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Neutron Scattering of Transuranium Materials

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Abstract

A number of neutron experiments on transuranium materials are reviewed. The purpose of these experiments, which range from studies of crystal-fields in the oxides to excitations in PuSb, is to increase our understanding of the 5f electron behavior across the first half of the actinide series. Comparisons are made with the more familiar uranium analogues.

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1. Introduction

Neutron scattering is by now a well-recognized technique for determining magnetic structures, locating light atoms in the presence of heavy ones, for examining either magnetic or structural correlations associated with phase transitions in actinide systems, and for determining the dynamics of both the nuclear and magnetic structures. For a complete review up to ~1983 see Rossat-Mignod, et al. [1] and Buyers and Holden [2]. Most of the examples in these two chapters concern experiments on uranium systems. A fair amount of work on transuranium materials, aimed at determining magnetic structures and associated moment values, took place at Argonne National Laboratory in the early 1970's but employed polycrystalline samples [1]. These suffer from the disadvantage that when large anisotropies are present experiments on polycrystalline samples yield only limited information. For uranium materials, particularly the chalcogenides and pnictides, single crystals became available in the late 1970's through the pioneering work of Oscar Vogt [3], and many different neutron experiments have been performed. Of particular importance have been the studies aimed at examining the magnetic structures as a function of applied field in systems such as UAs, $\text{USb}_{1-x}\text{Te}_x$, etc., and the behavior of the magnetic correlations near the ordering temperatures. These investigations prompted developments in the theory of anisotropic exchange interactions that are discussed by Cooper, et al. [4].

In the last few years, three rather new developments have taken place in neutron scattering of the actinides, and it is these, particularly those associated with transuranium materials, upon which I will concentrate:

(a) The discovery of heavy-fermion behavior in UBe_{13} [5], and subsequently in other uranium compounds, has led to a flurry of activity with neutrons on these compounds. The purpose of these studies has been either to investigate the magnetic structures, e.g., of U_2Zn_{17} [6], the magnetic form factors, e.g., UPt_3 and UBe_{13} [7], or the inelastic magnetic response function $S(\vec{Q}, \omega)$. The latter is of particular interest as it is

directly related to the imaginary part of the dynamic susceptibility $\chi''(\vec{q}, \omega)$, and it is commonly supposed that this reflects the correlations in the electronic system that give rise to the large anomalies in the many low temperature properties (e.g., the electronic specific heat) of heavy-fermions. Although this is a very interesting subject I shall not discuss it further as no work has yet been done in transuranium systems. An excellent recent review is by Shapiro [8]. Even more recent papers have appeared on UBe_{13} [9], UPt_3 [10], URu_2Si_2 [11], and UAl_2 [12]. Buyers [13] and myself [14] have also reviewed the similarity in the neutron inelastic response functions of systems such as US and UN, which order magnetically but exhibit no sharp spin waves, and the heavy-fermion systems.

(b) The capability of growing single crystals of transuranium materials has now been developed at the Euratom Institute, Karlsruhe and a large number of experiments on systems such as NpAs, NpSb, PuSb, PuAs, PuBi and PuTe have been performed. Some of these will be described below.

(c) The advent of spallation neutron sources [15] has resulted in an extension of the energy range available for inelastic studies. Although the so-called kinematic restrictions [16] are a serious limitation, energy transfers of ~250 meV can now be attained; e.g., spin-orbit splittings in rare-earth metals [17] and in both rare-earth and actinide oxides [18]. I shall discuss some of the recent work in this area below.

2. Experiments with Transuranium Single Crystals

2.1 Magnetic Structure and Anisotropy

The object of these experiments has been to investigate properties such as the magnetic structure, anisotropy, and nature of the phase transitions, and compare them with those found in uranium systems. For example, we recall that the many "planar" like magnetic structures in cubic uranium (and cerium) compounds [1] may be caused by the f hybridization, both with the conduction electrons and/or p electrons on neighboring

anions [4]. If, as we anticipate, the 5f electrons become more localized as we move across the actinide shell, then is the hybridization weakened as we proceed from U to Pu compounds? This question was partially answered by the early magnetization experiments and accompanying theoretical explanations [19]. A more positive answer was given by the neutron experiments [20], which showed that at high temperature in PuSb, for example, an incommensurate phase exists with the moments locked in planes and modulated from plane to plane in a longitudinal wave. This is exactly the signature of many uranium systems.

