Resonant Enhancements at Nonmagnetic Ions: New Possibilities for Magnetic X-Ray Scattering

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Synchrotron experiments with uranium antiferromagnetic compounds have discovered large (>1000) enhancements of the magnetic scattering intensities at the K edges of nominally nonmagnetic anions, e.g., Ga and As. The width in energy, the position with respect to the white line, and the azimuthal and polarization dependencies permit one to associate the signal with transitions of $E1$ dipole symmetry from $1s$ to $4p$ states. In momentum space, the signal exhibits long-range order at the antiferromagnetic wave vector. We discuss possible channels capable of generating the observed enhancements.

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When the photon energy is tuned near a resonant edge in either scattering or absorption experiments, a considerable change occurs in the cross section. Most importantly, an excited state, which corresponds to the promotion of a core electron into an intermediate level, is formed. This process is followed by the decay of the intermediate into the ground state with photon reemission. As pointed out over ten years ago [1,2], there is a special interest when the electron shells involved in the excited state are spin polarized. The resulting theories and experiments have given rise to two new fields of magnetic studies at synchrotron sources, x-ray magnetic circular dichroism (XMCD) and resonant x-ray magnetic scattering (RXMS). XMCD is sensitive to the imaginary part of the anomalous scattering amplitude, whereas RXMS measures the total scattering amplitude, including both the real and the imaginary contributions. Both techniques have the advantage (over neutron scattering) that they are element and electron shell specific. In the case of XMCD, sum rules [3], which are based on atomic models, are of assistance in extracting spin and orbital contributions to the effective magnetic moments. In the course of developing these techniques, practitioners have focused almost without exception on elements that have well-established magnetic moments.

In this Letter, we report x-ray measurements at the K edges of Ga and As in the antiferromagnetic compounds UGa_3 and UAs, respectively, in which enhancements greater than 10^3 over the nonresonant intensity are observed. A large enhancement has been observed also in XMCD at the K edge of S in ferromagnetic US [4]. Although a quantitative interpretation of these effects is lacking, the measurements open up a new form of spectroscopy which, in principle, can be exploited in other, nonactinide containing, materials.

The experiments reported in this paper were performed at the ID20 [5] and XMaS beam lines of the ESRF, Grenoble, France. At both beam lines, a double crystal, Si(111), monochromator selects the appropriate x-ray energy, harmonics of higher incident energy are eliminated by the use of mirrors, and the scattering plane was vertical with σ-incident photon polarization. The experiments were first performed at ID20 on single crystals of UGa_3. This itinerant $5f$ system (primitive cubic $AuCu_3$ crystal structure) orders below $T_N = 67$ K with a moment of $\sim 0.7\mu_B$ localized around the uranium site and with a propagation vector $\mathbf{Q}_0 = (\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$ [6]. Initial experiments were performed at the U $M_{4,5}$ edges, which involve transitions between the core $3d$ and unoccupied $5f$ states. The measurements confirmed the presence of long-range antiferromagnetic order at $\mathbf{Q}_0$. The nonresonant magnetic scattering signal, which is present at $\mathbf{Q}_0$ for *all* photon energies, is greatly enhanced (by a factor of at least 10^5) at the actinide $M_{4,5}$ edges due to the resonant process [1,7], and intensities of over 10^5 counts/s (at 200 mA synchrotron current) were observed.

The incident photon energy was then tuned to the K edge of gallium (10.37 keV). An analyzer [pyrolytic graphite (008) with ~10% reflectivity] was used to distinguish between photons scattered with ($\sigma \rightarrow \pi$) or without ($\sigma \rightarrow \sigma$) a change of polarization, and to reduce the strong background due to fluorescence. At $\mathbf{Q}_0$, a large (by a factor of ~1000) enhancement of the nonresonant intensity was observed. The integrated intensity as a function of incident photon energy is given in Fig. 1(a). Also shown is the Ga fluorescence yield spectrum measured in the same

