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Resonant magnetic X-ray scattering: a new probe for actinides

G.H. Lander
Commission of the European Communities, JRC, Institute for Transuranium Elements, Postfach 2340, D-76125 Karlsruhe (Germany)

W.G. Stirling, S. Langridge and C.C. Tang
Physics Department, Keele University, Keele, Staffordshire ST5 5BG (UK)

Doon Gibbs
Physics Department, Brookhaven National Laboratory, Long Island, NY 11973 (USA)

Abstract

The magnetic cross-section for photons is small and difficult to observe; however, when the X-ray energy is tuned to certain absorption edges an enormous enhancement of the magnetic scattering cross-section is observed. This process is now understood in terms of atomic resonances. By chance, the largest enhancements, and most convenient for diffraction experiments, occur at the M edges (3.5–4.5 keV) in the actinides. We shall give some examples of the work performed at the NSLS, Brookhaven National Laboratory. Our recent experiments have been on small single crystals of NpAs. The higher resolution available with X-ray synchrotron beams, compared with that at neutron sources, has allowed us to determine new features in both the magnetic structure and the critical fluctuations just above T_N. Because of the high absorption of the X-rays, the technique is extremely sensitive to the near-surface region, and the results often exhibit significant differences to those determined from neutron diffraction, which examines the bulk of the material. Thus, the two techniques are complementary. Very small samples are all that is required for the synchrotron experiments; we estimate that the beam illuminates no more than 1 μg of NpAs in this study, so that studies of the magnetic properties of transcurium materials become possible for the first time.

1. Introduction

One of the most important aspects of the actinide (5f) elements and compounds is that the 5f electrons are unpaired and may exhibit magnetic properties, like the compounds of the d or 4f series. Although the light actinides (U, Np, Pu, and Am) do not order magnetically many compounds of these, except for Am^{3+} which has a $J=0$ ($5f^6$) configuration, exhibit magnetic ordering. The heavier actinides are all magnetic, consistent with the idea that the series is analogous to the lanthanides. Even if the compounds do not order magnetically, the 5f electrons surrounding the nucleus are unpaired and thus exhibit "magnetic behavior", as observed, for example, in the magnetic susceptibility and the specific heat at low temperature. One of the most powerful probes of magnetism, whether it be ordered or not, is neutron scattering. The neutron has a spin which couples to that of the unpaired electrons and gives information directly on the wavevector-dependent dynamic and static susceptibility. Although other probes, susceptibility, nuclear magnetic resonance and muon precession, give information on part of this response function (or some integral of it) the information obtained by neutrons is unique, and has contributed enormously to our understanding of the lanthanide series (for a recent review see ref. 1). Great progress has been made with neutron scattering in uranium systems (see, for example, ref. 2), but for transuranium elements and compounds the situation is not so favorable. Two major reasons cause this situation. (1) The elements Np, Pu, and Am have high absorption (usually from the fission cross-section) for thermal ($\lambda \approx 1$ Å) neutrons. This can be avoided by the use of special isotopes in the case of Pu, but such isotopes are expensive. (2) Neutron cross-sections are small and the beams are weak, so that large samples are required. For elastic scattering to examine the structure (static susceptibility) single crystals of more than 1 mg are required and polycrystalline samples of more than 1 g. For inelastic scattering (to examine the dynamic susceptibility) the samples must be much larger. For any heavier actinides (beyond Cm) these conditions are prohibitive.

X-rays offer an alternative microscopic probe, at least for the structural aspects. However, the magnetic cross-

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section for photons, although it was first formulated 40 years ago [3], is very weak [4]. It has been only with the great intensity available from synchrotron sources that such experiments have been possible [5]. (Most of the magnetic scattering experiments have been performed at the NSLS, Brookhaven National Laboratory, NY, USA.) The exploitation of so-called non-resonant magnetic scattering has been described theoretically in some detail in ref. 4; experimentally it is testing the limits of present synchrotrons, and many practitioners await the development of the third-generation synchrotron beams with their intense insertion-device beams. However, during experiments on Ho metal Gibbs *et al.* [6] made the important discovery that the magnetic intensity increased when the energy of the photon beam was tuned near to the L_{III} absorption edge. This was understood immediately [7] in terms of atomic resonance spectroscopy, in which electric 2^L-pole resonances are stimulated and contribute to the coherent scattering amplitude. The largest enhancement of the magnetic signal occurs when the dipole ($L=1$) resonances are involved and these are L_{II} and L_{III} ($p \rightarrow d$) transitions for the d elements and M_{IV} and M_V ($d \rightarrow f$) transitions for the f elements. Since these experiments involve Bragg scattering conditions, for normal materials the wavelength must be less than about 4 Å. (The effects can also be seen in reflectivity experiments, and longer wavelengths can be used from multilayers.) When the relative energies are considered for the above transitions the most favorable conditions are found for the actinide M_{IV} and M_V resonances. Thus the first experiments on an actinide, by Isaacs *et al.* [8] on UAs, revealed a spectacular increase in the magnetic intensity when the energy was tuned near the M_{IV} resonance edge (3.727 keV for U). It is on the exploitation of this resonant magnetic scattering that we wish to focus in this review.

