K-edge resonant x-ray magnetic scattering from a transition-metal oxide: NiO

J. P. Hill
Department of Physics, Brookhaven National Laboratory, Upton, New York 11973

C.-C. Kao
National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York 11973

D. F. McMorrow
Department of Solid State Physics, Risø National Laboratory, DK-4000 Roskilde, Denmark

(Received 9 December 1996)

We report the observation of resonant x-ray magnetic scattering in the vicinity of the Ni *K* edge in the antiferromagnet NiO. An approximately twofold increase in the scattering is observed as the incident photon energy is tuned through a pre-edge feature in the absorption spectrum, associated with quadrupolar $(1s \rightarrow 3d)$ transitions. No enhancement is observed at the dipolar $(1s \rightarrow 4p)$ maximum. The quadrupolar resonant scattering amplitude is estimated to be $\sim 0.01 r_0$. [S0163-1829(97)50214-1]

Resonant x-ray magnetic scattering exploits enhancements in the cross section occurring when the incident photon energy is tuned through an atomic absorption edge. These enhancements are due to second-order processes in the interaction Hamiltonian.[1] Large enhancements were first observed at the L_{III} and L_{II} edges in Ho (Ref. 2) and explained in terms of electric multipole transitions.[3] The size of the enhancement is controlled by the matrix elements connecting the initial and intermediate states, the lifetime of the virtual core hole created, and the degree of polarization of the levels involved. Thus, in addition to the *L* edges of the rare earths ($2p \rightarrow 5d$ dipole and $2p \rightarrow 4f$ quadrupole excitations), much larger enhancements were expected, and observed, at the $M_{IV,V}$ edges of the actinides,[4] for which the dipole excitation is to the highly polarized $5f$ levels.

In contrast, resonant scattering at a *K* edge is expected to be considerably weaker and to date remains largely unstudied. Such investigations that have been performed include those of Namikawa *et al.*, who observed a weak *K*-edge resonance in the interference between the charge and magnetic scattering in ferromagnetic Ni metal,[5] and a study of antiferromagnetic Cr, for which no enhancement was observed.[6] Additionally Finkelstein *et al.* have observed resonant *charge* scattering at a quadrupole resonance at the Fe *K* edge in α-Fe_2O_3 (Ref. 7). *K* edge enhancements are expected to be weak because the strong dipole transitions involve *s* and *p* levels and there are no spin-orbit correlations of either level. However, *K*-edge quadrupole excitations couple to *d*-like states, which are the magnetic states in transition metals. This opens the possibility of observing an enhancement associated with these transitions. In the present work, we report just such an effect in NiO, for which an approximately twofold increase in the x-ray magnetic scattering is observed at an energy corresponding to a quadrupolar feature in the absorption spectrum.

In addition to the general interest in exploring resonant x-ray magnetic scattering phenomena further, *K*-edge studies would be of utility for a number of reasons. First, for $3d$ transition metal compounds, which rank among the most interesting of magnetic systems, only the *K* edge is typically accessible in the diffraction regime.[8] Second, successful observation of a *K* edge resonance would bring element specificity to x-ray magnetic scattering studies of such systems, of particular application in mixed spin compounds. Third, the polarization dependence of resonant scattering,[9] allows for the possibility of solving magnetic structures. Finally, it is possible that the technique could be utilized to recover site selective electronic information, for example in mixed valence systems.

We have chosen to investigate the type II antiferromagnet NiO, motivated in part by the recent observation of resonant enhancements in the inelastic x-ray scattering response.[10] At room temperature NiO is an antiferromagnetic Mott-Hubbard insulator with a filled O $2p$ band and a nominal Ni^{2+} $(3d^8)$ ionic configuration having localized Ni $3d$ electrons.[11] The orbital moment is quenched and the total magnetic moment is the spin only value, $2\mu_B$. The magnetic propagation vector corresponds to a doubling of the unit cell along the (111) direction and the spins lie in the plane perpendicular to the (111) axis, along a $\langle 112 \rangle$ direction. The crystal structure is fcc above $T_N = 523$ K, with $a = 4.177$ Å, and undergoes a slight rhombohedral distortion below T_N.[12] The sample was a large single crystal [mosaic=0.07° half width at half maximum (HWHM)] with a polished surface normal to the (111) direction. NiO was the first material in which nonresonant x-ray magnetic scattering was observed.[13]

