films[9] for $T > T_C$ also show an anomaly at $\epsilon = 2 \times 10^{-2}$ with almost all the data being taken for smaller ϵ. In addition it has been reported[10] that for Ni the exponent β characterizing the spontaneous magnetization changes from $\frac{1}{3}$ to $\frac{1}{2}$ at $\epsilon \approx 6 \times 10^{-3}$. We find that these observations are consistent with calculations of $(T_i - T_C)/T_C$ based on estimated or given impurity levels for these samples.

The spin correlation range in Fe deduced from neutron scattering[11] when plotted against $\ln\epsilon$ shows a deviation from $\nu \approx \frac{2}{3}$ behavior for $\epsilon < 6 \times 10^{-3}$. Again this change in behavior occurs at a value of ϵ consistent with the value inferred from the relation $\xi(\Delta T) \approx l_{ei}$. Also this is evidence that for $T - T_C < T_i - T_C$ the coherence length may depend on the mean free path.

In conclusion we have in this paper shown that the value of T_C as well as the detailed behavior of thermodynamic coefficients near a higher order phase transition as the supercritical region is entered may be strongly determined by impurity concentrations. By observing the values of ϵ for which $\xi \approx l_{ei}$ we have been able to infer the temperature dependence of the range of spin fluctuations in Gd.

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DIRECT OBSERVATION OF COHERENT EXCHANGE SCATTERING BY LOW-ENERGY ELECTRON DIFFRACTION FROM ANTIFERROMAGNETIC NiO

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Coherent exchange scattering has been observed in low-energy electron diffraction from antiferromagnetic NiO. Half-order diffraction beams which correspond to the translational symmetry of the magnetic cell occur below the Néel temperature, $T_N = 525°K$, and disappear at T_N. These beams are attributed entirely to exchange scattering because of their intensity, which is much too great to be accounted for by direct dipole-dipole and spin-orbit interactions.

This paper reports on the first experiment in which coherent scattering from an ordered magnetic spin system has been observed by electron diffraction. Not only does low-energy electron diffraction (LEED) from antiferromagnetic crystals provide an additional method for probing magnetic structure, but, perhaps more importantly, it is the most direct means now available for studying the role of exchange in electron scattering.

Spin ordering in antiferromagnetic NiO leads to a magnetic cell having dimensions twice that of the chemical cell. The arrangement of spins, as determined by neutron diffraction,[1] is represented in Fig. 1(a). If this spin configuration is not altered at the surface, the translational sym-

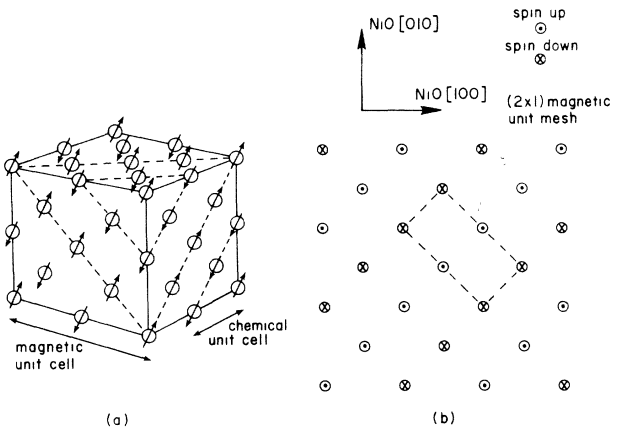

FIG. 1. (a) Ordered arrangement of spins of the Ni^{++} ions in NiO, as determined by neutron diffraction. The O^{--} ions are not shown. (b) Ordered arrangement of spins of Ni^{++} ions in a single layer parallel to the (100) plane of NiO.

metry of the spin system on the (100) surface is 2×1 with respect to the chemical unit mesh, as shown in Fig. 1(b). Coherent scattering of incident electrons by the ordered spin system produces half-order beams. If domains of both possible orientations exist within the cross-sectional area of the incident beam, the diffraction pattern illustrated schematically in Fig. 2 is expected. We shall show that the interaction of incident electrons with the magnetic structure is sufficiently strong to yield detectable half-order beams in NiO and that exchange between the incident electrons and the ordered spin arrangement accounts for their observed intensity.

