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The Magnetic Form Factor of Nickel Oxide*

HARVEY A. ALPERIN

U. S. Naval Ordnance Laboratory, Silver Spring, Maryland and Brookhaven National Laboratory, Upton New York, U.S.A.

Measurement of the magnetic form factor of a single crystal of nickel oxide to large values of $\sin\theta/\lambda$ reveals appreciable anisotropies in the unpaired electron distribution which are due to the effect of the crystalline electric field. Accurate temperature factors, B(oxygen)$=0.37$ and B(nickel)$=0.26$, were determined from powder data. Corrections to the inner magnetic reflections were made for secondary extinction and double Bragg scattering was removed from the outer reflections by measurement at two wavelengths. A direct Fourier projection of the data showed that the unpaired spin density has e_g-type symmetry. The form factor was put on an absolute basis by a method which requires no knowledge of either the absolute intensities or the moment on the Ni^{++} ion. The spherical and aspherical parts of the form factor were deduced directly from the data. The single crystal measurements, which agree with those obtained from a powder sample, yield an electron distribution more compact than is indicated by the latest free atom calculations.

The measurement, by means of neutron diffraction, of the form factor of a magnetic material enables one to determine directly the spatial distribution of the unpaired electrons which gives rise to the intrinsic moment of each magnetic atom. For an ionic compound the crystalline electric field of the anions can induce anisotropies in the unpaired electron distribution. We have investigated the form factor of a single crystal of nickel oxide, for which these asymmetries are expected to be large, out to large values of $\sin\theta/\lambda$. In a preliminary account of this work[1] we showed that the electron distribution has e_g symmetry and is more compact than is indicated by free atom calculations. In the present paper further details of the measurements are given and additional data is presented in order to put the spherical part of the form factor on a firmer footing for comparison with other measurements and with a recent refinement of the free atom calculation[2]. To accomplish this the data is reanalyzed in a new, entirely self-contained manner and a direct projection of the unpaired electron density is presented.

Preliminary to any form factor determination is a knowledge of the magnetic structure and the temperature factors. An accurate value for the nickel temperature factor is particularly important since an error in this quantity introduces an error in the form factor which becomes progressively worse with increasing $\sin\theta/\lambda$. The temperature factors were determined from the integrated intensities of the purely nuclear reflections obtained from a high resolution powder run* out to a value of $\sin\theta/\lambda=0.72$. The results, $B_O=0.37$ for oxygen and $B_{Ni}=0.26$ for nickel**, were checked by measuring the integrated intensity of the 844 reflection as a function of temperature between room temperature and 300°C. These values may be compared with those computed from specific heat measurements[5]: $B_O=0.31$ and $B_{Ni}=0.33$.

Several investigations of the magnetic structure of NiO[3,4,6,7,8] have been made in the past. The crystal used by the author in a previous study[4,8] was subjected to a low temperature stress anneal to reduce twinning in the crystal. Three-dimensional data collected for this crystal were consistent with a model where the spins lie in (111) planes and an isotropic distribution of antiferromagnetic domains is present within that plane. The crystal used for the present work was

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** These values differ greatly from those reported earlier.[3),4)]

not stress annealed and hence much twinning was present. The single $\bar{1}10$ zone measured yields magnetic reflections that arise from two of the four possible twins. Although the lack of three-dimensional data did not allow a direct determination of the domain distribution, the reflections from both twins were consistent with the previous model of isotropically distributed antiferromagnetic domains. We also investigated the effect on the form factor of tipping the spins out of the (111) plane. Taking in particular a model where the spins are in the $[\bar{1}11]$ direction (about a 20° tilt out of the (111) plane) we find no significant change in the form factor upon analyzing the data by the procedure described below, although the fit to the data is not quite as good as before*. In what follows, therefore, we adopt the model of spins lying in the (111) plane.

Integrated intensities of all nuclear and magnetic reflections were measured at room temperature and corrected for secondary extinction and effects of double Bragg scattering. The crystal was cylindrically shaped to enable accurate secondary extinction corrections to be determined from the nuclear reflections. A mosaic spread parameter of 130 seconds of arc led to corrections to the form factor of only 5.8% for the strongest 111 reflection, of only 1.4% for the $\bar{3}11$ reflection, of 1.0% for the $33\bar{1}$ reflection and of a completely negligible amount for all the other weaker reflections which occur at higher Bragg angles.

