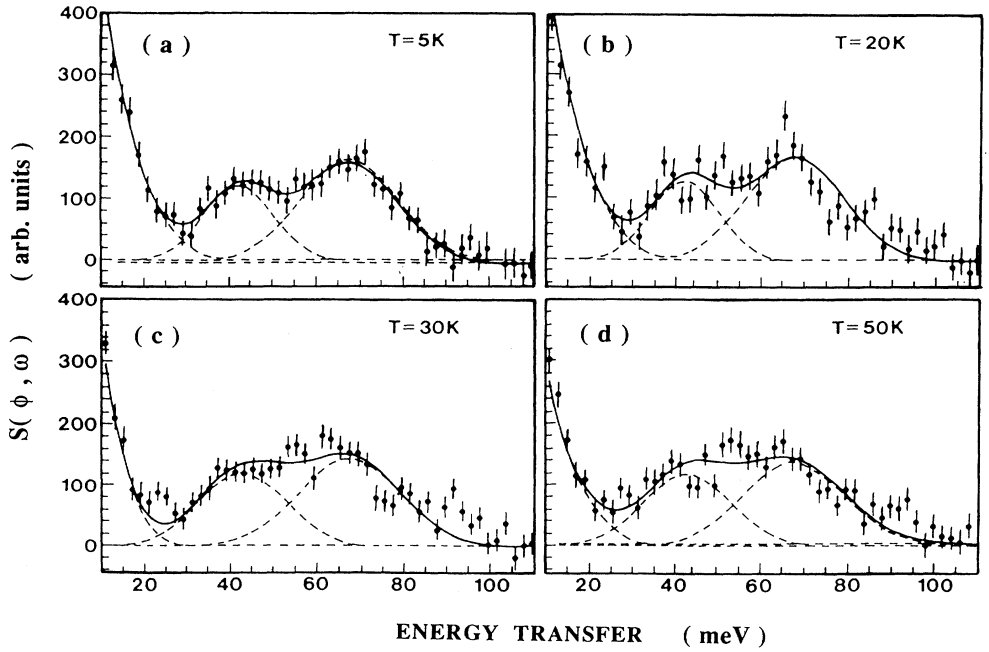

FIG. 2. Inelastic-magnetic-neutron-scattering cross section obtained for NpO_2 at (a) $T=5$ K, (b) $T=20$ K, (c) $T=30$ K, and (d) $T=50$ K. The incident energy was 180 meV and the average scattering angle $\phi=5°$. The phonon contribution has been removed following the procedure described in the text. The solid line is a fit to the data of Gaussian profiles and a sloping background (broken lines).

reason we expect to observe just one CF peak corresponding to the $\Gamma_8^{(2)}\rightarrow\Gamma_8^{(1)}$ excitation. However, two subpeaks separated by about 25 meV are observed in the experiment. This cannot be due to a splitting of the cubic quartets alone, since a structural distortion leading to such a peak separation would be easily observable by neutron diffraction.[3] In fact, if we assume a static Jahn-Teller distortion below the transition temperature similar to that considered for UO_2,[8] i.e., a monoclinic distortion of the oxygen cage surrounding the magnetic ion, we calculate a splitting of ~ 8 meV for $\Gamma_8^{(2)}$ and of ~ 4 meV for $\Gamma_8^{(1)}$. This corresponds to an oxygen-ion displacement of $\Delta=0.004a$, which is the maximum compatible with the results in Ref. 3. On this basis, it is hard to explain the measured splitting of the inelastic peak, although the order of magnitude of the ground-state splitting is in line with the quasielastic linewidths. Moreover, all the splittings due to this distortion mechanism should in principle disappear above T_c, which is not what is observed.

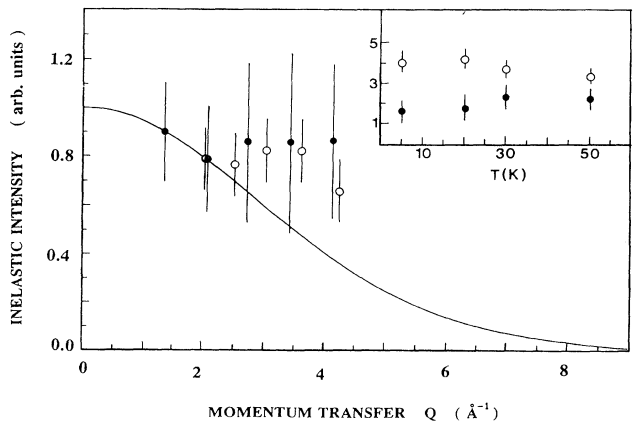

FIG. 3 Integrated intensity at $T=5$ K of the inelastic subpeaks as a function of Q. The dots correspond to the first subpeak at 42 meV, the open circles to the second subpeak at 67 meV. The solid line is the square of the Np^{4+} magnetic form factor. The inset shows the temperature variation of the intensity of the two subpeaks (in arbitrary units) at $\phi=5°$.

A more convincing hypothesis is that a bound state is formed between the $\Gamma_8^{(2)}\rightarrow\Gamma_8^{(1)}$ CF excitations and phonons lying in the 55 meV region (a vibrational band at this energy can indeed be seen in Fig. 1). Such an effect has already been observed in $CeAl_2$ (Ref. 12) and CeD_x (Ref. 13). In the case of $CeAl_2$, two peaks were observed with an average frequency very close to that of a peak in the phonon density of states (DOS). The situation is very similar in the present case: the triply degenerate phonon mode of Γ_{25}' symmetry at the Γ point gives rise, along the $[0,0,\xi]$ symmetry direction, to a flat doubly degenerate, transversely polarized, Δ_5 branch, ending in the M_5' optical mode at the (0,0,1) point with an energy of 56 meV in both UO_2 (Ref. 14) and ThO_2 (Ref. 15). As the phonon DOS deduced from the present neutron results for NpO_2 and ThO_2 are very similar (Fig. 1), it is likely that the phonon peak at ~ 55 meV in NpO_2 is of the same nature. Following the procedure outlined in Ref. 12 we calculated the relative weight of the coupling between the Γ_{25}'

mode and the different CF transitions. The results show that the $\Gamma_8^{(2)} \rightarrow \Gamma_8^{(1)}$ transition has the highest oscillator strength. The mixing of CF and vibronic states may also explain the unusual Q dependence of the inelastic intensities. These arguments strongly support this mechanism as responsible for the splitting of the magnetic signal in NpO_2.

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