High-resolution magnetic x-ray diffraction from neodymium

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High-resolution studies of antiferromagnetic ordering have been made on the rare-earth metal neodymium, using resonant magnetic diffraction at x-ray energies near the L_{II} and L_{III} absorption edges. A single domain of the double-**q** magnetic structure has been observed directly in zero magnetic field. Detailed measurements of the temperature dependence of the modulation vector over the temperature range 11.5–20 K showed no sign of any lock-in to commensurate values. The ordering was found to be double **q** over a wider temperature range than previous measurements would indicate.

I. INTRODUCTION

The magnetic ordering in rare-earth neodymium has been studied for over 30 years,[1] but continues to reveal new surprises. The principal technique has been neutron scattering. However, in recent years the availability of intense x-ray beams from synchrotron sources has allowed the investigation of magnetic structures using the weak magnetic x-ray interactions,[2–4] which may be enhanced by using x-ray energies close to certain absorption edges of the element being studied.[5,6] This paper reports an x-ray study of this element in the temperature range 11.5–20 K. The sample ordered into a *single magnetic domain*, allowing direct observation of the 2**q** magnetic structure of neodymium with no applied magnetic field. High-wave-vector-resolution measurements show no sign of any lock in of the wave vectors to commensurate lengths. Neodymium is the lightest rare-earth element to be investigated this way, and continues our work on the heavy and mid rare earths.[7–10]

On cooling below the Néel temperature of 19.9 K, neodymium has been shown to adopt a series of sinusoidally modulated magnetic structures with the number of modulation wave vectors increasing from one just below the Néel temperature to four in the lowest temperature phase.[1,11–14] These structures have been believed to be incommensurate with the crystal lattice. However, Lebech, Wolny, and Moon[15] have recently suggested that many of these apparently incommensurate structures are in fact ''higher-order commensurate,'' with modulation **q** vectors of specified length and angle, tilted so that they fit the crystal lattice. Magnetic x-ray scattering offers much higher wave vector resolution than neutron scattering, thus allowing us to distinguish more easily between incommensurate and commensurate structures.

The crystal structure of neodymium is double-hexagonal close packed (dhcp), in which there are two Nd sites, with local hexagonal and cubic site symmetry. Magnetic order occurs mainly at the hexagonal sites on cooling through $T_N = 19.9$ K, with weaker induced moments on the cubic sites.[16] Previous measurements[14,17] suggest that there is a weakly first-order transition at the Néel temperature to a single-**q** structure, with the **q** vector pointing along a {100}-type direction. This phase is also expected from a Landau-type theory.[18] Satellites appear at $\pm\mathbf{q}$, lying in the basal plane around reciprocal lattice points. If only one single-**q** antiferromagnetic domain is present, there will be just two satellites, but a hexagonal array of six satellites will result from occupation of all three possible domains. The single-**q** phase is believed to persist for about 1 K below T_N; then, there is another weakly first-order transition at which the **q** vectors move away from these symmetry directions, and a 2**q** structure is formed.[11,12,18–20] This would give the satellite pattern shown in Fig. 1. Our measurements were carried out in the range 11.5–20 K so are restricted to the 1**q** and 2**q** regions.

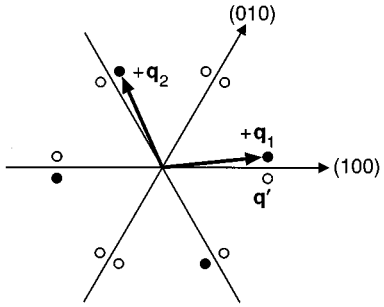

FIG. 1. Pattern of magnetic satellites seen around a reciprocal lattice point in the 2**q** phase of neodymium. When all three antiferromagnetic domains are present there are 12 satellites, shown as the solid and open circles. A single-domain sample will produce only four satellites, for example, those represented by the solid circles. Also shown are the coupled **q** vectors that give rise to these four satellites.

