Resonant x-ray scattering in 5f magnetism

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Large enhancements of the magnetic cross section of photons occurs when the energy is tuned near to an absorption edge. Examples of this effect in the actinides at the M_{IV} edge are presented. The excellent resolution available with x-ray synchrotron beams has allowed new features in both the magnetic structure and the critical regime to be determined. The technique is also sensitive to the near-surface region. Some of the possibilities with the new 3rd-generation synchrotrons will be discussed.

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1. Introduction

The fact that photons are scattered from magnetic distributions of both spin and orbital density has been known for 40 years [1], but the cross sections are weak, on average a factor of at least 10^{-6} less than the standard Thomson scattering cross-section that arises from the photon interaction with the charge density. Pioneering experiments to measure some of these magnetic cross sections were undertaken by de Bergevin and Brunel [2], but it was not until the advent of intense photon beams from synchrotron sources that magnetic photon scattering became more than a curiosity. The first material to be studied was Ho which has a complicated magnetic spiral structure, but the advantage of a large magnetic moment of $10 \mu_B$ at low temperature. A series of important discoveries was made about the antiferromagnetic (AF) structure of Ho, in particular the presence of the so-called 'spin-slip' structures [3]. The investigators used both the high q-space resolution available with synchrotron radiation as well as the fact that charge and magnetic scattering may be separated by their polarization dependence of the scattered photon beam. Shortly after the first experiments on Ho it was noticed [4] that a large enhancement of the magnetic scattering occurred near the L_{III} absorption edge at an energy of 7.847 keV. This effect is now understood [5] as a *x-ray resonant exchange scattering (XRES)*. The energy is such that the incident photon energy excites a $3p$ electron to the $5d$ unoccupied level. Under these conditions electric $2L$ -pole resonances (EL) are stimulated and contribute to the coherent scattering amplitude. The strongest transitions with the largest matrix elements is dipole ($L=1$), and this is the $p-d$ transitions described above. Weaker electric quadrupole ($L=2$) also occur resulting in $3p$ to $4f$ transitions. The intensity as a function of photon energy probes the energy dependence of the spin-polarized density of empty states above the Fermi level. This paper will be limited to examples drawn from such experiments on $5f$ systems; somewhat longer reviews of the experimental situation also exist [6].

2 Energy dependence of scattering

The work by Hannon et al. [5] showed that we could simply deduce the strongest resonant effects, and these are given for representative elements in the d and f series in Table 1. A 'normal' monochromatic beam at a synchrotron facility has a wavelength range of from ~ 5 to ~ 16 keV. The $4f$ L transitions are conveniently in this range, but the Fe L edges have a wavelength that will not satisfy Bragg's law, in which $\lambda < 4 \text{ \AA}$ except for multilayers. The Fe resonance has been seen using reflectivity [7], but the energy excludes normal XRES of $3d$ materials. For the $4f$ series the L edges couple to a small density of d states and the enhancement will be correspondingly small. The same will be true for the actinide L edges. The scattering at the L edges is a mixture of dipole and quadrupole (linking the p to f transitions) terms, as has been shown in extensive studies of holmium [8]. The L edges for the $5d$ series are clearly suitable, but the $5d$ electrons are seldom spontaneously polarized. A recent experiment on CoPt [9] illustrates the information that can be extracted. Much greater enhancements will be found in the f series when the E1 matrix element couples to a f state. Here the M edges in the lanthanides are at too low an energy (except for scattering from multilayers perhaps), but those in the actinides are accessible. An enormous enhancement of at least 10^6 was found in the first experiments on U/As [10]. It should be emphasized that these effects are *site specific*, so they represent a technique of focusing on one atom species in a compound or alloy. To illustrate this we show the results [11] for the U and Np M edges in Fig. 1. The energy of < 4 keV is accessible, but not easy to use. Such beams are easily absorbed, the number of Bragg reflections that can be measured is small, and the flux of these photons from the synchrotron are much reduced compared to those at higher energies. The solid lines through the points in Fig. 1 represent fits with atomic resonances, specified by a position, amplitude, and width. The ratio of the amplitudes of the M_{IV} and M_V resonances is called the 'branching ratio' and contains information

on the ground state of the ions. Similarly, the widths give information about the core-hole lifetime. Unfortunately, absorption corrections make the measurement of the branching ratio difficult, and the instrumental resolution (presently ~ 3 eV) is too great to give a reliable value for the lifetime, so that both these effects remain to be explored in the future. Aspects of this are discussed in McWhan et al. [10] and Tang. et al. [12]. There is, however, the expected difference in the branching ratio between USb and NpAs - confirming our belief that in these compounds both actinide ions are trivalent.