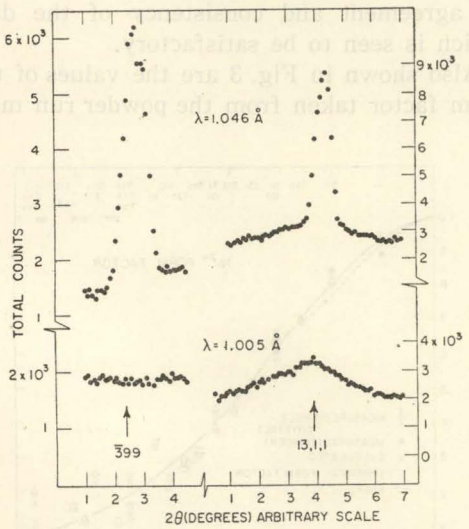

Fig. 1. The effect of double Bragg scattering on the $\bar{3}99$ and 13, 1, 1 reflections at 1.046Å. The arrows designate the counter settings at which the reflections are expected.

Double Bragg scattering[10] (DBS), which occurs when more than one reciprocal lattice point lies on the sphere of reflection, was noticed for some of the very weak outer magnetic reflections. Here one expects the effect to be an enhancement of the primary reflection. The method used for correcting for DBS consisted of measuring all magnetic reflections at two wavelengths, 1.046Å and 1.005Å. In Fig. 1 the results are illustrated for the $\bar{3}99$ and 13,1,1 reflections where the reflections seen at the higher wavelength are probably due to DBS from the 111, $\bar{4}88$ and 111, 12, 0, 0 reflections respectively*. It is to be noted that these reflections are slightly displaced from the Bragg angles at which

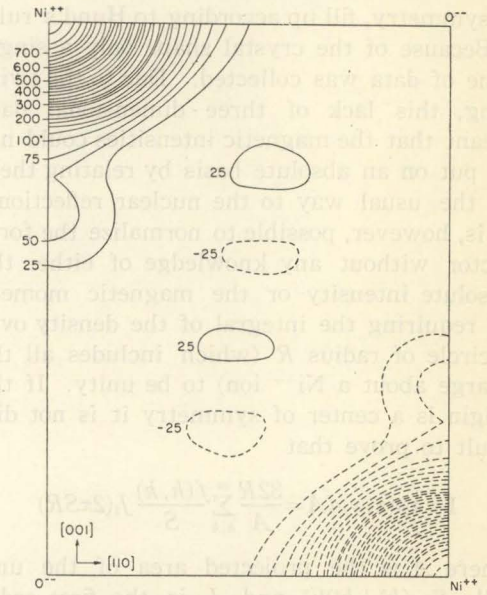

Fig. 2. The relative unpaired spin density in antiferromagnetic NiO. The solid and dashed contours denote positive and negative density respectively. The circle-like contours in the center are diffraction effects arising from series termination error. The zero contour has been omitted for the sake of clarity.

* The relative insensitivity to tipping of the spins out of the plane is due to the averaging effect of the antiferromagnetic domains.

* It was ascertained that these anomalies are not due to primary reflections from a higher layer line.

the primary reflections are expected and are considerably narrower (due to the focusing action of the DBS) than the primary reflection. By thus noting the differences (if any) in peak shape and position for the two wavelengths, estimates of DBS were made for all magnetic reflections.

The necessary experimental corrections to the data having been made, it is possible without any further analysis to obtain by a Fourier inversion a direct projection of the unpaired spin density, as shown in Fig. 2. The compactness and non-sphericity of the distribution is clearly seen. The effects of series termination errors have been investigated by varying the number of reflections used in the sum and the results indicate that the major features of Fig. 2 are real. The symmetry is clearly e_g (i. e. lobes along the cubic axes) and is just what one expects according to crystal field theory if the energy levels, which are split by the electric field of octahedral symmetry into a low-lying triplet of t_{2g} symmetry and a higher double of e_g symmetry, fill up according to Hund's rule.

Because of the crystal shape only a single zone of data was collected. Due to the twinning, this lack of three-dimensional data meant that the magnetic intensities could not be put on an absolute basis by relating them in the usual way to the nuclear reflections. It is, however, possible to normalize the form factor without any knowledge of either the absolute intensity or the magnetic moment by requiring the integral of the density over a circle of radius R (which includes all the charge about a Ni^{++} ion) to be unity. If the origin is a center of symmetry it is not difficult to prove that

$$1=\int\rho(x,y)dA=\frac{32R}{A}\sum_{h,k}^{\infty}\frac{f(h,k)}{S}J_1(2\pi SR)$$

where A is the projected area of the unit cell, $S=(h^2+k^2)^{1/2}$ and J_1 is the first order Bessel function*. Applying this equation to our measurements for which $f(h,k)=K(I(h,k))^{\frac{1}{2}}$, where $I(h,k)$ is the measured relative intensity of a reflection, we can determine the constant K and hence normalize the form factor. This procedure assumes no overlap between nickel atoms, a conclusion seen to be fully justified from Fig. 2. In addition, the effect of including only a finite number of reflections in the sum can be shown to introduce only a negligible error because of the relatively rapid fall-off of the form factor with Bragg angle. The normalized experimental values of the form factor are shown in Fig. 3. The error bars shown on the points are estimates which include such factors as reproducibility, statistical errors, and corrections for DBS.