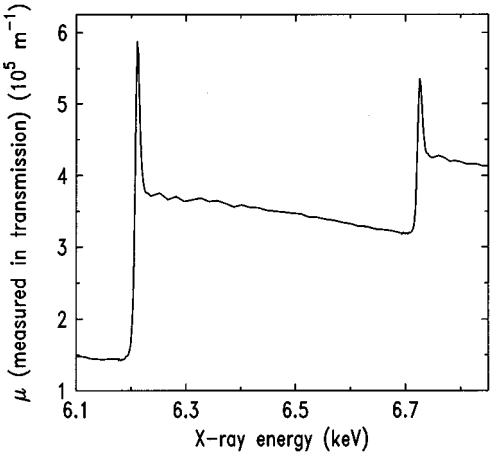

FIG. 2. L_{II} and L_{III} absorption edges of Nd, measured in transmission with a foil.

II. EXPERIMENTAL DETAILS

Our first observations of resonant magnetic diffraction were made on station 9.4 at Daresbury SRS. The data reported in this paper were collected at station X22C at the NSLS, Brookhaven National Laboratory. Incident x-ray energies were in the range 6.1–7.2 keV; this includes the L edges of neodymium. A solid-state detector was used to discriminate elastically scattered x rays from a fluorescent background. Our sample was a high-purity single crystal prepared by the solid-state strain-anneal technique at elevated temperatures in UHV.[21] A face a few mm^2 in area was cut perpendicular to the (001) direction. The sample surface was etched using concentrated nitric acid, and then washed with water and acetone immediately before mounting under vacuum in a closed-cycle refrigerator. The crystal had a mosaic spread of 0.03° full width at half maximum (FWHM) and was initially oriented so that the scattering plane contained the (001) and (100) directions, although the cryostat and sample could be tipped a few degrees away from this plane.

Since the x rays must enter and leave the sample through the **c** face, only scattering vectors fairly close to $(00l)$ were obtainable. The satellites we investigated were of the form $(q_h q_k l)$. Detailed measurements were performed on satellites around (005); we also observed similar intensity satellites around (007) and (009). The FWHM resolution in the basal plane at the charge peak (004) was $\sim 0.0005\tau_{100}$ in the (100) direction and $\sim 0.007\tau_{100}$ in the (120) direction, perpendicular to (100) and to the scattering plane. The positions of satellite peaks could be determined to an accuracy 5–10 times better than this. The maximum count rate for the $+\mathbf{q}_1$ satellites around (005) was $\sim 3000\ \mathrm{s}^{-1}$ near the L_{II} edge; this was $\sim 10^{-6}$ that of the (008) charge peak.

III. RESONANT ENHANCEMENTS

Magnetic satellites about the reciprocal lattice point (005) were observed using x-ray energies close to the L_{II} and L_{III} absorption edges, 6.722 and 6.208 keV, respectively. In order to correct these results for sample absorption, which varies strongly near the edges, the transmission of a thin (approximately 4 μm) Nd foil was also measured as a function of energy. After normalization at one energy, these transmission results, shown in Fig. 2, gave good agreement with earlier measurements[22,23] over the whole energy range. The energy dependence of the absorption-corrected magnetic signals at the L_{II} and L_{III} edges are shown in Figs. 3(a) and 3(b). The energies were linked to the known values of the L edges to an accuracy ~ 1 eV by observations of fluorescence from the sample.