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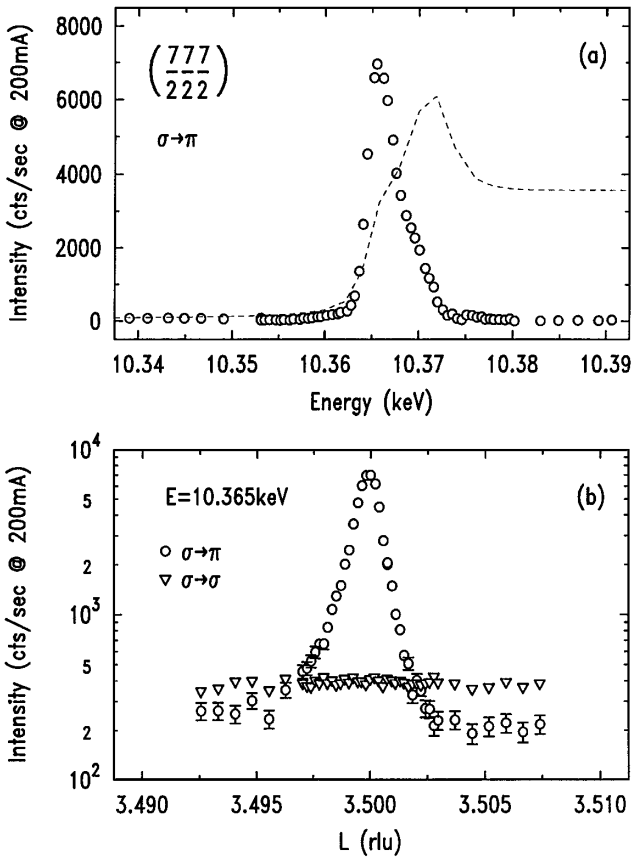

FIG. 1. Resonant intensity associated with Ga K edge in the antiferromagnetic UGa_3. (a) Data points ($T = 10$ K) are integrated intensity as a function of incident photon energy. The dashed curve superposed is the fluorescence yield spectrum. The tabulated value of the Ga K edge is 10.37 keV. All are measured in the $\sigma \rightarrow \pi$ channel. (b) Intensity at a photon energy of 10.365 keV for the antiferromagnetic Bragg reflection as a function of the longitudinal wave vector $[\xi\xi\xi]$, where these are coordinates in reciprocal space. The peaks occur at the antiferromagnetic wave vector, and their narrow width (in q space) indicates long-range real space correlations. The higher background in the $\sigma \rightarrow \sigma$ channel arises from the specular charge truncation rod.

experiment (dashed line). The position of the resonant peak in energy strongly suggests that the scattering is electric dipole ($E1$) in nature, i.e., involves $4p$ intermediate states of gallium. The signal is present only in the $\sigma \rightarrow \pi$ channel; again consistent, within the elementary atomic picture, of the $E1$ resonant process [1]. The energy width is $\sim$4 eV. This is greater than the expected inverse core-hole lifetime of $\sim$1.5 eV, and represents the extent (bandwidth) of $4p$ states contributing to the excitation process. Figure 1(b) shows the intensity as a function of position in reciprocal space. The signal has the periodicity $\mathbf{Q}_0$ and a width in momentum space indicative of long-range order.

Experiments were performed subsequently at the K edge of As (11.861 keV) in the compound UAs (fcc NaCl crystal structure), which has an ordered moment of $\sim 2\mu_B$ associated with the uranium ion at low temperature [8]. Close to the As K-edge energy, intensities of up to 8×10^4 counts/s in full polarization mode [LiF (440) with 6% reflectivity] were measured on ID20 at positions in reciprocal space defined by the antiferromagnetic structure. In energy, the width and position with respect to the As K edge are similar to the observations in UGa_3. An additional experiment (Fig. 2) was performed at the XMaS CRG beam line at the As K edge to determine the azimuthal dependence of the signal. Both these results, and the scattering angle dependence of the Bragg intensities, are consistent with the proposed $E1$ symmetry of the scattering potential, and make the possibility that the signal could arise from orbital ordering effects, such as found in $LaMnO_3$ [9] and V_2O_3 [10] or with an associated Templeton-like signal arising from charge scattering [11], remote. In addition, UGa_3 and UAs have different crystal and magnetic structures, making it unlikely that orbital ordering would be similar in the two materials.

