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Neutron Diffraction Observation of Heat Treatment in Cobalt Ferrite

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The effect on cobalt ferrite of heat treatment in a magnetic field has been studied by neutron diffraction. The data indicate that the magnetic moments are, in general, displaced from the directions which would be expected from consideration of crystalline anisotropy alone. The effect is greater in ferrites that are iron rich than it is in stoichiometric ferrites. The results are consistent with magnetic data.

INTRODUCTION

IN a recent paper,[1] Bozorth, Tilden, and Williams have discussed observations of magnetic anisotropy and magnetostriction in cobalt ferrite and cobalt zinc ferrite. In particular, they have described the changes in apparent anisotropy which result when single crystals and polycrystalline samples of these substances are annealed in a strong magnetic field. In the early stages of a study of the mechanism of this phenomenon, it appeared as if neutron diffraction evidence might answer two specific questions. First, if the response to heat treatment involved ordering of iron and cobalt ions, then the comparatively large difference in neutron scattering power of iron and cobalt nuclei might lead to extra diffraction effects that would not be observed with x-rays, and, second, the sensitivity of neutrons to the internal arrangements of magnetic moments on a unit-cell scale might shed further light on the basic mechanism.

EXPERIMENTAL OBSERVATIONS

Neutron-diffraction powder patterns were obtained from cobalt ferrites having the formula $Co_{1-x}Fe_{2+x}O_4$, with several values of x from 0 to 0.5. The samples were provided by F. J. Schnettler, and were ceramic cylinders about 2 cm in diameter and 5 cm long. Chemical analysis showed that the metal-ion ratios were within 1% of their nominal values, although all compositions were slightly oxygen rich. The samples having values of x of 0, 0.15, and 0.23 were first measured as received and then heat-treated with a magnetic field of several thousand oresteds along a diameter. After heat treatment, two patterns were run on each sample, one with the direction of the heat-treating field, H_T, perpendicular to the reflecting planes, and one with H_T lying in the reflecting planes. A typical pair of such diffraction patterns, those for $x=0.15$, is shown in Figs. 1 and 2.

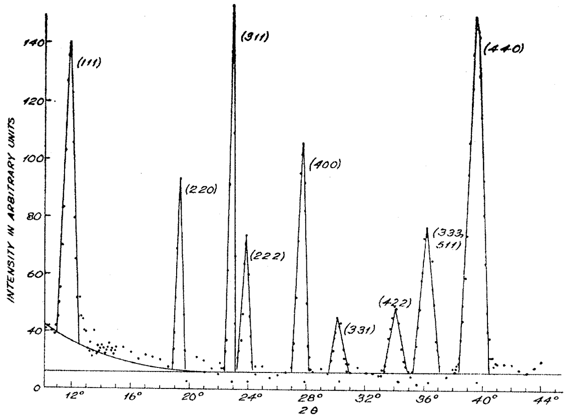

FIG. 1. Neutron diffraction powder pattern for $Co_{0.85}Fe_{2.15}O_4$. H perpendicular to reflecting planes.

Cobalt ferrites have the spinel structure, which is based on cubic close packing of oxygen ions. The unit cell contains 32 oxygen ions, 8 metal ions in "A" sites with tetrahedral coordination, and 16 metal ions on "B" sites with octahedral coordination. The "normal" structure has divalent ions on the A sites and trivalent ions on the B sites, while the "inverse" structure has trivalent ions on the A sites and the B sites are occupied by divalent and trivalent ions distributed at random. On the basis of saturation magnetization measurements, cobalt ferrite has been assumed to have the inverse structure. Table I shows a list of observed and calculated intensities for the $x=0.15$ sample, as measured before heat treatment. In these calculations it has been assumed that the structure is completely inverse, that

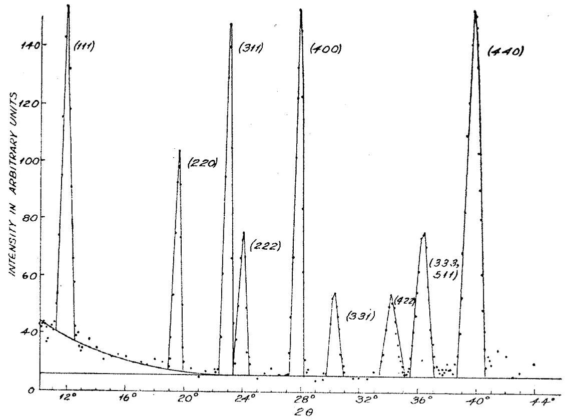

FIG. 2. Neutron diffraction powder pattern for $Co_{0.85}Fe_{2.15}O_4$. H in reflecting planes.