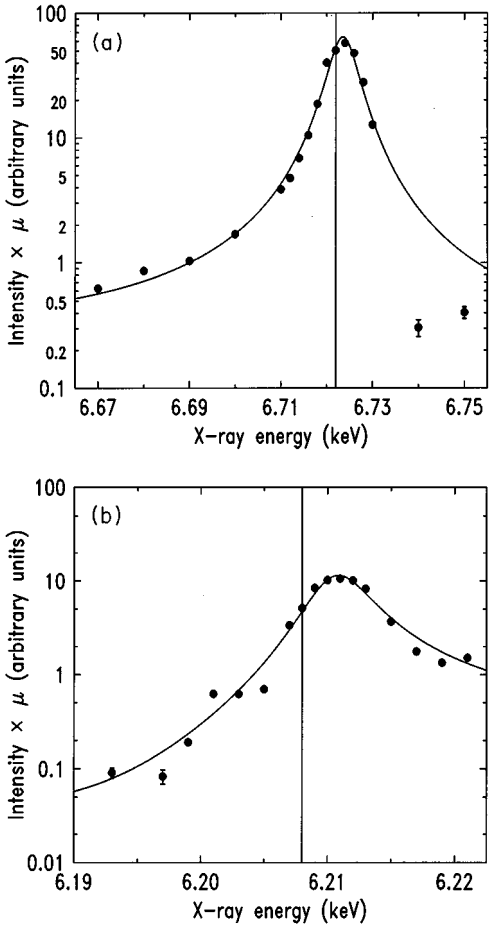

FIG. 3. Absorption-corrected resonant magnetic scattering intensity as a function of energy near (a) the L_{II} edge, (b) the L_{III} edge. The data are the height of a fixed-width Lorentzian peak fitted to a (100) scan through the $+\mathbf{q}_1$ satellite of (005) at 11.5 K, normalized to incident beam intensity. Note the logarithmic scale. The vertical lines indicate the positions of the absorption edges. Each solid curve is a least-squares fit using the square modulus of the sum of a Lorentzian amplitude (which varies in phase over the resonance) plus a constant amplitude of fixed phase. In (a) the center of the Lorentzian is 6723.6(3) eV, the width is 6.8(5) eV, and the enhancement over the nonresonant background is 17^2. The 6.74 keV point, which was verified by repeating the measurements, is significantly below the line and has been excluded from the fit. This suggests that our resonant line shape is only a good first approximation to the data. In (b) the corresponding values are 6210.6(3) eV, 5.3(4) eV, and 8^2.

It will be noted that the peak in the L_{II} response occurs ~ 2 eV above the edge and the L_{III} peak is ~ 3 eV above the edge. This can be compared with the other light rare-earth element in the literature, Sm,[7,10] where the L_{II} peak is just above the edge, but the L_{III} peak is ~ 4 eV below the edge. The "branching ratio" between the L_{II} and L_{III} intensities is

TABLE I. Absorption-corrected L_{II}/L_{III} branching ratios for the rare earths, where available.

Rare earth	Sample used	Absorption-corrected L_{II}/L_{III} branching ratio	Reference
Ce			
Pr	Ho-Pr alloy	>1	25
Nd	element	6	this work
	Nd_2CuO_4	~100	24
Pm			
Sm	element	<0.5	7, 10
Eu	$EuAs_3$	~0.5	26
Gd	GdSe	~1	9
	$GdNi_2B_2C$	~1[a]	27
Tb	element	~1	28
Dy	$Dy_{0.6}Lu_{0.4}$ alloy	[b]	29
Ho	element	~0.1	30
	$HoNi_2B_2C$	<1	31
Er	element	<1	32, 33
Tm	element	<0.02	34
Yb			
Lu	$Dy_{0.6}Lu_{0.4}$ alloy	[b]	29

[a]Not absorption corrected.
[b]Only data at the L_m edge reported.