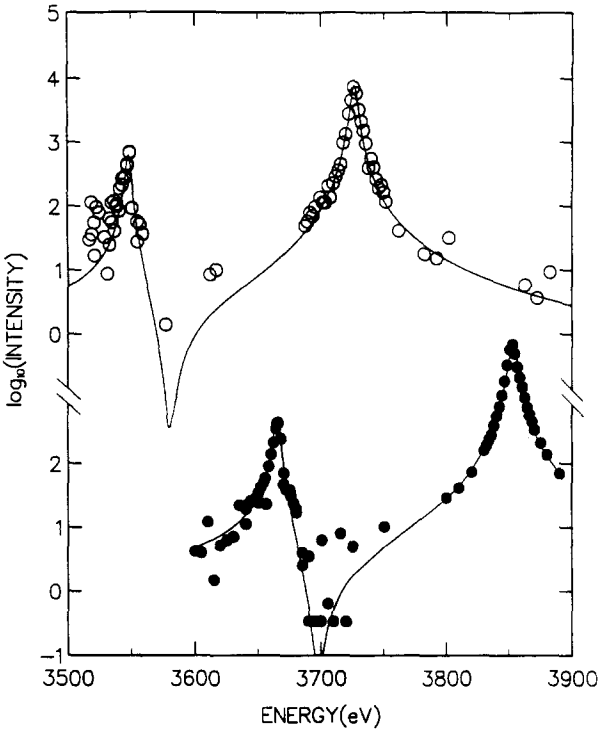

Fig. 1. Intensity of the scattered X-ray intensity from single crystals of USb (○) and NpAs (●) as a function of the photon energy: ——, fits to two resonances as suggested by atomic physics (see ref. 7).

2. Examining the resonant energy and intensity

The enhancement of the intensity at the resonant energy depends on a number of factors, including the density of 5f states at the Fermi level, so that it contains important information on the solid state properties of the actinide [9] being examined. We show in Fig. 1 the intensity of antiferromagnet reflections as a function of the photon energy for uranium and neptunium compounds. The aspects of these curves that are interesting are the energies and widths of the resonances, and the ratio of the two peak intensities (the so-called branching ratios). The increase in energy between U and Np reflects the increase in nuclear charge, and the energies appear to correspond well to those of the absorption edges. The instrumental resolution (about 3 eV) is still too large for broadening effects due to the core–hole lifetime properties of the resonance to be observed, but this resolution can be improved. The branching ratios have been discussed at length in refs. 10 and 11 and can be used to determine the ionic state, *i.e.* Np^{3+} or Np^{4+}, of the actinide ions. The fact that the resonances are atom specific implies, for example, that the individual moments on different actinides can be determined in solid solutions. This is not possible with neutrons.

3. Studies of the magnetic ordering

We shall now concentrate on the studies of the magnetic ordering. Despite the large enhancement of magnetic scattering that occurs at resonance, the normal Thomson charge scattering is always much stronger. In a ferromagnet, or a paramagnet in applied field, the elastic magnetic response coincides with the charge scattering because the repeat unit cell is the same as for the crystal structure. The separation of the magnetic and charge contributions is thus difficult. It requires the use of circular-polarized radiation and has been done successfully for the transition metal ferromagnets at Daresbury Laboratory, UK [12]. Further progress will be made when new insertion devices capable of

changing the degree of circular polarization are operating. We note in passing that circular dichroism provides identical information except that it corresponds to a $Q=0$ (where $Q=4\pi \sin\theta/\lambda$ is the scattering vector or momentum transfer) measurement (for experiments see ref. 13 and for theory see ref. 14). No measurements of circular dichroism have yet been reported at the actinide M edges, but there are plans for such measurements.