More recent experiments (still unpublished) on single crystals of NpAs and PuBi at Grenoble by Paul Burlet, Jean Rossat-Mignod and their group have shown even more unusual behavior. In PuBi the ordering ($T_N = 57K$) is antiferromagnetic but the wavevector is $\vec{k} = (0,0,0.233)$, i.e., we again find ferromagnetic planes with the moment modulation parallel to the spin direction, which is always [001]. The wavevector k is independent of temperature, which is rather unusual, but at lower temperature third-order satellites are seen that indicate a squaring of the modulation wave. The value of 0.233 is close to $3/13 = 0.2308$ so we can think of the modulation as three repeats in 13 unit cells.

2.2 Magnetic Form Factors

One of the very fundamental questions that still remain unanswered in metallic uranium systems, including the heavy fermions, is "how many 5f electrons are there outside the radon core?" The answer should be 2 or 3, or maybe somewhere in between if one adopts a band or intermediate valence approach. Debates over this continue to flood the literature and no one technique can make the identification. For example, our inability to observe crystal-field transitions in most metallic uranium systems [2,13,14], render this usually unambiguous neutron technique useless. Form factor studies of uranium systems [1] are usually ambiguous

because the $5f^2$ and $5f^3$ configurations are very similar [21]. However, in the case of plutonium a very interesting situation arises and form factor studies can give unique information if the $5f^5$ state is present. This is because both the spin and orbital contributions are very large ($L = 5$ and $S = 5/2$ in RS coupling) and they oppose each other. The result (and this is also true for $4f^5$ ions) is a form factor that has a maximum at $Q(=4\pi\sin\theta/\lambda)$ greater than zero. This is illustrated for PuSb in Fig. 1 from Ref. [22]. In this figure the solid curve $\mu\langle j_0 \rangle$ would be for a spin-only system, whereas the total induced moment at a value of Q is

$$\mu f(Q) = \mu[\langle j_0 \rangle + C_2\langle j_2 \rangle + \dots] \quad (1)$$

and must include the large orbital scattering to fit the data. In fact the large value of $C_2 = 3.80$ points unambiguously to a trivalent $5f^5$ configuration with intermediate coupling. The anisotropy about the broken curve (see insert) also tells us that the Γ_8 is the ground state. A simple analogy with lanthanide systems would expect a Γ_7 ground state, but the strong f hybridization lowers the energy of the Γ_8 state compared to the Γ_7 state [23].

We are now in the process of using this form factor technique to look at PuTe [24]. This is a particularly interesting system because the ground state is nonmagnetic and it is not clear why this is the case [25]. If the configuration is $Pu^{3+}:5f^5$ a magnetic ground state is expected, and if it is $Pu^{2+}:5f^6$ a different lattice parameter is expected. Preliminary neutron measurements suggest, in fact, that the $5f$ electrons do not have the large orbital moment we found in PuSb, but more experiments (and careful chemical analysis of the ^{239}Pu) are needed before a conclusion can be drawn.

2.3 Dynamics of Transuranium Systems

This subject is naturally in its infancy. To perform inelastic neutron experiments on transuranium systems requires special preparations.

We need large samples and for the most detailed work single crystals are needed. In this respect, the work of J. C. Spirlet and his collaborators at Karlsruhe [3] is unique in that large ($\sim 0.5 \text{ cm}^3$) crystals of some transuranium systems have been produced. For the first experiments we chose PuSb. As discussed earlier, this has the advantage that the system is apparently predominantly localized so we expect to be able to understand the excitation spectrum. Since the ^{239}Pu strongly absorbs thermal neutrons the crystals were grown with the ^{242}Pu isotope, which was loaned by the U.S. Department of Energy. Measurements have now been done on the IN8, IN1, and IN20 triple-axis spectrometers at the ILL. A brief report of this work has appeared [26].