The experiments were performed on the bending magnet beamline X22C and the wiggler beamline, X25 at the National Synchrotron Light Source (NSLS). Beamline X22C is comprised of a Ni coated focusing mirror, a double bounce Ge(111) monochromator and a Ge(111) analyzer. Unfortunately, the Ni mirror causes complications in the vicinity of the Ni *K* edge and the energy resolution of ~5–10 eV is not optimal. At X25 a double bounce Si(220) monochromator was employed with a Pt coated focusing mirror, for which the energy resolution was 1.8 eV (HWHM). The λ/2 com-

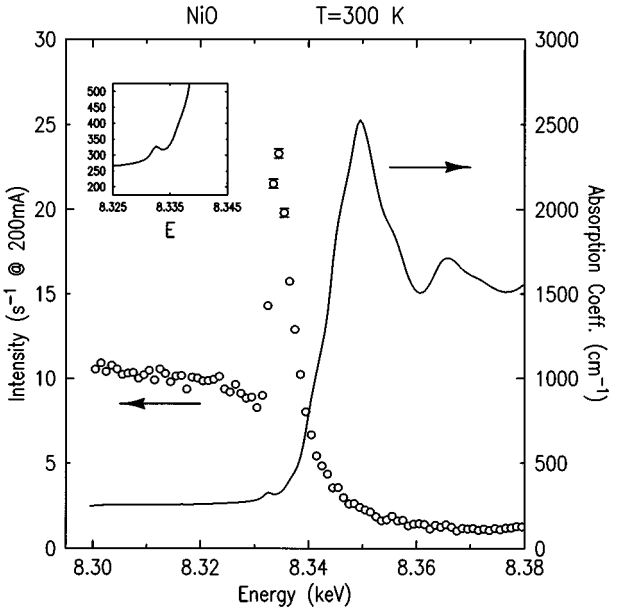

FIG. 1. The magnetic scattered intensity at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ (open circles) as a function of incident photon energy. These data are not corrected for absorption. Data were taken at beamline X25. The solid line is a high resolution absorption spectra of NiO powder showing the presence of a quadrupolar pre-edge feature coincident with the resonant enhancement observed in the magnetic scattering. The inset shows this feature in more detail.

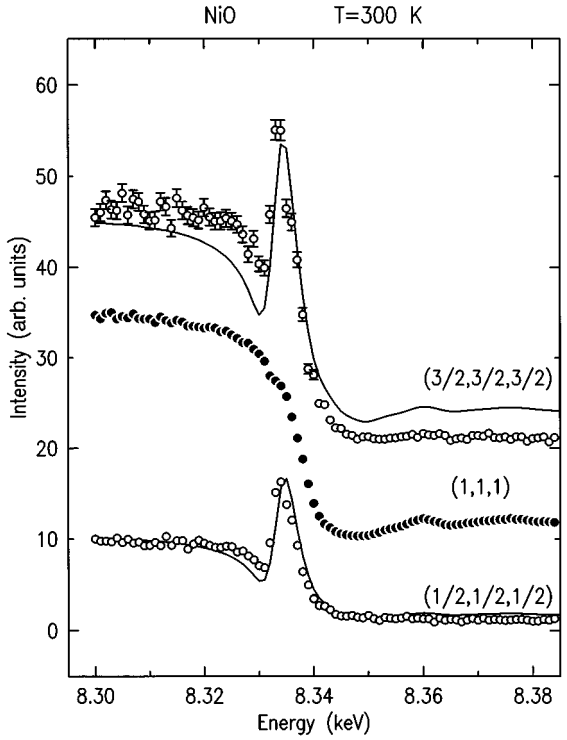

FIG. 2. Energy dependence of magnetic (open circles) and charge (closed circles) Bragg peaks at room temperature. Data were taken at beamline X25. The solid lines are simulations, discussed in the text.

ponent of the scattered beam was filtered out by a triple bounce Si(111) analyzer, together with an energy dispersive solid state detector. The configurations at beamlines X22C and X25 gave similar nonresonant intensities, though the energy and reciprocal space resolution was higher at X25 by factors of ~ 3 and 2, respectively. In each case the absolute energy scale was calibrated by measuring the absorption of NiO powder, characterized by a strong white line maximum at $E = 8350$ eV.

The central result of this work is shown in Fig. 1, in which the intensity of the $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ antiferromagnetic Bragg peak is plotted as a function of incident energy. A resonant enhancement of approximately a factor of 2 is observed at $E = 8333$ eV. The underlying, nonresonant magnetic scattering is constant below the edge and appears to rapidly fall to background levels above the edge. The nonresonant cross section has no strong energy dependence and this intensity variation is due to changes in the absorption length. No enhancement in the magnetic scattering was observable near the peak of the absorption, $E = 8350$ eV.