Before leaving the energy dependence of the scattering, we should note the equivalence of these types of measurements to the technique of magnetic circular dichroism (MCD). The latter occurs at $Q=0$ (i.e. absorption) and to separate the magnetic effect circular polarized radiation has to be used [13]. This is because magnetic and charge photon cross sections are out of phase by π . By using circular-polarized radiation this factor of π is recovered, allowing interference between the two effects. A similar technique must be used in scattering from ferromagnets [14] and in Compton scattering [15]. The measurements discussed in this paper are on *antiferromagnets* in which the charge and magnetic scattering occur at different Q vectors and there is no interference between them.

3 Investigations of magnetic structures

Starting from the work on Ho, the number of lanthanides that have been examined is considerable, and we cannot cover them here. The site-specific nature of the scattering has been exploited in a study of a random $\text{Ho}_{0.5}\text{Er}_{0.5}$ alloy by Pengra et al. [16]. We show in Fig. 2 the experimental scan along the specular direction from the surface, here called $[00L]$, from a single crystal of NpAs [11]. It is clear that the magnetic peaks are strong and sharp - in fact their width gives us information on the spatial correlations in the magnetic structure. The

magnetic structure of NpAs (with the NaCl crystal structure) is complex. Between $T_N = 172.8$ K and $T_0 \sim 130$ K the structure is the single-q type, in which the crystal consists of three physically separate domains. In each one the AF structure propagates along a certain cube direction $\langle 100 \rangle$ with the moments parallel to the propagation direction. When neutrons are used [17] the domain population is found equal to $1/3$, as would be expected from a random distribution. However, the x-rays see a different situation, as shown in Fig. 3. On cooling through T_N there is a reduction in the population of the C domains, which have their spins perpendicular to the surface, because these domains are not favored by dipole interactions. At lower temperature a dramatic change takes place with the material illuminated becoming a single C-domain state. This can be understood by realizing that the material is distorted tetragonally in this phase and there is a necessity to minimize the strain, even at the cost of dipole energy. At T_0 the structure becomes triple-q [11,17]. These are novel effects in this 5f material, and show that the *near-surface* region is important in defining the x-ray signal. Because of the high absorption of these beams (the μ coefficients approach $25,000 \text{ cm}^{-1}$) the penetration depth is ~ 1200 Å. An equally complex magnetic structure, and somewhat different from found on the same crystal with neutrons, was found in a pseudo-binary $\text{U}_{0.85}\text{Th}_{0.15}\text{Sb}$ [18] - again, no doubt, reflecting features of the near-surface region.

4 Measurement of correlation lengths

The excellent q-space resolution available at synchrotron sources, which is often between 5 and 10 times better than possible with neutrons, is reflected in the sharpness of the peaks in Fig. 2. If the long-range order is infinite, then the peaks are delta functions and the measured width is the 'resolution function' of the instrument. This is the case in the commensurate state of NpAs illustrated in Fig. 2. However, it is not always the case; a good example being the study of the

heavy-fermion superconductor URu_2Si_2 [19] in which the magnetic correlation lengths in the ordered state do not exceed $\sim 500 \text{ \AA}$.

The large intensities of XRES mean that measurements can also be made in the so-called 'critical regime', i.e. before the material orders, to measure the spatial correlations. Such effects are shown in Fig. 4, as observed near T_N in NpAs [20]. Note 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. Earlier measurements on Ho [21] showed that the scattering in that case could not be fit with a simple Lorentzian function, as is usually the case in neutron scattering, but a second component (with a Lorentzian-squared form) had to be introduced. Such a function describes a 'sharp' component. This was found also in NpAs [20] and is currently an active area of research, with the general belief that this 'sharp' component comes from the near-surface or 'skin' region [22]. That the near-surface region may be different from the bulk should not come as a surprise [23].