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[1] Bozorth, Tilden, and Williams, Phys. Rev. 99, 1788 (1955).

TABLE I. Calculated and observed intensities in the neutron diffraction powder pattern for $Co_{0.85}Fe_{2.15}O_4$ before heat treatment.

Plane	Calculated intensity Nuclear I_n	 Magnetic I_m	 Total I_c	Observed intensity I_0
111	0.6	54.8	55.4	55.4
220	16.9	9.2	26.1	27.8
311	45.6	0	45.6	47.0
222	7.8	10.7	18.5	17.8
400	32.6	11.6	44.2	45.0
331	1.0	10.9	11.9	12.5
422	11.0	2.9	13.9	16.9
333 511	37.5	0	37.5	38.0
440	100	0	100	100

TABLE II. Observed intensities in the neutron diffraction powder pattern for $Co_{0.85}Fe_{2.15}O_4$ after heat treatment.

hkl	$I_\perp$	$I_\parallel$	$(I_{mag})_\perp$	$(I_{mag})_\parallel$
111	58.0	50.3	57.4	49.7
220	26.4	21.8	9.5	4.9
222	19.1	17.9	11.3	10.1
400	52.4	34.2	19.8	1.6
331	14.0	8.8	13.0	7.8
422	16.2	13.7	5.2	2.7

the oxygen parameter u, which measures the space available for an A-site ion, is 0.381, and that the magnetic moments are 88% oriented at room temperature. This last assumption is inferred from the intensity of the (111) reflection. All intensities are referred to the intensity of (440), which is entirely due to nuclear scattering, and is quite insensitive to any of the variable parameters. The magnetic calculations assume the magnetic form factor given by Corliss, Hastings, and Brockman.[2] I_n is the calculated nuclear scattering, I_m is the calculated magnetic scattering, I_c is the total calculated scattering, and I_0 is the observed intensity.

The agreement is quite satisfactory, indicating that the assumptions listed above are essentially correct. Table II lists the observed intensities after heat treatment. The total intensity is listed in the first two columns, while the magnetic intensity, obtained by subtracting the calculated, nuclear intensity from the observed intensity, is listed in the third and fourth columns. Here $I_\parallel$ refers to the case where the normal to the reflecting planes is parallel to the treating field, H_T, while $I_\perp$ refers to the case where the normal is perpendicular to H_T.

Similar diffraction patterns for cobalt ferrites with values of x of 0 and 0.23 showed the same general features, although the effect of heat treatment on the magnetic intensities of the patterns taken in the two orientations increased markedly with increasing values of x, which is consistent with the magnetic observations.[1] These three samples, as well as additional samples with nominal values of x of 0.40 and 0.50, were examined for evidence of extra diffraction peaks that would indicate ordering of iron and cobalt. No such extra peaks occur in any pattern. The data do not eliminate the possibility of some short-range order.

DISCUSSION OF RESULTS

The most significant features of the data lie in the comparative effects of the heat treatment on the intensities of peaks which have different orientations with respect to the directions of easy magnetization in the crystallites. In cobalt ferrite the directions of easy magnetization lie along the cube axes. The magnetic contribution to neutron diffraction intensity is proportional to the average value of $\sin^2\alpha$, where α is the angle between the magnetic moment and the normal to the reflecting plane. In cases where the magnetic moments are distributed at random along the three cube directions, this average value is equal to 2/3, and is independent of the orientation of the plane. Since the angle between a cube direction and a [111] direction is equal to $\cos^{-1}(1/\sqrt{3})$, the value to $\sin^2\alpha$ must be equal to 2/3, irrespective of the distribution of the moments among the cube directions, for any order of reflection from a (111) plane. Therefore, any mechanism of heat treatment that implies only a redistribution of moments among the three cube directions also implies that heat treatment should have no effect on the magnetic intensities of the (111) and (222) peaks. A difference does occur, however, which is far beyond the limits of experimental error. This difference can only be explained by the assumption that the moments are rotated toward the direction of the heat treating field, H_T, by an angle which averages about 3° in the $x=0.15$ sample, and nearly 6° in the $x=0.23$ sample. In the $x=0$ sample the rotation is small but visible. By contrast, the behavior of the (400) is quite different. Here $I_\parallel$ is essentially zero, while $I_\perp$ is in substantial agreement with the value to be expected for $\sin^2\alpha=1$. Other reflections show intermediate behavior.