In order to ascertain the origin of the enhancement, a high resolution measurement of the absorption was performed on NiO powder at beamline X21, at the NSLS (solid line, Fig. 1). The incident resolution was 0.35 eV (HWHM). Close inspection reveals the presence of a weak pre-edge feature at 8333 eV, usually associated with $1s \rightarrow 3d$ transitions (inset Fig. 1).[14] Such transitions are dipole forbidden and can only occur via quadrupole processes (unless there is some hybridization with p states, prohibited here by the inversion symmetry of the Ni site). The main peak is assigned to the Ni $1s \rightarrow 4p$ dipole transitions. The weak pre-edge feature is coincident with the resonant enhancement in the magnetic scattering to within calibration errors.

The presence of this enhancement implies that the magnetic $3d$ levels are being probed, and thus confirms the quadrupole $1s \rightarrow 3d$ assignment of the pre-edge feature. That is in this case, the small size of the quadrupole matrix elements is compensated by the large polarization of the $3d^8$ electrons resulting in a significant resonant scattering amplitude.

Further evidence that this resonant enhancement is magnetic scattering is found in Fig. 2, in which energy scans at the $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and $(\frac{3}{2},\frac{3}{2},\frac{3}{2})$ magnetic Bragg peaks are presented (open circles), together with the scattering at the (111) charge Bragg peak (closed circles). Only the magnetic peaks show the resonant feature at 8333 eV. The energy dependence of the charge scattering reflects the changes in the absorption; the features observed above the edge are associated with diffraction anomalous fine structure (DAFS).

One may estimate the resonant scattering amplitude by comparing the ratio of observed nonresonant and resonant scattering intensities to that expected for the NiO spin structure. In order to properly estimate this, the data are simulated utilizing a generic scattering amplitude

$$f = -iA + \frac{iB}{x - i}, \tag{1}$$

where $x = 2(E_c - E_A - \hbar\omega)/\Gamma$ is the deviation from resonance in units of the core-hole lifetime. We take $\Gamma = 1.5$ eV.[15] A and B are the nonresonant and quadrupolar resonant scattered amplitudes, respectively. The calculated intensity is then convolved with the experimental energy resolution, a

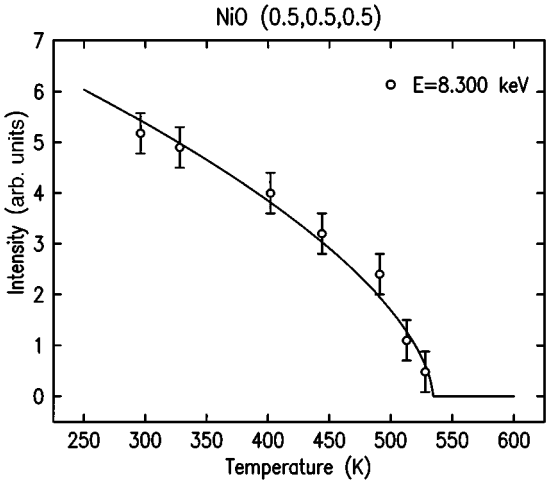

FIG. 3. Temperature dependence of nonresonant magnetic scattering, as measured at $E=8300$ eV on beamline X22C.

Guassian of HWHM=1.8 eV, and divided by the measured absorption. The resulting model (solid lines Fig. 2) provides a reasonable description of the data, with the ratio $B/A=1.3$ for the $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ peak.

We next make several simplifying assumptions. (1) The incident polarization is taken to be perpendicular to the scattering plane. (2) In the absence of any information on the in-plane moment direction, the spins are taken to have equal components perpendicular to, and in, the scattering plane. The spin component along the momentum transfer is zero, and the moment is taken to be spin only. (3) Higher-order terms in the resonant cross section which produce scattering at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ are ignored. This is difficult to justify rigorously without theoretical input, however, if one looks to the rare earths for guidance, we see that at the L_{III} edges of Ce ($S=1/2$) and Nd ($S=3/2$), the third-order quadrupolar intensities are 4–9 times weaker.[16] Hence we suggest that for Ni ($S=1$) this approximation is a reasonable one.