At low temperature PuSb is a ferromagnetic with $\vec{\mu}$ along a cube axis [19,20]. By field cooling the sample a single magnetic domain was produced and this allows the separate components of the total $S(\vec{Q}, \omega)$ response function to be measured. Figure 2 shows some inelastic spectra from PuSb. We are reasonably sure that this excitation is within the Γ_8 ground state, as the excitation cannot be seen for $T > 100\text{K}$. The excitation has almost no dispersion in the direction $[00q]$, i.e., between the ferromagnetic sheets. In the $[q00]$ direction the mode $S^{yy}[q00]$ is also dispersionless but if we separate $S^{xx}[q00]$, which has displacements longitudinal with respect to the wave propagation, then we find this has a sudden drop near the zone boundary ($q = 1$). It is rather unusual that the frequency within the $[001]$ plane is not different from that for spin waves perpendicular to the plane, particularly in view of the bulk anisotropy observed. The minimum at $q = 1$ for the $S^{xx}[q00]$ component is also unusual, but is rather reminiscent of what happens in CeSb [27]. Banerjee, et al., [23] have successfully predicted the exchange splitting of the Γ_8 as $\sim 4 \text{ THz}$ (as observed) but have not yet reproduced the minimum at the X-point ($q = 1$), which is shown in Fig. 2. Note that $1 \text{ THz} = 4.14 \text{ meV}$. Attempts to measure

the $\Gamma_8 \rightarrow \Gamma_7$ splitting, predicted in Ref. [23] as ~20 THz with the IN1 spectrometer were not successful either because the matrix elements (remember these are modified from the simple single-ion values by hybridization effects) are too small, or we didn't have enough material. The crystal size is ~350 mm³. Perhaps of more interest has been our efforts to prove with neutron polarization analysis techniques that the component $S^{xx}[q00]$ is, in fact, a linearly polarized wave as the above discussion suggests. Unfortunately, our first effort on IN20 failed because of technical difficulties.

3. Crystal-Field Transitions in Actinide Oxides

The advent of spallation neutron sources, as described earlier, has opened up the possibility of extending the available range of energy transfer up to ~300 meV, from the ~50 meV available for magnetic excitations at reactor sources. Naturally, one of the first materials we tried at IPNS at Argonne was UO_2 . Twenty years ago Rahman and Runciman predicted the splitting as 170 meV between the Γ_5 triplet ground state and the excited Γ_3 doublet [28]. To our surprise not one, but two peaks were seen at ~160 meV in the early experiments at IPNS [18,29]. More recently, using higher resolution at the ISIS source at Rutherford-Appleton Laboratory, Hayes, et al., [30] have shown that there are at least 3 and possibly 4 peaks between 150 and 170 meV. Kern, et al., proposed [29] that the two peaks resulted from a dynamical splitting of the excited Γ_3 doublet, probably a dynamical Jahn-Teller effect. However, the observation of more peaks at the Rutherford clearly indicates that we are also seeing transitions to the next excited Γ_4 triplet as well as intramultiplet splitting. This result forces us to lower the magnitude of the fourth order potential V_4 in crystal-field theory from ~400 meV (as predicted by Rahman and Runciman) to ~180 meV and also to increase the magnitude of sixth order term, which is positive, to ~20% of V_4 . Both of these effects are rather unexpected, but possible if one considers the spatial extent and potential overlap of the 5f

electrons with the anion p states. Even more puzzling, of course, is the multiplet structure. It should be noted that the phonon-spectrum cuts off ~ 80 meV so it is difficult to see how this splitting can come from direct phonon-exciton interaction, as is the case in CeAl_2 [31].

More recently we have performed an experiment at IPNS on polycrystalline NpO_2 . This material is particularly interesting because the results of specific heat and magnetization measurement suggest a phase transition at 25K, but microscopic techniques (including neutron diffraction) have been unable to verify such a transition. Friedt, et al., [32] have reviewed all the measurements on NpO_2 and concluded that a dynamical internal distortion occurs at 25K as a result of strong quadrupolar effects. They predict a $\Gamma_8^{(1)}$ quartet ground state within the $5f^3$ configuration with the excited $\Gamma_8^{(2)}$ some 86 meV above. Our experiments at IPNS [33] were relatively disappointing, considering the effort required to make a sample and perform the experiments, since they showed one very broad (5 times the resolution or ~ 20 meV full width at half maximum) at 60 meV energy transfer. This is lower than we expect. However, we have shown from complete intermediate coupling calculations involving all the excited S and L components, that this value can be understood if $V_4 = -(160 \pm 30)$ meV and $(V_6/V_4) \sim 0.2$. These parameters are indistinguishable from those of UO_2 , which is very gratifying, and gives us confidence that the potentials are more effectively screened even in the ionic oxides than we had thought. However, this does not explain the very broad peak in NpO_2 . We can speculate that this is broadened by the quadrupole mechanism of Friedt, et al., [32] but a more quantitative argument is needed. Moreover, if the quadrupole interaction is like that in UO_2 then the effect in NpO_2 is quite different. In the former sharp peaks are seen, whereas in NpO_2 only a very broad peak, which is essentially independent of temperature, is seen.