In order to deduce the spherical form factor from the data we can make use of the fact that Blume[2] has shown for NiO (even if there is an orbital contribution to the form factor) that one can still write the form factor as the sum of a spherical and an aspherical part: $f=f_S+C(h,k,l)f_A$ where $C(h,k,l)$ depends on the cubic symmetry of the lattice. At each value of $\sin\theta/\lambda$ where there exists more than one reflection we can solve for f_S and f_A. The smooth curve drawn through the values of f_S arrived at in this way is shown in Fig. 3. The virtue of this method is that the spherical part of the form factor is deduced directly from the data. One can now compute f for every reflection; these points are designated by the triangles in Fig. 3. Comparison of the experimental and calculated points gives a measure of the overall agreement and consistency of the data which is seen to be satisfactory.

Also shown in Fig. 3 are the values of the form factor taken from the powder run men-

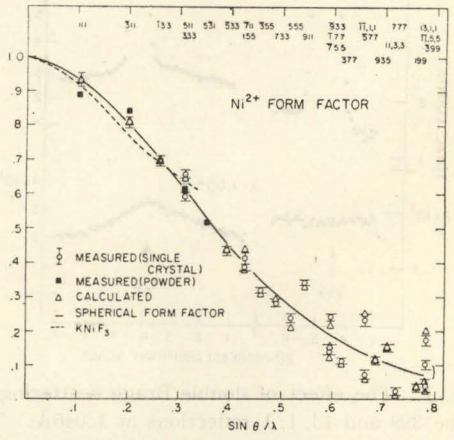

Fig. 3. Magnetic form factor of Ni^{2+} in NiO. The indices at the top of the figure correspond (in the order shown) to the points directly below. Error bars have been omitted from the powder data for the sake of clarity.

* It should be remembered that $f(0, 0)=0$ for an antiferromagnet.

tioned earlier. It should be noted that these values have been normalized in an entirely different manner from the single crystal data, namely, by putting the magnetic reflections on an absolute basis relative to the nuclear reflections and then extrapolating to $\sin\theta/\lambda=0$. The agreement between the two sets of measurements is good. The form factors for Ni^{++} in $KNiF_3$[11] (also in an octahedral site as in NiO) and for Ni^{++} in $NiTiO_3$[12] (not shown) are also in agreement with the single crystal results for NiO.

The experimental curve for the spherical form factor is compared with free atom calculations in Fig. 4. The lower curve is due to Watson and Freeman[13]. The middle curve combines the corrections for spin polarization and an octahedral point charge environment by Watson and Freeman[14] with a 10% contribution to the total moment due to orbital angular momentum by Blume[2]. It is clear that a large difference between the experimental and calculated curves still remains to be explained. The significance of these results for Ni^{++} and a comparison with Mn^{++} and Fe^{3+} are given more fully in an accompanying paper[15].

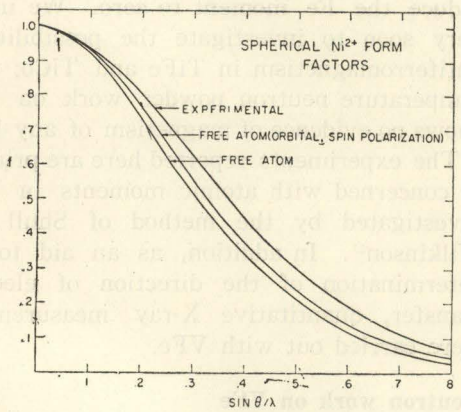

Fig. 4. Comparison of calculated free atom form factors for Ni^{2+} with that deduced from measurements on NiO.

A determination of the intrinsic moment gS was made for Ni^{++} where g is the ordinary 'g-factor' and S is the spin quantum number. From an extrapolation of the powder measurements to $\sin\theta/\lambda=0$ we find the quantity $gSB_s=1.72\pm.20$. B_s, the ratio of the moment at room temperature to that at 0°K, was evaluated by measuring the intensity of the 111 reflection at room and helium temperatures. The result was $B_s=.95\pm.05$ and hence $gS=1.81\pm0.20\mu_B$. If we use the value $g=2.2$ as a typical value for Ni^{++} then the effective moment $\mu_{eff}=g(S(S+1))^{1/2}=2.71\pm.16\mu_B$.

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