A standard display-type Varian LEED system was employed for this investigation. The crystal manipulator, similar to that described earlier,[2] was used to cleave the NiO crystal[3] in ultra-

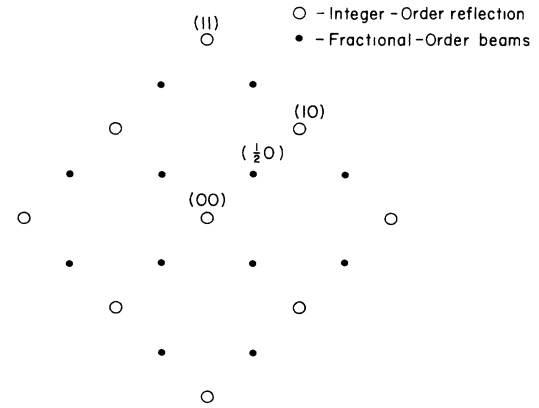

FIG. 2. Schematic representation of expected diffraction pattern from NiO (100) surface.

high vacuum and to control sample temperature from −195 to 500°C. The background pressure during cleavage and observation was in the low 10^{-10} Torr range.

Diffraction patterns taken above and below the Néel temperature (525°K) from the vacuum-cleaved NiO (100) surface are presented in Fig. 3. At 400°K half-order beams appeared at the positions indicated by Fig. 2. These half-order beams disappeared when the temperature of the crystal was raised above the Néel temperature, and reappeared on cooling below the Néel temperature. For incident beam energies from 25 to 70 eV and a crystal temperature of 400°K, the intensity of the half-order beams was 1-3% of the integer order beam intensities. The half-order beams were visible only below 100 eV.

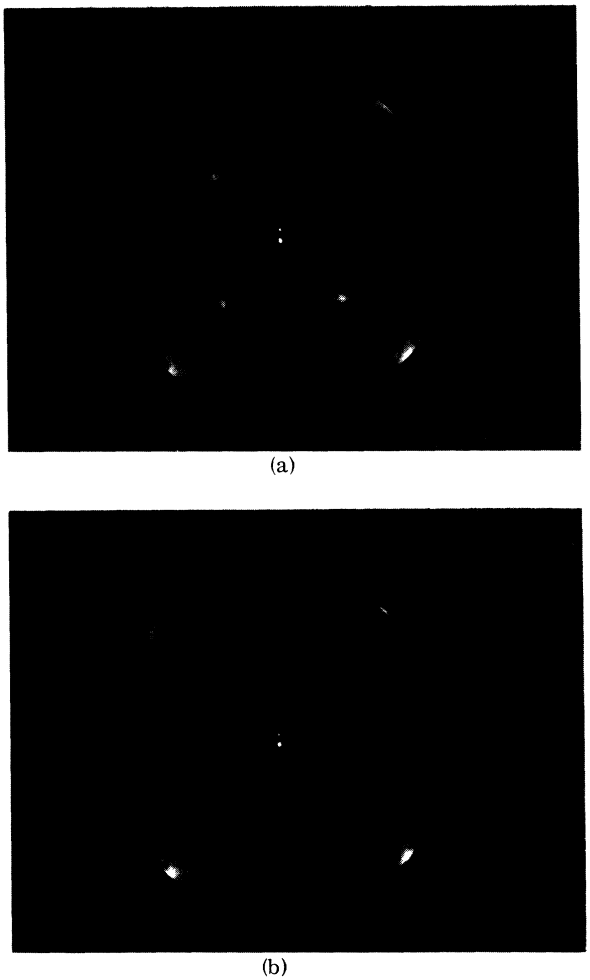

FIG. 3. Low-energy electron diffraction pattern at 33 eV from NiO (100) surface; (a) 400°K, (b) 535°K. Integer-order beams are partially visible at edge of fluorescent screen. Note that half-order beams in (a) are not visible at 535°K.

Although the appearance of half-order beams below the Néel temperature at positions corresponding to the ordered magnetic structure leaves little doubt that these beams result from diffraction from the ordered spin system, other possibilities deserve consideration. Additional diffraction features frequently result from adsorption of gases or through atomic rearrangement of the clean surface. The latter possibility is extremely unlikely for NiO because the surfaces of similar ionic crystals such as MgO,[4] KCl,[4] and NaCl[5] are all characterized by their bulk atomic arrangement. Because the half-order beams were observed immediately after cleavage in vacuum near 10^{-10} Torr, adsorption of gases can be ruled out. With the elimination of these possibilities, it is concluded that observation of half-order beams below the Néel temperature must be attributed to the magnetic structure.