The greatest advantage of resonant scattering is when the material is an antiferromagnet, in which case the magnetic and charge scattering are usually separated by the fact that the repeat unit cell of the antiferromagnet is different from that of the crystal structure. This is illustrated by the data presented in Fig. 2 from a single crystal of NpAs. The first-order satellites for this phase, in which the repeat unit cell of NpAs is 4 times bigger than the crystal unit cell, are very strong. Despite the encapsulation (involving Be windows) we measured over 20×10^3 counts s^{-1} in the magnetic peak. The antiferromagnetic arrangement of NpAs at this temperature is a series of ferromagnetic planes of Np moments stacked in the sequence 4+, 4−, 4+, 4− etc., with the moments parallel to the stacking direction. Much of this was known from neutron experiments [15]. The new information from the synchrotron experiments arises from both the intensity and the resolution. By resolution we mean the narrowness of the peaks in Fig. 2. The excellent resolution (which can be up to a fact of 5–10 better than in neutron experiments) can be illustrated with the measurement of the magnetic q vector (where $1/q$ is the repeat of the magnetic unit cell) in NpAs as shown in Fig. 3. The two domains, depending on whether the moments are parallel or

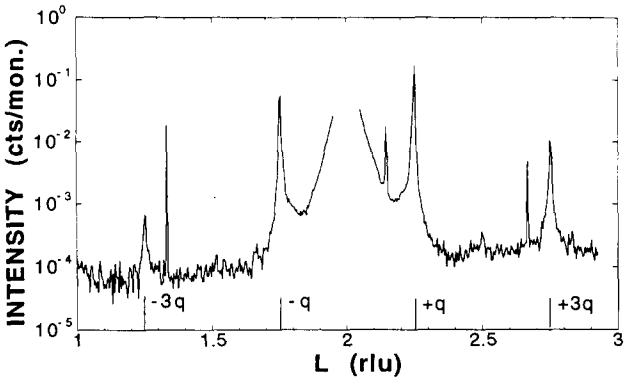

Fig. 2. Complete scan with X-rays of $E=3.852$ keV (the Np M_{IV} resonant energy) along the L direction from the (001) face of a small NpAs single crystal at $T=135$ K. The logarithmic scale should be noted. The large peak in the center at $L=2$ is the charge scattering. Peaks at $\pm q$ and $\pm 3q$ are magnetic in origin (as can be demonstrated by both their temperature and energy dependences). Peaks at $L=1.333$ (4/3) and $L=2.667$ (8/3) are from the third-order contamination of the primary beam. The peak at $L=2.1$ is from the sample holder.

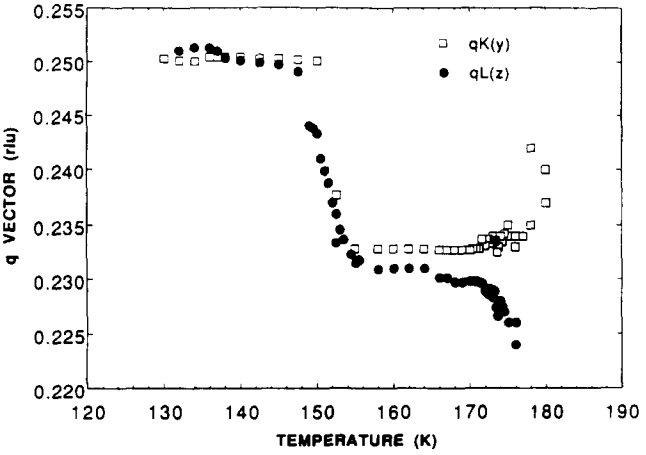

Fig. 3. Values of the magnetic wavevector q as a function of temperature for NpAs. The points correspond to different domains with the moments parallel (□) or perpendicular (●) to the surface of the material.

perpendicular to the surface, have different values. This unusual sensitivity to the near-surface behavior arises because of the large absorption of the X-ray beam at resonance. The 1/e penetration depth of these photons is about 1200 Å so that the technique is near-surface sensitive, and there is increasing evidence that the nature of the magnetism of the actual surface itself has a pronounced effect on the observations. Experiments on a single crystal of the pseudobinary compound $U_{0.85}Th_{0.15}Sb$, for example, show [16] that the near-surface volume actually has a slightly different magnetic structure from that of the bulk, as measured by neutrons.

Figure 3 shows that the q vector of NpAs has two constant values; one at low T of the commensurate $q=1/4$ structure, and another where $q\approx0.230$ before the ordering disappears at $T_N\approx173$ K. In fact the plateau at about 0.230 probably corresponds to an arrangement with special faults. Such a model predicts structures of the form $q=6/26$ (=0.2308) or 7/30 (=0.2333), which are very close to the observations.

