

LETTER TO THE EDITOR

Large enhancement of x-ray magnetic scattering at the L edges of the 5d transition metal antiferromagnet K_2ReCl_6

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Online at stacks.iop.org/JPhysCM/15/L59**Abstract**

The x-ray resonant scattering cross-section of K_2ReCl_6 has been studied for energies near the L edges of rhenium. Below the Néel temperature of $T_N \sim 11$ K, additional peaks appear when the photon energy is tuned to the L_{II} or L_{III} edges. The peaks are found to rotate the incident (linear) polarization, and have a Lorentzian lineshape in energy. The peaks are ascribed to resonant magnetic scattering, where a dipolar transition connects 2p–5d states. At resonance the scattering amplitude is of order $\sim r_0$ per atom, roughly two orders of magnitude greater than that of the bare magnetic scattering.

(Some figures in this article are in colour only in the electronic version)

X-rays now play a pivotal role in our understanding of magnetism in solids [1]. In many situations the enormous brightness of modern synchrotron sources overcomes the weakness of the non-resonant magnetic scattering amplitude. This is of order $\approx 0.01 r_0$ for a single electron, where r_0 is the Thomson scattering length [2]. However, when all factors are included the measured magnetic intensity is typically 10^{-7} of the charge intensity, as was the case in the pioneering experiments of de Bergevin and Brunel on NiO [3]. A second key characteristic of synchrotron radiation, the freedom to tune the incident x-ray energy to any desired value, has led to the discovery of resonant processes, where the sensitivity to magnetism is greatly enhanced for photon energies in the vicinity of certain absorption edges [4]. Values of the resonant magnetic scattering amplitude per atom range from $\sim 0.05 r_0$ in the case of the L_{II}/L_{III} edges of the rare earths, $\sim 10 r_0$ for the M_{IV}/M_V edges of the actinides [5], and up to $\sim 100 r_0$ for the M_{IV}/M_V edges of the rare earths [4]. This increased sensitivity to magnetism is of course evident in both scattering and absorption geometries, which are related to each other by the optical theorem [1].

In the hard-x-ray regime, the largest resonances occur in the 5d transition metal series. To date most of our experimental knowledge of such effects in this series comes from x-ray magnetic circular dichroism (XMCD) experiments [6]. Large effects in a scattering geometry were first predicted by Carra *et al* [7] for a ferromagnet, and later confirmed through experiments on a CoPt alloy [8]. Here we extend this work with the first study of a 5d antiferromagnetic compound using x-ray resonant scattering techniques. Our results show that the magnetic scattering amplitude at the L edges of 5d ions can exceed r_0 , opening up new possibilities for the study of the magnetic properties of antiferromagnets containing ions from this row of the periodic table.

In contrast to that of the 3d and 4f series, the magnetism of compounds containing elements from the 4d/5d series is distinguished by the fact that the 4d/5d electrons are much more delocalized. One consequence of this is that in certain compounds the magnetic electrons can form part of a covalent bond. In K_2IrCl_6 , for example, neutron scattering experiments have shown that as much as 30% of the Ir moment is transferred onto the Cl site [9]. More generally, an increasing number of 5d compounds are being discovered that show novel effects. Examples include: the continuous metal-insulator transition in $\text{Cd}_2\text{Os}_2\text{O}_7$ [10], which is posited to be driven by antiferromagnetic correlations, making it a rare example of a Slater transition; $\text{Er}_5\text{Ir}_4\text{Si}_{10}$, where an unusual coupling has been discovered between a charge-density wave and local moment magnetism [11]; CuIr_2S_4 , where the Ir ions are coordinated in 3D, and yet the system undergoes a simultaneous charge-ordering and spin-dimerization transition [12], behaviour normally confined to 1D compounds. Particular interest in rhenium-based compounds has been stimulated by the discovery of the pyrochlore superconductor $\text{Cd}_2\text{Re}_2\text{O}_7$ [13, 14].

One attractive feature of using x-ray resonant scattering to probe the magnetism of 5d compounds is that the L edges involve 2p-5d transitions, so any resonant process yields a direct measure of the ordering of the 5d electrons. In addition, the L edges of the 5d compounds fall in the hard-x-ray region, resulting in the use of complicated in-vacuum diffractometers, etc, being unnecessary and thereby considerably simplifying the experiments.