of great interest: Hill *et al.*[24] point out that there is some tendency for a systematic variation of this quantity along the rare-earth series. Rare-earth ions with more than seven $4f$ electrons seem to favor enhancement at the L_{III} edge, and those with less than half filling of the $4f$ shell tend to have larger L_{II} enhancements. Table I summarizes for the rare earths the L_{II}/L_{III} branching ratios presently known to us. The number of $4f$ electrons cannot be the only factor determining these ratios. Sm^{3+} ions have only five $4f$ electrons but the L_{III} response is greater than the L_{II}.[7,10] The cases of Eu^{2+} ions [in $EuAs_3$ (Ref. 26)] and Gd^{3+} ions [in GdSe (Ref. 9)] are particularly interesting, since both have seven $4f$ electrons yet they have different branching ratios. The very recent work of Hill *et al.*[24] on resonant enhancement of magnetic scattering from Nd^{3+} ions in Nd_2CuO_4 gives an L_{II}/L_{III} enhancement ratio of ~100. Their results were not corrected for absorption, but after applying our absorption data to the intensities they report, the ratio remains ~100. This is a very significant difference from metallic Nd.

A preliminary theoretical analysis of resonant magnetic x-ray scattering in rare-earth metals has been carried out[35] and systematic calculations are underway.[36] It appears that we still have much to learn about the influence of ionic structure and surroundings on the resonant enhancement of magnetic scattering in the rare earths.

IV. TEMPERATURE DEPENDENCE OF THE 2q MAGNETIC STRUCTURE

X rays with an energy of 6.722 keV were used to investigate the magnetic structure and temperature variation of the modulation vector $\mathbf{q}_1$. Within the volume of the sample illuminated by the x-ray beam (~1 mm^2 × a few micrometers depth), well below T_N we observed a *single* domain of a double-**q** structure; i.e., a series of scans around (005)

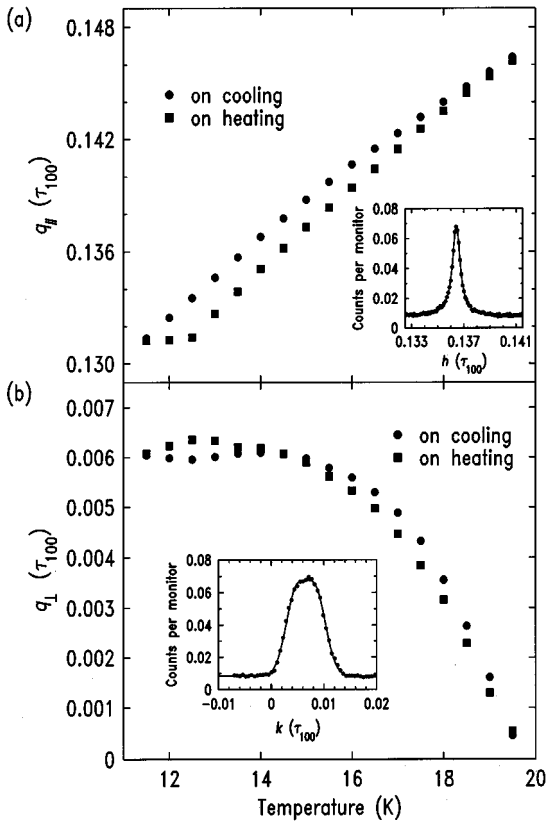

FIG. 4. Temperature variation of the components of $\mathbf{q}_1$ (a) parallel and (b) perpendicular to the (100) direction. (A temperature calibration shift of 1.5 K has been applied to obtain the correct T_N of 19.9 K.) The insets show data taken at 15.5 K on cooling. In (a) is a (100) scan through the $+\mathbf{q}_1$ satellite of (005) fitted with a variable-width Lorentzian, and in (b) is a (120) scan through the same satellite; this was fitted with a flat-topped line shape to represent the angular acceptance of the detector. This inset also shows no satellite centered at $k \sim -0.007\tau_{100}$ (the position labeled $\mathbf{q}'$ in Fig. 1), which would arise from a different domain to the single one observed.

showed that only the magnetic satellites represented as solid circles in Fig. 1 had measurable intensity. For example, scans through the $+\mathbf{q}_1$ satellite are shown as insets in Fig. 4; the inset to Fig. 4(b) shows that the $\mathbf{q}'$ satellite, which would indicate the existence of a second domain, was not present. A multidomain double-**q** structure would produce the 12 satellites shown in Fig. 1, and up until now, the 2**q** nature of the ordering has only been indicated indirectly by the observation of weak harmonics[11] or by the application of a magnetic field.[12] In this experiment we have observed a single domain of the double-**q** structure in zero field. The double-**q** character of the ordering was confirmed by the fact that the two **q** vectors were not exactly along the symmetry directions and were tilted in the expected directions. The surface of the sample was nominally perpendicular to **c** so should not favor a particular domain orientation, but this same domain was always observed on several temperature cycles through T_N.