In summary, studies of the magnetic ordering of actinides with synchrotron radiation will greatly improve our understanding of the microscopic interactions, benefitting from both the increased intensity and the resolution of resonant scattering. A good example of the questions answered by the synchrotron experiments concerns the heavy fermion material URu_2Si_2 and the nature of the long-range order at low temperature. Isaacs *et al.* [17] were able to show that ordering is not truly long range in nature; the correlation length of the moments was about 500 Å.

4. Studies in the critical regime near the ordering temperatures

One of the great successes of condensed matter theory has been to formulate ideas connected with the

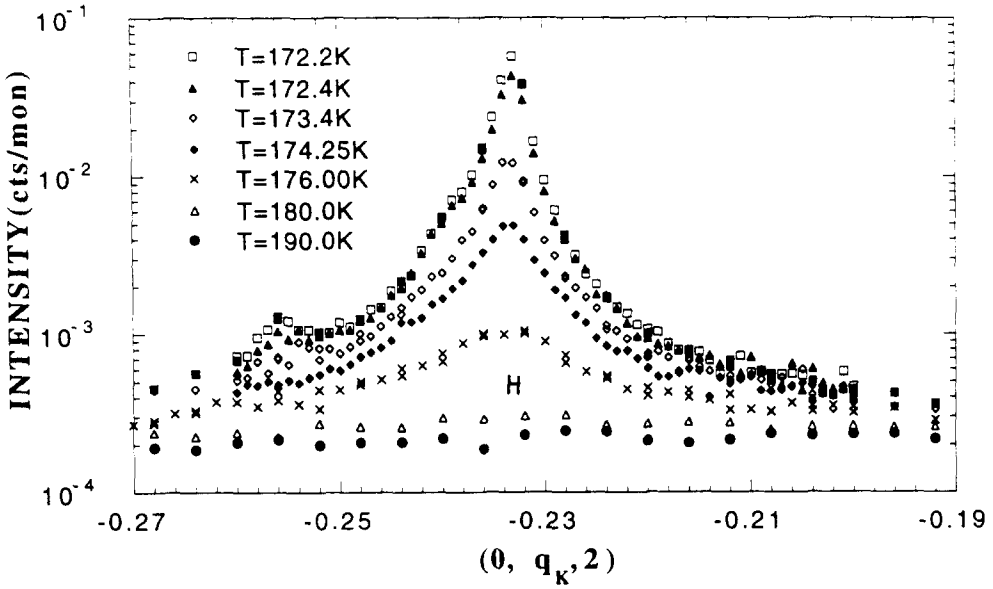

Fig. 4. Scans in the [0K2] direction showing how the magnetic scattering in NpAs changes with K (the ordering wavevector, see Fig. 3, is $q_K = 0.233$) and with temperature. The logarithmic scale should be noted. The horizontal width of the small bar indicates the instrumental resolution. The ordering temperature $T_N = 172.8$ K. Scans above this temperature are sensing the spatial correlations of the magnetic components. It should be noted that the scattering is strong enough to observe even at 180 K. A detailed analysis can be made from scans such as these to investigate the parameters in the critical regime.

spatial and temporal behavior of fluctuations of parameters near a phase transition. To observe spatial coherence over a long length scale one needs good q space resolution, so with the excellent resolution of the synchrotron instruments it was natural to apply the new technique to the observation of the fluctuations near phase transitions. The first observations on Ho metal provided a surprise [18]; an additional component was observed in the critical fluctuations. Although a detailed analysis is necessary before a two-component structure is evident, we show the quality of the data in the so-called critical regime taken in NpAs in Fig. 4. In NpAs we have also clear evidence for a two-component structure of the correlation lengths near the ordering temperature [19]. This behavior is at odds with current theories, so this is naturally an active experimental area. It appears most likely that the behavior may be related to the surface or near-surface region [20] of the crystal. These questions will probably not be answered until real grazing-incident surface magnetic scattering measurements are performed, and, given the intensity in the resonant scattering, it seems likely that such experiments will be performed first on an actinide sample.

5. Study of the lattice behavior with high resolution

The charge scattering is, of course, extremely strong with a synchrotron source, so strong in fact that an attenuator normally has to be used in the beam. The advantage of studying the lattice behavior simultaneously with the magnetic scattering is that magnetoelastic effects may be identified unambiguously in the sense that the same sample and temperature sensors are being used. The early studies of holmium and the development of the "spin–slip" model (for a review see ref. 21) showed the importance of such measurements. We show in Fig. 5 the scans through the charge (002) and (004) Bragg peaks of NpAs at three different temperatures. Although it was known from early experiments on polycrystalline material that NpAs exhibited a number of unusual lattice distortions [22] these new measurements [11] confirm the earlier work in a dramatic way.