K_2ReCl_6 was chosen for our experiments as it is a simple insulating, commensurate antiferromagnet. At room temperature, K_2ReCl_6 adopts the cubic antiferroite structure (space group $Fm\bar{3}m$, $a = 9.861 \text{ \AA}$). On cooling, it undergoes a series of displacive structural phase transitions at 111, 103, and 76 K [15]. These transitions are driven by correlated, rigid-body rotations of the Cl octahedra surrounding each Re ion. As the atomic displacements associated with these transitions are very small [15, 16], it will suffice here to label reciprocal space using cubic notation. Around 12 K a further transition is observed to an antiferromagnetically ordered state. In this phase the moments on the Re^{4+} ions order into a type I structure, with a magnitude equal to $2.7(3) \mu_B$ [16, 17]. Neutron scattering measurements show a significant deviation from the free ion form factor, indicating large covalency effects [17].

Preliminary x-ray experiments were performed at the X22C beamline, NSLS, Brookhaven National Laboratory, USA. All of the data presented here were taken in a second experiment at the XMaS beamline, ESRF, France [18]. A single crystal of K_2ReCl_6 was mounted in a cryostat (base temperature 1.7 K) so as to allow access to reflections of the type $(hk0)$ in the vertical scattering plane of the instrument, and oriented such that the $[hh0]$ direction was vertical when $\theta = 0$. The mosaic spread of the crystal was 0.15° . Experiments were performed either in a two-axis geometry, or when required a polarization analyser was employed. The bending magnet radiation feeding the diffractometer is predominantly plane polarized (97.5%) in the horizontal plane. By mounting an analyser crystal set for 90° scattering, and then rotating around the scattered beam, it is possible to isolate the unrotated ($\sigma-\sigma$) from the rotated ($\sigma-\pi$) components in the scattering. The analyser crystals used in our experiments were LiF(440) and pyrolytic graphite (008) at the L_{II} (11.958 keV) and L_{III} (10.535 keV) edges, respectively.

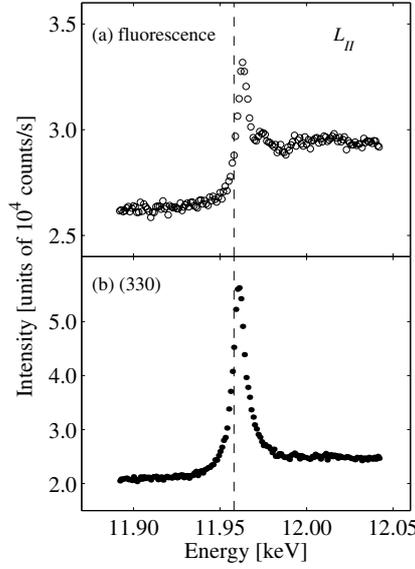


Figure 1. Two-axis measurements in the vicinity of the Re L_{II} edge. (a) The energy dependence of the fluorescent radiation measured in the background, away from any Bragg peaks. (b) The energy dependence of the (330) peak at $T = 1.7$ K. The dashed vertical line is the nominal position of the L_{II} edge (11.958 keV). For the fluorescence measurements the beam-defining slits were opened from 1.5×2.5 to 6.0×6.0 mm².

With the diffractometer configured in a two-axis mode and the incident photon energy set to that of the Re L_{II} edge, a search was made at $T = 1.7$ K for peaks of type $(hh0)$, h odd, which are known to be magnetic from earlier neutron scattering measurements [16, 17]. Peaks were found at all positions investigated with intensities of order $50\,000$ counts s^{-1} . Once the orientation of the crystal had been optimized for a given reciprocal-lattice point, the energy of the photon beam was scanned keeping the wavevector transfer constant. In figure 1(b) we show the energy dependence of the (330) peak, which exhibits a sharp resonance a few electron volts above the nominal position of the L_{II} edge. The fluorescence from the sample was measured by rotating it a few degrees off the Bragg condition and repeating the energy scan, with the results shown in figure 1(a). A strong ‘white line’ is evident, peaking at approximately the same energy as the resonance of the (330) peak.