Using expressions for the nonresonant amplitude from Blume and Gibbs[17] and for the first-order quadrupolar resonant amplitude, $A_{E2}^{(1)}$, from Hill and McMorrow,[9] we obtain $A_{E2}^{(1)}\sim 0.01\ r_0$, where r_0 is the classical electron radius. While this estimate is necessarily very approximate, it is interesting to compare with calculations of the same term for the $2p_{3/2}\rightarrow 4f$ transition at the L_{III} edges of the rare earths. For Ce, $A_{E2}^{(1)}=0.017\ r_0$ and $A_{E2}^{(1)}=0.046\ r_0$ for Nd.[16] We conclude that the quadrupolar effects are of similar magnitude in transition metals and rare earths.

The temperature dependence of the nonresonant and resonant magnetic scattering was also investigated. The nonresonant studies were performed at X22C with $\hbar\omega=8300$ eV. A thermocouple was placed in direct contact with the crystal, and the sample heated by passing hot air over the surface. Temperature stability was ± 5 K. The integrated intensity of the $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ peak is shown in Fig. 3. The intensity disappears, to within errors, at the published $T_N=523$ K. The temperature dependence of the resonant scattering was studied at X25 in a small x-ray oven. Unfortunately, large temperature gradients were present and detailed measurements of the order parameter were not possible. However, the resonant scattering did disappear at T_N, as determined by the temperature at which the splitting of the (111) charge peak reached zero (and the cubic symmetry of the crystal is recovered).

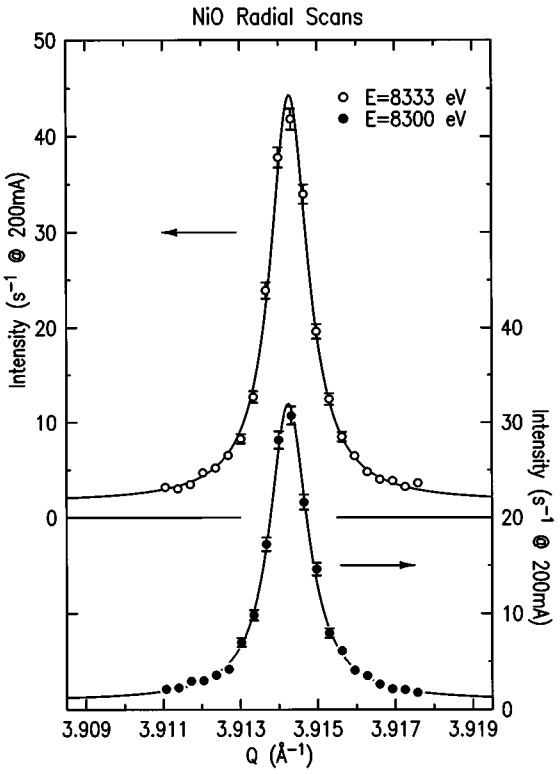

FIG. 4. Radial scans, along the magnetic propagation vector at $(\frac{3}{2},\frac{3}{2},\frac{3}{2})$ taken on and off resonance. The scans have identical widths, corresponding to a correlation length in excess of 1700 Å. Data were taken on beamline X25.

Representative resonant and nonresonant longitudinal scans are shown in Fig. 4. In each case the scan is close to resolution limited and of identical width. From fits to Lorentzian line shapes (solid lines), a lower bound on the longitudinal magnetic correlation length was extracted, $\xi_{\text{long}}>1700$ Å. These data were taken at room temperature at X25. No change in width was observed at higher temperatures, to within errors. The nonresonant intensity was 1800 counts per min, with a signal to noise of $>30{:}1$.

Finally, we mention possible applications of K-edge resonance enhancements. First, in mixed spin systems involving e.g., a rare-earth and transition metal magnetic sublattice [e.g., R_2BaNiO_5, (Ref. 18) RNi_2B_2C (Ref. 19), and $DyFe_4Al_8$ (Ref. 20)] it is frequently of interest to resolve the magnetic behavior of the two sublattices. The polarization properties and element specificity of resonant x-ray magnetic scattering would facilitate such a measurement in a model independent fashion. Second, there are large classes of extremely interesting transition metal compounds including, notably, the high-T_C cuprates and the colossal magnetoresistance maganates, for which nonresonant x-ray magnetic scattering is prohibitively weak, and a factor of 2 increase in count rates could prove useful. Third, there are certain cases for which electronic structural information may be derived. An example would be the mixed valence doped maganates,

in which Mn^{3+} and Mn^{4+} ions are believed to order, giving rise to additional charge and magnetic reflections. In principle at least, it ought to be possible to observe such effects directly. Similar studies have been performed at the Tm L_{III} edge in TmSe.[21]

In conclusion, we have reported an approximately twofold resonant enhancement in the x-ray magnetic scattering in the vicinity of the Ni K edge in the antiferromagnet NiO. The enhancement is associated with quadrupolar excitations to the magnetic $3d$ levels. No enhancement was observed at the dipole resonance, due to a combination of extremely weak magneticsensitivity of the levels involved and the strong absorption. In contrast, similar resonance phenomena was not observed previously in Cr (Ref. 6) in which the $3d$ electrons are itinerant, suggesting that the localized nature of the Ni $3d^8$ electrons may be important.