Changes in the correlation length are, of course, most pronounced near T_N , but they may not be confined to this temperature range. In Fig. 5 we show some recent results [24] from a study of the pseudo-binary alloy $\text{USb}_{0.8}\text{Te}_{0.2}$. This material has an incommensurate structure throughout the AF range. The large variation in the widths near T_N reflects the 'critical regime', but notice that the widths actually have a minimum at T_N , and then slowly increase as the temperature is further lowered. Similar effects have been seen in the incommensurate region of Ho [25] and are probably caused by magneto-elastic interactions. It is interesting in this particular study to note that the same material was examined with neutrons and nothing unusual was observed below T_N ; however the neutron resolution width was $\sim 0.015 \text{ rlu}$. When the system was

examined with x-rays with a resolution of 0.003 rlu a clear trend (Fig. 5) is seen in the widths below T_N .

5 Conclusions

Magnetic scattering with x-rays is now an active field of research at many synchrotrons world wide. Efforts will certainly increase with the commissioning of the ESRF in Grenoble, and soon the APS at Argonne. Efforts to extend our work on Np to Pu compounds (and possibly Cm) are under discussion at the NSLS. Cm represent an interesting challenge - it is an antiferromagnet with an unknown magnetic structure - so finding that would be a real first for x-rays!

Apart from Cm, and perhaps the heavier actinides, which do not exist in sufficient quantities for neutron experiments, the work with x-rays will almost certainly be confined to *details* of the magnetic structures. Neutrons will remain the technique of choice for solving unknown magnetic structures. New possibilities open up in using XRES to examine surface magnetism with grazing incidence, to examine magnetic multilayers, and to search for transferred small moments in random alloys using the site specificity. More speculative is to extend the measurements into the *inelastic* regime. An energy resolution of ~ 8 meV appears possible with inelastic x-ray scattering, and without the kinematic restrictions present in neutron inelastic scattering, attempts could be made to see excitations in the region 0.1 to 1 eV.

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Table I

Representative elements of the different possible magnetic series, together with the possible strong (E1) dipole transitions for resonant magnetic scattering, and the relevant x-ray energies and wavelengths ($E=12.398/\lambda$).

transition			edge	E (keV)	λ (Å)	edge	E (keV)	λ (Å)
3d	Fe	p-d	LII	0.72	17.22	LIII	0.707	17.54
4d	Rh	p-d	LII	3.146	3.94	LIII	3.004	4.13
5d	Pt	p-d	LII	13.27	0.93	LIII	11.56	1.07
4f	Gd	p-d	LII	7.93	1.56	LIII	7.24	1.71
4f	Gd	d-f	MIV	1.22	10.16	MV	1.19	10.42
5f	U	p-d	LII	20.95	0.592	LIII	17.17	0.722
5f	U	d-f	MIV	3.73	3.32	MV	3.55	3.49

Figure Captions

Fig. 1 Intensity of the scattered x-ray intensity from single crystal of USb (open points - upper) and NpAs (filled points - lower) as a function of the photon energy. The solid lines are fits to two resonances as suggested by atomic physics, (Taken from Ref. [11] and [12])

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. Note the logarithmic scale. 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 dependence). Peaks at $L=1.333$ ($4/3$) and $L=2.667$ ($8/3$) are from the 3rd-order contamination of the primary beam. The peak at $L=2.1$ is from the sample holder. (Taken from Ref. [11])

Fig. 3 Calculated "C domain fraction" in NpAs as a function of temperature. The C domains have their moments perpendicular to the surface of the crystal. The vertical arrows indicates phase transitions in NpAs, and the horizontal arrow indicates the value of $1/3$ expected for a random domain distribution. (Taken from Ref. [11])

Fig. 4 Scans in the $[0K2]$ direction from a single crystal of NpAs showing how the magnetic scattering changes with wavevector q and with temperature. Note the logarithmic scale. The horizontal width of the small bar indicates the instrumental resolution. The ordering temperature is $T_N = 172.8$ K. (Taken from Ref. [20])

Fig. 5 The width of the x-ray scans parallel to the magnetic propagation vector from a single crystal of $USb_{0.8}Te_{0.2}$ as a function of temperature. The symbols represent measurements around different peaks. Near 184 K the material exhibits two AF wavevectors, and the widths of both are plotted. (Taken from Ref. [24])

fig 1.
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fig 2. Jander et al. ICM-94

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fig. 4 Lander ICM-94
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