To establish the origin of the (330) peak, polarization analysis was performed of the $(hh0)$, h odd, peaks at the L_{II} edge. For this part of the experiment a LiF(440) analyser was mounted in the scattered beam. The results for the (330) and (550) peaks are summarized in figure 2. It is clear that the peaks are predominantly found in the $(\sigma-\pi)$ channel. We note that the analyser has the effect of removing the fluorescence from the sample, which is evident as a high-energy tail in the two-axis experiments. It is also apparent from the fact that the resonance falls close to the position of the L_{II} edge, and does not exhibit any additional structure, that the resonance corresponds to a dipolar (E1) transition, 2p–5d.

For a commensurate antiferromagnet, the x-ray magnetic resonant scattering amplitude for a dipolar transition can be expressed in the form

$$A_{res} = -a_{mag} \frac{(1 - ix)}{(1 + x^2)} \begin{pmatrix} 0 & z_1 \cos \theta + z_3 \sin \theta \\ z_3 \sin \theta - z_1 \cos \theta & -z_2 \sin 2\theta \end{pmatrix}. \quad (1)$$

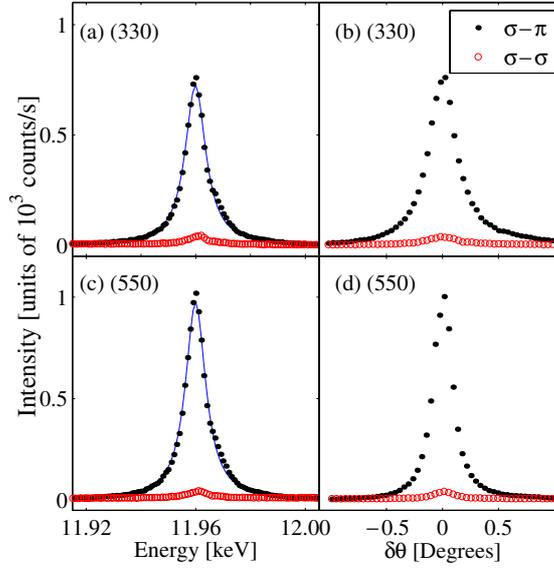


Figure 2. A summary of the energy and polarization dependence of the scattering near the Re L_{II} edge. (a) and (b) show the variation with energy and θ of the (330) peak for the two polarization channels. (c) and (d) show data for the (550) peak. The solid curves in (a) and (c) are fits to the resonant lineshape discussed in the text with a full width $\Gamma = 9.0(1)$ eV.

Here x is defined by

$$x = \frac{(E_f - E_i) - \hbar\omega}{\Gamma/2}.$$

a_{mag} is the magnetic scattering amplitude per atom, Γ is the full width of the resonance, and θ is the scattering half-angle [4, 19]. Following the usual convention, we have expressed the amplitude as a matrix in a basis of the linear components of the polarization perpendicular (σ) and parallel (π) to the scattering plane, for the incident and scattered beams. Equation (1) shows that the scattering amplitude in the (σ - σ) channel is zero, while in the rotated (σ - π) channel it has a value equal to $(z_3 \sin \theta - z_1 \cos \theta)$. Here z is a unit vector along the direction of the magnetic moment, with Cartesian components defined such that z_3 is antiparallel to the direction bisecting the incident and scattered beams, z_2 is perpendicular to the scattering plane, and z_1 is related to the other two components in a right-handed sense. Thus our observation that the predominant response occurs in the (σ - π) channel is explicable in terms of a resonant magnetic scattering processes, involving a dipolar 2p-5d transition. The ratio of intensities in the (σ - π) to (σ - σ) channels is observed to be approximately 17. This ratio is much smaller than expected from the efficiency of the polarization analyser measured at the (660) reflection, which would lead to a leakage signal into the (σ - σ) channel suppressed by a factor of 85 relative to the (σ - π) response. From this we conclude that either a very weak structural distortion accompanies the magnetic transition, or that the scattering process involves higher-order transitions beyond the dipolar one considered here. Further experiments are required to clarify this point. The full width of the resonance deduced from a fit of equation (1) to the data is $\Gamma = 9.0(1)$ eV. This is much greater than the value of 4 eV found to give a good account of the data in a study of ferromagnetic CoPt. The reason for this discrepancy is unknown, and cannot be explained by instrumental resolution which is ~ 1.8 at 12 keV. Neither can it be explained by the rather weak absorption corrections at the L_{II} edge. Unlike the case of the L_{III}