We are grateful to F. de Bergevin for the loan of the NiO sample, J. Bohr for the loan of his x-ray oven, and D. Gibbs for helpful discussions. The work at Brookhaven National Laboratory was carried out under Contract No. DE-AC02-76CH00016, Division of Materials Science, U.S. Department of Energy.

[1] M. Blume, J. Appl. Phys. **57**, 3615 (1985).
[2] D. Gibbs, D.R. Harshmann, E.D. Isaacs, D.B. McWhan, D. Mills, and C. Vettier, Phys. Rev. Lett. **61**, 1241 (1988).
[3] J.P. Hannon, G.T. Trammell, M. Blume, and D. Gibbs, Phys. Rev. Lett. **61**, 1245 (1988).
[4] E.D. Isaacs, D.B. McWhan, C. Peters, G.E. Ice, D.P. Siddons, J.B Hastings, C. Vettier, and O. Vogt, Phys. Rev. Lett. **62**, 1671 (1989); D. B. McWhan, C. Vettier, E. D. Isaacs, G. E. Ice, D. P. Siddons, J. B. Hastings, C. Peters, and O. Vogt, Phys. Rev. B **42**, 6007 (1990).
[5] K. Namikawa, M. Ando, T. Nakajima, and H. Kawata, J. Phys. Soc. Jpn. **54**, 4099 (1985).
[6] J.P. Hill, G. Helgesen, and D. Gibbs, Phys. Rev. B **51**, 10 336 (1995).
[7] K. D. Finkelstein, Qun Shen, and S. Shastri, Phys. Rev. Lett. **69**, 1612 (1992).
[8] The exceptions are long period structures, where large enhancements in antiferromagnetic Bragg peaks have been observed at L-edges, e.g., J. M. Tonnerre *et al.*, Phys. Rev. Lett. **75**, 740 (1995).
[9] J. P. Hill and D.F McMorrow, Acta Crystallogr. Sec. A **52**, 236 (1996).
[10] C.-C. Kao, W.A.L. Caliebe, J.B. Hastings, and J.-M. Gillet, Phys. Rev. B **54**, 16 361 (1996).
[11] The Ni ground state is estimated to be an admixture of 82% $3d^8$ and 18% $3d^9L$, where L represents a hole on the oxygen ligand, J. Van Elp $\overline{e}t$ *al.*, Phy$\overline{s}$. Rev. B **45**, 1612 (1992).
[12] S.J. Joshua, *Symmetry Principles and Magnetic Symmetry in Solid State Physics* (Adam Hilger, Bristol, UK, 1991).
[13] F. de Bergevin and M. Brunel, Phys. Lett. **39A**, 141 (1972).
[14] Z. Tan, S.M. Heald, S-W. Cheong, A.S. Cooper, and A.R. Moodenbaugh, Phys. Rev. B **47**, 12 365 (1993).
[15] M.H. Chen, B. Crasemann, and H. Mark, Phys. Rev. A **21**, 436 (1980).
[16] M.D. Hamrick, Ph.D. thesis, Rice University, 1994.
[17] M. Blume and D. Gibbs, Phys. Rev. B **37**, 1779 (1988).
[18] A. Zheludev, J.P. Hill, and D.J. Buttrey, Phys. Rev. B **54**, 7216 (1996).
[19] C. Detlefs, A.I. Goldman, C. Stassis, P.C. Canfield, B.K. Cho, J.P. Hill, and D. Gibbs, Phys. Rev. B **53**, 6355 (1996). J.P. Hill, B.J. Sternlieb, D. Gibbs, C. Detlefs, A.I. Goldman, C. Stassis, P.C. Canfield and B.K. Cho, *ibid.* **53**, 3487 (1996).
[20] S. Langridge *et al.* (unpublished).
[21] D.B. McWhan, E.D. Isaacs, P. Carra, S.M. Shapiro, B.T. Thole, and S. Hoshino, Phys. Rev. B **47**, 8630 (1993).