Further information on the origin of the scattering process is provided by the (normalized) temperature dependence of the signal associated with the antiferromagnetic state measured with various probes in UGa_3, and shown in Fig. 3. The neutron signal, sensitive to the total ordered magnetic moment, is shown as crosses [12]. With $T_N = 67.2 \pm 0.2$ K, this is in good agreement with the susceptibility [6] and previous work [12]. The results at the M_4

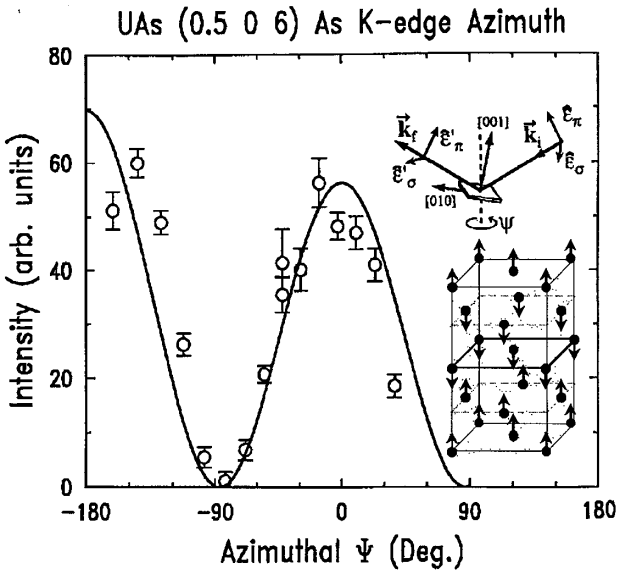

FIG. 2. Measurements at the As K edge of the integrated intensity in the $\sigma \rightarrow \pi$ channel of the $(0.5, 0, 6)$ reflection in UAs at $T = 20$ K as a function of the azimuthal angle around the normal to the [001]. See insets for geometry and schematic of the Fourier component of the magnetic structure of UAs that gives rise to this reflection, where the propagation vector of the structure is [100]. The azimuthal angles $\Psi = 0°, 180°$ correspond to the [100] axis lying in the scattering plane, defined by incident and scattered wave vectors $\mathbf{k}_i$ and $\mathbf{k}_f$, respectively. In the $\sigma \rightarrow \pi$ channel the cross section for $E1$ processes reduces to $(\mathbf{k}_f \cdot \mathbf{z})^2$, where $\mathbf{z}$ is the direction of the dipole, and this is shown as a solid line.

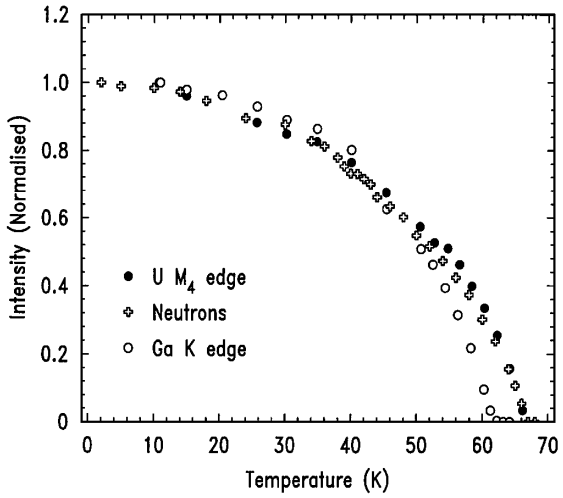

FIG. 3. The integrated intensity as a function of temperature for the following quantities in UGa_3. (i) Crosses: The magnetic $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ peak as measured by neutron diffraction on the D15 diffractometer at the Institut Laue Langevin [9]. (ii) Closed circles: The $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ reflection as observed (ID20) at the U M_4 energy. (iii) Open circles: The $(\frac{7}{2}, \frac{7}{2}, \frac{7}{2})$ reflection as observed (ID20) at the Ga K energy.

edge of U are shown as solid circles, and are in excellent agreement with the neutron results. Such agreement eliminates any potential problems of thermometry between the two experiments as well as considerations of sampling depth. The open circles give the temperature dependence of the signal at the Ga K edge. Measurements at a different Bragg reflection gave identical results. The signal at the Ga K edge clearly disappears at T^*, some 6 K *below* T_N. (The discontinuous nature of the magnetic phase transitions [8] in UAs make such measurements as a function of temperature more difficult to perform and interpret.)