The advantage of a single domain lies in the reduction of the number of satellites a given structure will produce. This is very helpful when attempting to identify an unknown magnetic structure. The pattern of satellites produced by a multidomain sample may not allow the structure to be deter-

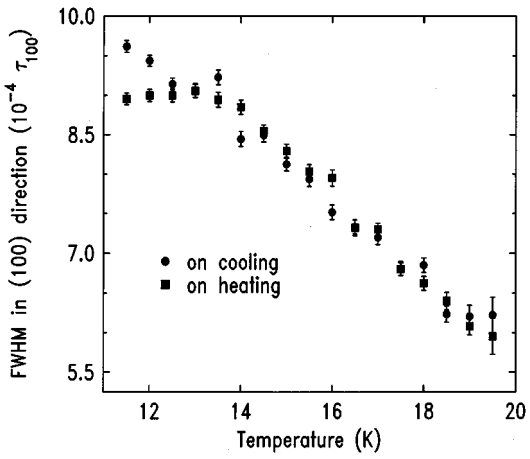

FIG. 5. Temperature variation of the width in the (100) direction of the $\mathbf{q}_1$ satellite of (005) on heating and cooling.

mined: There could be several possible structures that would produce the same pattern. A single domain may give a pattern unique to one structure. Early experiments on neodymium would have benefited enormously from the clarity offered by single-domain samples.

We observed the satellites at $\pm\mathbf{q}_1$ in order to determine $\mathbf{q}_1$ with high accuracy. The values of the components of $\mathbf{q}_1$ parallel and perpendicular to the (100) direction are shown in Fig. 4 as a function of both increasing and decreasing temperature. The parallel component of $\mathbf{q}_1$ has the greater accuracy because of the smaller width of the resolution ellipsoid in that direction. It is clear that there is hysteresis in the length of $\mathbf{q}_1$ and that this hysteresis decreases towards T_N. We attribute this hysteresis to pinning of the modulation repeat distance by minor inhomogeneities in the crystal; we would expect this pinning to be less effective near T_N. We also note that the wave vector width of the satellites decreases towards the expected resolution width as T_N is approached (Fig. 5): This is also what would be expected if pinning of the **q** vector to nonequilibrium lengths decreases towards T_N. No sign of lock in of the **q** vectors was observed at any temperature, and the parallel component goes smoothly though the value of 1/7 near T_N; thus, there is no evidence for the applicability of ''higher-order commensurate'' ideas[15] in this temperature region.

The 2**q** character of the ordering persisted up to ~0.2 K from T_N. This leaves a much smaller temperature region than has been previously reported for the single-**q** structure. However, it is possible that the ''near-surface'' region of our crystal, which is probed by x rays, behaves somewhat differently from the bulk of crystals that have been investigated by neutrons.

V. CONCLUSION

This work has shown the technique of resonant magnetic x-ray scattering to be a very useful complement to magnetic neutron diffraction. The ability of x rays to probe a small region of the crystal has allowed us to observe a single domain and hence to observe directly in zero field the double-**q** magnetic structure of neodymium. The high wave vector resolution of the measurements of the temperature dependence of the **q** vector in the double-**q** phase casts doubt on the claim that this structure is ''higher-order commensurate.'' We look forward with interest to extending these measurements into the lower-temperature region, where a further series of fascinating phase transitions takes place.

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