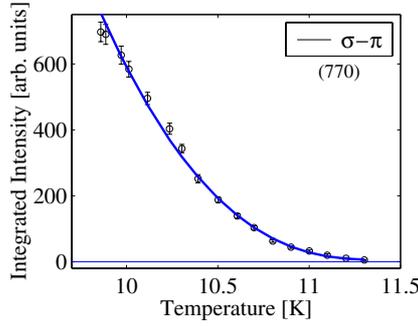


Figure 3. The temperature dependence of the integrated intensity of the (770) peak measured in rocking scans. The solid curve is a guide for the eye.

edge discussed below, the absorption corrections at the L_{II} edge were found to have negligible effect on the energy lineshape.

Attempts were made to determine the temperature dependence of the magnetic order parameter. It only proved possible to obtain data over a range of temperature below T_N , due to problems with the cryostat. Figure 3 displays the temperature dependence of the integrated intensity of the (770) reflection. The intensity is seen to drop smoothly to zero above ≈ 11.2 K, with no clear evidence for a first-order transition reported in earlier studies [17]. The reason for this discrepancy is unknown.

Experiments were also performed with the incident photon energy tuned to the L_{III} edge, with the results shown in figure 4. The energy dependence of the (330) peak is plotted in figure 4(b), where the resonance now appears to have two distinct components, one near the nominal energy and a second weaker component lying approximately 6 eV higher in energy. On first inspection it might be thought that this structure reflects some feature in the electronic structure of the material, or the opening up of a new resonant channel. However, we believe neither of these to be the case. Instead we consider that the structure arises from an increase in absorption at the energy of the strong white line. To estimate the effect of the white line on the shape of the resonance we have used the fluorescence to derive the energy dependence of the absorption coefficient, μ , using a standard method [20]. In a kinematical model of the scattering process, the integrated intensity is corrected by multiplying by μ [21]. In figure 4(c) we show the outcome of this procedure. The resonance now has a single component, and a fit of the lineshape to equation (1) yields a width of $\Gamma = 8.6(2)$ eV, similar to the value found at the L_{II} edge.

The scattering was also investigated for photon energies around the L_I edge (12.527 keV). In this case no magnetic peaks were detected. Moreover, it proved not to be possible to detect any non-resonant magnetic scattering with the configuration used in this experiment, probably due to the very low reflectivity ($\sim 1\%$) of the polarization analyser crystal.

It is valuable to obtain an estimate of the amplitude of the resonant magnetic scattering (a_{mag} in equation (1)), to compare it to that found in the other series of the periodic table. To achieve this we have attempted to scale the intensity of a magnetic Bragg peak to the closest-lying charge peak. The main problem with this method is the difficulty in correcting for extinction effects, so our value should be viewed as an order-of-magnitude estimate. The integrated intensities of the (770) magnetic and (660) charge peaks were obtained from rocking scans in a two-axis geometry at the L_{II} edge. The intensities were corrected for the Lorentz factor, and the geometrical factor which appears in the absorption correction. The ratio of