In this context, we note that, in NMR/NQR experiments sensitive to the field at the Ga site, Ikushima *et al.* [13] have found a temperature interval of $\sim$6 K below T_N over which the Ga nuclear quadrupole resonance (NQR) signal shows a splitting, but no temperature dependence, whereas at lower temperature the splitting follows a standard Brillouin dependence. Although the unusual temperature dependence of the x-ray and NQR signals at the Ga site are not reflected in a change of lattice symmetry at either T_N or T^*, evidence for a change in the magnetic symmetry is provided by the thermal evolution of the field dependence of the bulk susceptibility [14]. In these latter experiments, the response for fields in the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions are equivalent for $T < T_N$, whereas this symmetry is broken below T^*. In parallel with this, a series of experiments and theory [15] have shown that the magnetic structures of the UX_3 (X = Ga, In, Pb) compounds are more complex than originally considered. In summary, we are persuaded that the x-ray experiment is indeed sensitive to an effect involving quasistatic long-range ordering on the Ga sublattice.

Since the interest in this paper is in signals at nominally *nonmagnetic* elements, it is useful to summarize previous experiments of this type. The first were those performed at the L edge of Pt in CoPt [16]. L-edge resonances involve transitions from core p states to unoccupied $5d$ states. In the case of Pt, these experiments were interpreted as an indication of an induced magnetic moment in the $5d$ shell. Similarly, a weak signal found at the L edge of Lu [17] was interpreted as indicating a small ($0.20\mu_B$) induced moment in the $5d$ band of Lu in the Dy-Lu alloy under investigation. More recently at ID20, a weak signal was found at the K edge of Ge and L edge of Pt in the compound UPtGe [18]. Thus, signals at these edges are not zero; the surprise in the present experiments is the oscillator strength. An alternative perspective is to realize that dipolar ($1s \rightarrow 4p$) enhancements over the nonresonant signal at *magnetic* transition-metal K edges, such as elemental Ni [19] or the ionic compound $RbMnF_3$ [20], have been found to be less than 1 order of magnitude, even though a substantial moment exists in the $3d$ shell. Such enhancements are thus at least 2 orders of magnitude smaller than we find on the *nonmagnetic* ions As and Ga.

In neither UGa_3 nor UAs is a large polarization expected in the $4p$ bands. No such effects are reported in neutron diffraction [8,12], and measurements of the Mössbauer effect on Sn doped into UGa_3 [21] have given a limit of $\sim 0.02\mu_B$ on the Ga site. Theory also suggests polarizations of this order of magnitude at the anion sites in the UX_3 compounds [15,22]. Thus, the origin of the enhancement must be sought elsewhere.

RXMS arises from an asymmetry in transition probabilities between the up and down spin channels. For a resonant signal on the Ga site, a number of conditions need to be met. The first requisite is that the dipole overlap integral between the $1s$ core and $4p$ intermediate state must be finite; this is the case. The second requisite, the existence of an asymmetry, may arise in a number of ways: (i) differences in the up/down spin dipole overlap integrals as induced by polarization of the orbitals [23]; (ii) differences in the occupation of the orbitals appropriate to the up/down spin channels (we note that these differences may be dynamic, i.e., on the scale of the intermediate state lifetime); (iii) differences in the resonant energies (or lifetimes) of the up/down spin channels.

Whereas we cannot identify the precise combination of (i) to (iii) that gives rise to the anomalous enhancement, we consider briefly some of the factors. For (i), further band structure calculations may establish its significance at the anion site. For mechanism (ii), a possible dynamic origin of the enhancement may be found in the short time scale of the resonant process (10^{-15} s). This opens the discussion to the sensitivity of the probe to bare electron states rather than the time-averaged correlations in quasiparticle bands, and questions the relevance of the small thermodynamic moment at the Ga site [15,21,22]. Finally, for (iii), we note that the hybridization of electronic states implies that the

antiferromagnetic character of the $5f$-projected states will polarize the wave functions at the anion site, as evidenced by the transferred hyperfine field measured in Ga NQR [13]. The resulting Zeeman splitting of the Ga $1s$ core levels will be a source of RXMS enhancement not seen by probes of the valence polarization.

In conclusion, the observation of unexpectedly large enhancements at the K edges of certain anions in uranium antiferromagnets opens up further possibilities for diffraction experiments (and XMCD) as an element specific probe. For example, studies at the K edges of anions allow more momentum space to be accessed than at the restrictive actinide M edges of $\sim$4 keV ($\sim$3.1 Å), as well as possibilities to perform pressure or very low temperature experiments, both of which require sample containment opaque to low energy photons. We may also ask whether such large effects are present when uranium is replaced with other cations. Finally, these experiments stimulate a growing need to examine, in a critical fashion, the basic formalism of the resonant scattering process.

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