The neutron data are consistent with the magnetic data of Bozorth *et al.*, which indicate that the effect of heat treatment is to superimpose an additional anisotropy term which has uniaxial symmetry about H_T on the crystalline anisotropy. Thus if H_T is parallel to a particular easy direction of magnetization in the crystal, the additional term makes that direction easier than the others, giving the large change in the (400) intensity. Conversely, if H_T makes an angle with the crystalline easy directions, the effect is to displace the minima in the resultant anisotropy surface away from those easy directions.

Nesbitt, Williams, and Bozorth[3] have shown that some of the magnetic properties of single crystals of Fe_2NiAl may be explained by the presence of a pre-

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[2] Corliss, Hastings, and Brockman, Phys. Rev. **90**, 1013 (1953).

[3] Nesbitt, Williams, and Bozorth, J. Appl. Phys. **25**, 1014 (1954).

cipitate oriented along certain crystallographic directions. Bozorth, Tilden, and Williams have suggested that the presence of such an oriented precipitate in cobalt ferrite may explain their results obtained by heat treatment of this material in a magnetic field. More recently Williams, Nesbitt, and Heidenreich[4] have found more direct experimental evidence for this idea by the use of torque curves and electron diffraction. It is possible that this view could be confirmed by a study of the diffuse scattering of x-rays from single crystals of these substances.

ACKNOWLEDGMENTS

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[4] Williams, Nesbitt, and Heidenreich (to be published).

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Resistivity of Interstitial Atoms and Vacancies in Copper[*]

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The residual resistivity associated with the presence of interstitial atoms or vacancies in copper is studied with particular attention devoted to the scattering of conduction electrons resulting from lattice distortions surrounding the imperfections. For interstitials this scattering is found to be an order of magnitude larger than that from the defect itself. For vacancies it is smaller but still important. Interference between scattering from the defect and the surrounding lattice distortion is computed and found to be very small. The calculated resistivity associated with one atomic percent of interstitial atoms is 10.5 μohm cm. The corresponding value for vacancies is 1.5 μohm cm. Using nominal values for the energy of formation of these defects, the stored energy to resistivity ratios associated with interstitials, vacancies, and interstitial-vacancy pairs are 1.4, 3.4, and 1.6 cal/g per μohm cm, respectively.

I. INTRODUCTION

THE increase in the residual resistivity of copper arising from the presence of interstitial atoms or vacancies has been studied by several workers. Dexter[1] approximated the scattering potential associated with the imperfections by a shielded Coulomb interaction, $(e^2/r)\exp(-\mu r)$, and computed electronic transition matrix elements by the Born approximation. The shielding constant μ was adjusted so that the computation yielded experimental values when applied to the analogous problem of substitutional impurities having adjacent atomic number. The estimated resistivity change for 1% of interstitials was 0.6 μohm cm, and for 1% of vacancies was 0.4μ ohm cm. Dexter also investigated the scattering arising from the elastic distortion of the lattice surrounding the imperfections. He concluded that such effects probably contribute less than 10% to the scattering cross sections for both types of imperfection. In making this estimate the discrete positive ion lattice was approximated by a smeared-out positively charged continuum.

In treating the same problem, Jongenburger[2] used for the scattering potential of a lattice vacancy a shielded Coulomb interaction with constants adjusted so as to fit as closely as possible the Hartree field of a copper atom. The scattering cross section was computed by the partial wave method. Jongenburger obtained a resistivity of 1.8 μohm cm per atomic percent of vacancies. (Jongenburger gives a value of 1.3, but apparently a numerical error was made in converting phase shifts to resistivity.) He estimated the contribution arising from elastic distortions by comparing the displacement of nearest neighbors of the vacancy with the root mean square atomic displacements caused by lattice vibrations, which are responsible for the temperature dependent electrical resistivity. A value of 0.04 μohm cm was obtained. Jongenburger[3] has also estimated by the same method the extra resistivity caused by interstitial atoms. For the contribution of the interstitial scattering potential alone a value of 1 to 2 μohm cm was found, and an additional 3.5 μohm cm resulting from nearest neighbor displacements was obtained.

More recently, Blatt[4] has computed the resistivity associated with one atomic percent of interstitial atoms, assuming that the scattering effects of elastic strains can be neglected. An appropriately screened Hartree

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[1] D. L. Dexter, Phys. Rev. 87, 768 (1952).

[2] P. Jongenburger, Appl. Sci. Research B4, 237 (1953).

[3] P. Jongenburger, Nature 175, 545 (1955).

[4] F. J. Blatt, Phys. Rev. 99, 1708 (1955).