We turn now to some brief considerations of the scattering mechanism involved. Electron scattering from an antiferromagnetic crystal arises from four principal interactions[6]: Coulomb, exchange, dipole, and spin-orbit. The spin-orbit interaction has two contributions, one from a magnetic term involving the spins of the magnetic electrons of the host ions and the other from a nonmagnetic term involving only the spin of the incident electron. The exchange, dipole, and magnetic spin-orbit interactions are magnetic in origin and will therefore display the structure of the magnetic cell, while the Coulomb and nonmagnetic spin-orbit interactions display the structure of the chemical cell. It is well known that the Coulomb interaction dominates the nonmagnetic part of the low-energy scattering. As discussed previously,[7] the exchange interaction dominates the magnetic scattering processes at low energies; for low energies the ratio of the dipole and magnetic spin-orbit differential scattering cross sections to that of the exchange is proportional to $(e^2/\hbar c)^4 \sim 10^{-8}$ for temperatures below the Néel point.

To determine whether exchange scattering accounts for the observed intensity of half-order beams, it is useful to estimate the ratio of the magnetic to nonmagnetic scattering intensities. For this purpose we will use the Born approximation to calculate the intensity ratio of "magnetic" and Coulomb diffraction beams. Since the Coulomb and exchange scattering factors for individual ions may be factored from the summation over lattice sites, it is sufficient to calculate the ratio of exchange to Coulomb scattering for a single Ni^{2+} ion (because of its much lower atomic number, scattering from O^{2-} ions will be neglected). Although it is recognized that a more complete dynamical theory is essential for accurate results, the Born approximation will be used to estimate the order of magnitude of "magnetic" beam intensities.

We start from a one-electron Hamiltonian containing the potential energy of all nuclei plus an exchange potential[8]

$$g(\vec{r}) = -e^2 \int \frac{\psi_i^*(r)\varphi_\rho^*(\vec{r}')\varphi_\rho(r)\psi_i(\vec{r}')dr'}{|\vec{r}-\vec{r}'|\psi_i^*(r)\psi_i(\vec{r})}, \qquad (1)$$

where e is the electronic charge in cgs units. This potential depends explicitly on the wave function $\psi_i(r)$, representing the scattered electron, and the wave function $\varphi_\rho(r)$, representing the magnetic electrons. To determine the scattered intensity, it is necessary to solve the Schrödinger equation self-consistently for the one-particle wave functions. However, to make an order-of-magnetiude calculation, we evaluate[7,8] $g(r)$ by representing the incident electron by a plane wave. For the case of the $3d$-state magnetic electrons of the Ni^{2+}, we calculate the low-energy limit of the Fourier transform $G(\vec{K})$ of the exchange potential to be

$$G(0) = 36\pi e^2 \langle r_d \rangle^2, \qquad (2)$$

where $\langle r_d \rangle$, the mean radius of the d-electron orbitals, is calculated[9] to be 0.2 Å. The electron energies used in our experiment make this low-energy approximation valid for order-of-magnitude purposes. Then the ratio of the magnetic differential scattering cross section to that of the nonmagnetic scattering from NiO at low energies for temperatures below the Néel point is found (in the Born approximation) to be

$$\frac{(\partial\sigma/\partial\Omega)_{\text{exch}}}{(\partial\sigma/\partial\Omega)_{\text{Coul}}} = \left[\frac{G(0)}{V(0)}\right]^2, \qquad (3)$$

where $V(0)$ is the $K=0$ Fourier transform of the Coulomb potential. From the Hartree-Fock effective potential[10] for Ni^{2+} we obtain $V(0) = 416$ eV Å. From Eq. (2) we estimate $G(0) = 65.0$ eV Å^3. Thus for NiO the intensity of the magnetic scattering is estimated to be 2.5% of the nonmagnetic scattering, in reasonable agreement with the observations.

To summarize: (1) The magnetic structure of

antiferromagnetic NiO has been detected with a display-type LEED apparatus. (2) Exchange scattering accounts for the intensity of the observed "magnetic" beams.