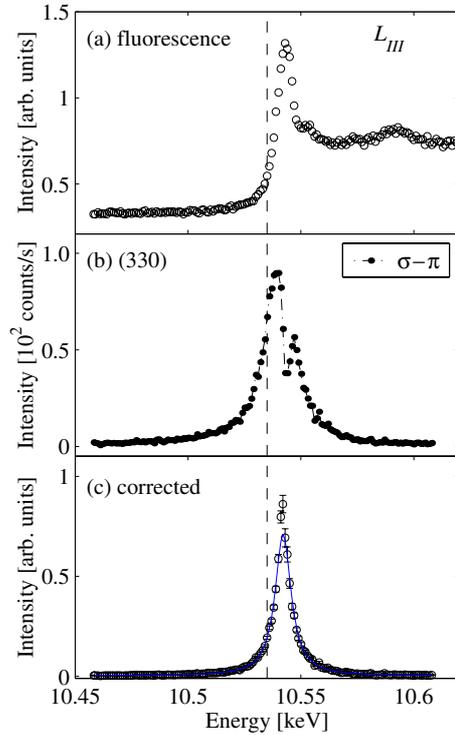


Figure 4. (a) The energy dependence of the fluorescent radiation near the Re L_{III} edge. (b) The energy dependence of the (330) peak in the ($\sigma-\pi$) channel measured at $T = 1.7$ K with a polarization analyser. The dot-dashed curve is a guide for the eye. (c) The intensity of the (330) peak corrected for the absorption derived from the fluorescence shown in (a). The solid curve is a fit to the resonant lineshape discussed in the text. The vertical dashed curve is the nominal position of the L_{III} edge (10.535 keV).

integrated intensities was then found to be $R_{measured} = I_{(770)}/I_{(660)} = 0.0022(1)$. To calculate the expected intensity of the charge peak, a cubic unit cell was assumed, the dispersion corrections were taken from Cromer and Liberman [22], and the atomic form factors calculated from the parametrization given in the *International Tables of Crystallography* [23]. These calculations yielded a value of $I_{(660)} = 2(1) \times 10^4 r_0^2$, where the large uncertainty reflects the difficulty of calculating accurate dispersion corrections at an absorption edge. For the four magnetic Re^{4+} ions in the unit cell of the type I antiferromagnetic structure, $I_{(770)} = 16 a_{mag}^2$. From these considerations we deduce the value $a_{mag} = 1.7 r_0$.

Thus far we have neglected the trigonometric factors which appear in equation (1). While the inclusion of these terms will increase our estimate of a_{mag} , without knowing the detailed magnetic domain structure of the sample, this cannot be done in a reliable way. (It is perhaps worth noting that experimentally the intensities of the magnet peaks varied only very slowly with the scattering angle 2θ (figure 2). This suggests that due to the magnetic domain structure the $\sin \theta$ and $\cos \theta$ terms cancel out as the scattering angle is increased.) Our estimate of a_{mag} is the of same order of magnitude as that reported for ferromagnetic CoPt alloys from scattering and XMCD experiments [6, 8]. This is a somewhat surprising result, as the moment carried by the Pt atoms is approximately an order of magnitude smaller than that carried by the Re ions in K_2ReCl_6 .

Finally, we address the question of the branching ratio of the intensities of the magnetic scattering at the L_{II} and L_{III} edges. For dipolar processes these arise from $2p_{1/2} \rightarrow 5d_{3/2}$ and $2p_{3/2} \rightarrow 5d_{5/2}$ transitions, respectively. For the rare earths the branching ratio varies across the series: it exceeds unity for the light rare earths, while for the heavy rare earths it is less than unity. These results (from both scattering and XMCD experiments) stand in contrast to band structure calculations, which provide a constant ratio. It has been shown that it is only when the ‘breathing’ of the spatial extent of the 5d states, due to interactions with the localized 4f moments, are included in the calculations that satisfactory agreement with experiment is achieved [24]. In the case of the 5d series, the only systematic study of the branching ratio that we are aware of is the XMCD study of Os, Ir, Pt, and Au in Fe [6]. Here it was found that the ratio was approximately equal to -2 , in agreement with a simple one-electron picture, with the exception of Os where it was closer to 1. (In very general terms, the scattering cross-section is proportional to the absolute square of the XMCD signal.) In our case the ratio $I_{L_{II}}/I_{L_{III}}$ was obtained from the integrated intensities of the (770) peak, corrected for absorption, measured in two-axis mode at the two edges. We obtain a value of 2.3(0.5), with the large uncertainty arising from the need to correct the data for the absorption due to the presence of the intense white line (see, for example, [20]).

In conclusion, we have observed x-ray resonant magnetic scattering from the 5d antiferromagnet K_2ReCl_6 at the L edges of the Re ions. Our results are consistent with the existence of a 2p–5d dipolar transition, which yields a scattering amplitude of order r_0 per Re atom. This represents an enhancement of approximately a factor of 10^4 in the cross-section over the bare magnetic scattering, which makes feasible experiments on other interesting antiferromagnets containing 5d transition metals.

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