High resolution neutron experiments can be performed also, but it usually requires a subsidiary experiment. The advantage of the X-ray studies is that they can be performed quickly with the same experimental configuration.

6. Summary

We have tried, in this short paper, to give an idea of some of the recent advances in our understanding of actinide magnetism due to synchrotron resonant magnetic X-ray scattering. The technique is very new: the first experiments were reported on an actinide in 1989 [8]. We emphasize that the actinides are uniquely suited to this technique as the M edges, at which strong enhancements of the magnetic scattering are found,

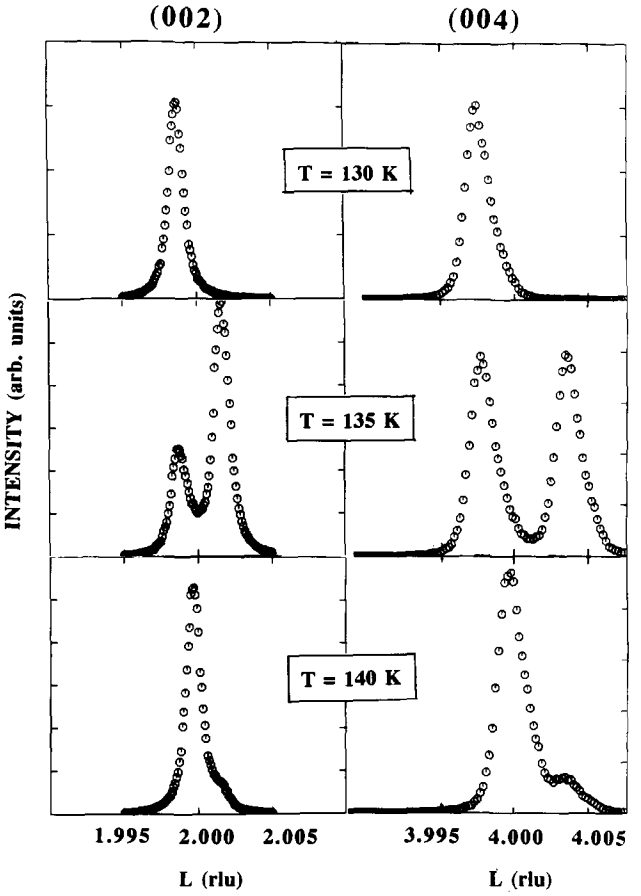

Fig. 5. Profiles of the diffraction peaks from the (002) and (004) reflections of NpAs taken with the high resolution configuration (8 keV, Ge analyzer) at 140, 135, and 130 K. NpAs is tetragonal in the temperature range 132 K $< T <$ 173 K and the bottom two sets of profiles illustrate this by showing two peaks in each: these correspond to the d spaces from the (H00)- (or (0K0)-) and (00L)-type reflections. At T = 132 K NpAs becomes cubic, so that a single peak is observed.

occur between 3.5 and 5 keV. Diffraction experiments can be undertaken at these energies. Moreover, the quantity of material required is extremely small. For example with a beam of 1×0.5 mm^2 and a penetration depth of about 1200 Å the volume of material irradiated is 10^{-4} mm^3, corresponding to no more than 1 μg. This technique is clearly matched exactly to scarcity of the heavier actinides. This is also the quantity of material used in diamond pressure cells, so that the technique can be used to examine the changes in the magnetic configuration under pressure up to pressures in the gigapascal range.

So far the experiments have been performed on single crystals. However, polycrystalline materials can be also examined provided that detectors covering a large solid angle to intercept the Debye–Scherrer cone are used. This is the only way to make up for the large absorption. Such an instrument has yet to be constructed but is simple in conception. Although inelastic scattering experiments with photons are extremely difficult, for excitations above about 100 meV the resonant scattering technique offers some advantages over neutron techniques. Apart from the difficulty of obtaining adequate resolution, the main problem will be the absorption of the incident beam on resonance. This extension of the technique remains a challenge.

The new third-generation synchrotron machines, such as the ESRF in Grenoble and the APS at Argonne, offer beams 1000 times brighter than the NSLS. This will allow totally new types of investigations in both absorption spectroscopy (circular dichroism) and scattering from the actinides. Indeed, we dare to predict that this technique will revolutionize our understanding of the magnetic and structural aspects of the heavier actinides, leading at long last to their being characterized properly rather than remaining the domain of the theorists.

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