Summary

I have tried in this short review to give a flavor of the many different aspects of neutron scattering on actinide systems that are now underway. There is little space for detail and I hope, at least, that the reader will find the references useful. I have chosen to concentrate on work on transuranium systems, because there are already a number of reviews on uranium compounds, and by extending the work beyond uranium we begin to get an idea of the systematics of the actinide series.

Certainly the magnetic structure studies, which we hope soon to extend to curium metal and compounds, show much of the features already found in U-systems. New systematics are emerging in discussing these planar arrangements, which have now been found to be typical of Ce, U, Np, and Pu compounds. One obvious analytical framework for discussing their behavior is that of Ising systems [34], and this can provide useful predictions as to the nature of the anisotropic interactions. Such theories do not, of course, address the microscopic interactions producing the anisotropy, and it is here that the hybridization theories play an important role. The form factor studies (of at least PuSb) point to a localized trivalent state, although the ground state is reversed from that found in the analogous rare-earth compounds. The dynamical behavior of PuSb again points to unusual anisotropic interactions. Of particular interest is the ability to measure the individual components of $S(\vec{Q}, \omega)$, and this is of great value in constructing detailed theories. It also raises questions about the dynamical behavior of other actinide systems in which one measures the general rather than specific components. For example, measurements on a single domain sample of CeAs [35] also indicate a more complicated situation than previously thought.

In the oxides the new work on spallation sources is providing us with major surprises. Optical methods do not work well with such systems because they are opaque, the cation is at a center of inversion symmetry, and the technique is

very sensitive to vibronic effects. Nevertheless, we do have a rough idea of the crystal-field potentials in dilute systems doped with actinide ions and these vary over a wide range depending on the system being studied. Such dilute systems lack, of course, the direct interactions that are so important in compounds. Normally the effective charges, which can be deduced from the crystal-field potentials, in actinide systems are between 2 to 5 times as great as in analogous lanthanide compounds. However, the new values of V_4 for UO_2 and NpO_2 are now similar to effective charges found in PrO_2 [29], but with larger V_6 terms than commonly found in the lanthanides. Even more puzzling are the nature of the spectra that appear to indicate strong quadrupolar interactions. Far from being understood, these oxides clearly have much physics left to yield.

The heavy-fermion systems present very important challenges, but I have referred to the review of Shapiro [8] rather than discuss this subject in detail. New experiments are being reported almost daily, and no doubt more are presented in this Proceedings. So far, at least, the neutron results have been rather disappointing, except perhaps for the very interesting spectrum that has been found in URu_2Si_2 . Single crystal experiments are now in progress at a number of Laboratories (Brookhaven, Risø, Chalk River, and ILL) and no doubt will be reported in due course.

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Figure Captions

Figure 1.

Magnetic amplitudes as a function of $\sin\theta/\lambda$ ($=Q/4\pi$) for ferromagnetic PuSb at 10K. The moment direction is [001]. Open points correspond to reflections {hko}, i.e., in the scattering plane. The dashed curve, which is approximately the sum of the two solid curves is the best fit to the open points. Reflections out of the scattering plane ($l \neq 0$) are given by solid points and calculations for them are represented by crosses. The bulk magnetization value [19] is represented by a cross on the ordinate axis.

Figure 2.

Inelastic spectra from a single crystal of $^{242}\text{PuSb}$ taken at ILL [26]. The three spectra indicate (a) that there is little dispersion across the zone since a peak appears throughout at ~ 4 THz ($1 \text{ THz} = 4.14 \text{ meV}$) and (b) at the zone boundary [102] two peaks are seen because a mode $S^{xx}[\text{q}00]$ is measured, whereas at [201] this mode cannot be seen and only one peak is observed.

Fig 1

Fig 2