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EXCITON STRUCTURE OF TlCl AND TlBr †

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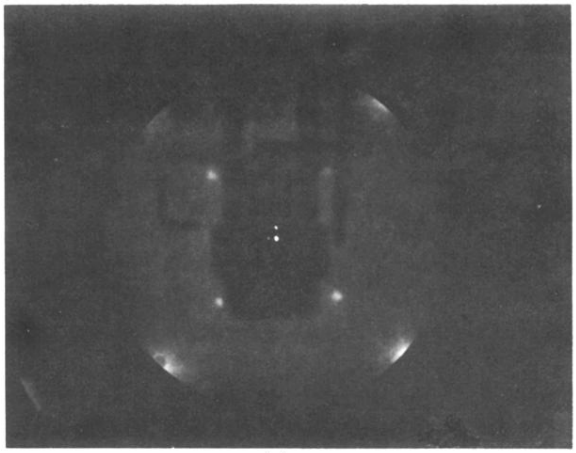
A study of both thick-crystal and thin-film optical absorption data for the thallous halides (CsCl crystal structure) indicates a direct band gap associated with the excitation of the thallous rather than the halide ions. Extremely narrow and very strong exciton lines exhibiting sidebands have been observed in thin films which are relatively free of strain. A very small exciton binding energy, a high polarizability, and large electron-lattice interaction favor this sideband structure which is probably due to coupled exciton-phonon states.

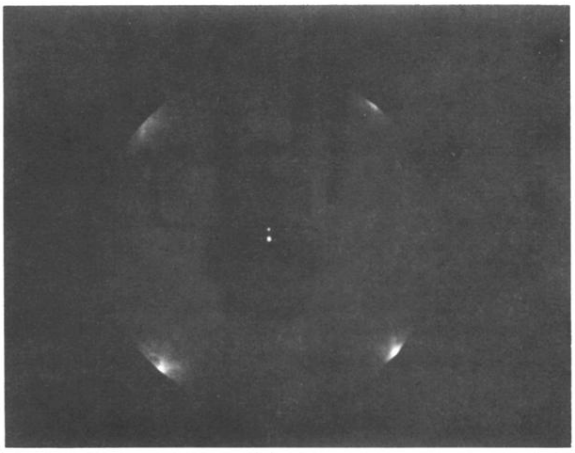
The thallous halides TlCl and TlBr are highly polarizable ionic crystals with characteristic optical absorption which begins in the near-ultraviolet region of the spectrum. A variety of optical data on these interesting materials can be found in the literature,[1-4] and most of this indicates a direct band gap although indirect transitions have also been suggested.[1] Recently two-photon absorption has been reported.[5] Transport experiments[6] on TlCl indicate that both electrons and holes are mobile, and even cyclotron resonance for photocarriers has recently been observed.[7] In this Letter we describe optical measurements at helium temperature on both thick crystals and thin films. Very strong and extremely narrow exciton lines can be observed in thin films of TlCl and TlBr by utilizing a new technique to control the effects of strain. It is found that both TlCl and TlBr have a direct gap with first exciton lines due to excitations centered upon the Tl^+ ions rather than upon the halogen ions as in the alkali and silver halides. Moreover, sidebands, probably due to coupled exciton-phonon states, are observed.[8]

A cryostat and Cary Model 14R spectrophotometer were used to study the absorption edge of thick polished samples of the thallous halides from room down to liquid-helium temperatures. No structure was found in the thick-crystal data, and the edge obeyed Urbach's rule. Entirely similar behavior was observed in crystals of TlBr as well as in TlCl.[9] As the temperature is lowered the edge becomes steeper but this apparent shift of the tail to shorter wavelengths is opposed by the shift of the first exciton peak to longer wavelengths as noted by earlier workers.[1,2] The origin of a positive $(\partial E/\partial T)_P$ for the exciton peak is discussed by Brothers and Lynch[10] who also show that the sign and magnitude of the pressure coefficient is rather similar for both the peak and the tail as would be the case for a direct exciton material with no underlying absorption process toward long wavelengths.

To study the strong optical absorption beyond the tail and edge region, one can use either transmission with thin films or reflection from single crystals. The latter is difficult to carry out with precision since the thallous halides do not readily cleave and highly polished undamaged surfaces are difficult to prepare. We have employed thin films and used the two-thickness subtraction method which corrects for surface re-



(a)



(b)

FIG. 3. Low-energy electron diffraction pattern at 33 eV from NiO (100) surface; (a) 400°K, (b) 535°K. Integer-order beams are partially visible at edge of fluorescent screen. Note that half-order beams in (a) are not visible at 535°K.