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Magnetic Susceptibility of NiO and CoO Single Crystals*

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The magnetic susceptibility of a NiO single crystal grown by the flame fusion method was found to be isotropic below the Curie temperature as it is for the case of powdered material. Such characteristics can be explained by twinning or domain structure within the crystal. Stressing the crystal along a [111] direction, while annealing, produces an anisotropic susceptibility with the maximum and minimum values found when the applied field was parallel and perpendicular, respectively, to the direction of stress. By using the Van Vleck theory, the results can be explained on the basis that the stress rotates some of the atomic spins from the direction of the [111] stress axis to the perpendicular planes. An assignment of spin direction to (111) planes of each domain agrees with the most recent neutron diffraction interpretation.

The antiferromagnetic susceptibility of a single crystal of CoO was found to decrease when measured along one cubic edge and remain approximately constant along the other two [100] directions for temperatures down to 77°K. At liquid helium temperatures the susceptibility increases for all [100] directions.

I. INTRODUCTION

FROM powder measurements of magnetic susceptibility by La Blanchetais,[1] and neutron diffraction experiments by Shull, Strauser, and Wollan,[2] nickel monoxide and cobalt monoxide have been found to be antiferromagnetic. Rooksby[3] has made x-ray studies which show that, above the Curie temperature, the crystals have cubic symmetry, while below the Curie temperature NiO exists in a rhombohedral form and CoO exists in a tetragonal form. It is believed that the lattice distortion is intimately related to the spin ordering and direction in antiferromagnetic materials.

In an attempt to orient the spins of NiO and CoO, we employed annealing with forces applied along various crystallographic directions. The forces established a preferred direction for phase distortion and hence removed a directional degeneracy. This technique changed the susceptibility in such a way that it enabled us to select a probable spin direction for single crystals of NiO.

The single crystals were grown by Scott[4] by using the Verneuil (flame fusion) technique. They were cleaved from the boule to parallelopipeds with masses of approximately 0.2 grams. The cleavage planes were [100] directions of the cubic form as determined by means of Laue back-reflection x-ray patterns. The single crystals were relieved from strains by annealing from 1000°K at a cooling rate of 1° per minute before measurements were commenced.

II. NiO MEASUREMENTS

The magnetic susceptibility measurements were made by the body-force method[5] using field strengths from 6000 to 10 500 oersteds (in an attempt to determine the anisotropy energy). Figure 1 shows susceptibility values for an annealed crystal as a function of temperature from 4 to 700°K. The Curie temperature is characterized by a broad maximum in the region of 600 to 700°K. Susceptibility was found to be independent of field strength and also independent of the crystal orientation in the magnetic field at all temperatures. These characteristics are almost identical with those of a polycrystalline sample.

Force was then applied along a [111] direction while annealing from 1000°K. This direction was chosen because it is the axis which contracts at change of phase. Use of a spring clamp having extension legs so that the compression spring was exterior to the furnace, permitted pressures from 200 pounds/inch^2 to 5000 pounds/inch^2 to be kept constant while annealing the crystal.

Figure 2 illustrates the susceptibility data obtained following stress annealing. The lower branch of the curve is susceptibility measured in the (111) plane perpendicular to the [111] direction which had been stress annealed. The susceptibility is isotropic in this (111) plane. The upper branch of the curve is the susceptibility measured along the stressed [111] direction.

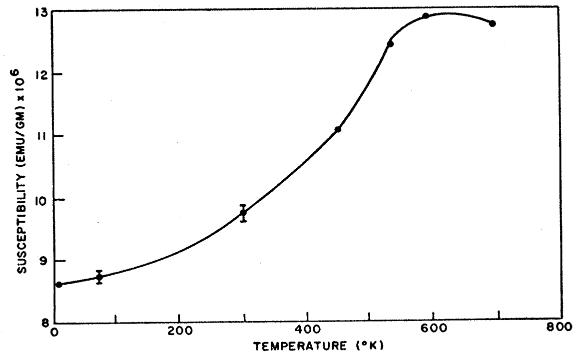

FIG. 1. Isotropic susceptibility of NiO.

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[1] C. H. La Blanchetais, J. phys. radium 12, 765 (1951).

[2] Shull, Strauser, and Wollan, Phys. Rev. 83, 333 (1951).

[3] H. P. Rooksby, Acta Crystallographica 1, 226 (1948); N. C. Tombs and H. P. Rooksby, Nature 165, 442 (1950).

[4] E. J. Scott, J. Chem. Phys. 23, 2459 (1955).

[5] T. R. McGuire and C. T. Lane, Rev. Sci. Instr. 20, 489 (1949).

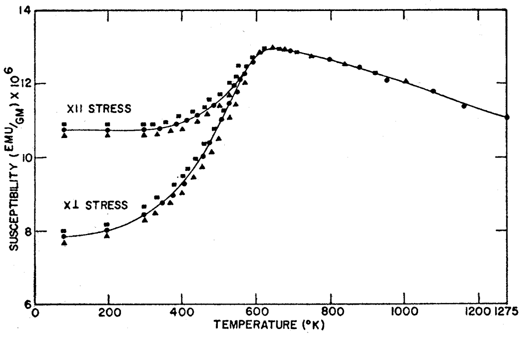

FIG. 2. Stress annealed susceptibility of NiO measured paralle and perpendicular to the stressed direction. The three curves represent values found after annealing with stress along three different [111] directions.

Neither the magnitude of the force nor the particular [111] axis of application was found to be significant since successive annealings with 200 pounds/inch^2 to 5000 pounds/inch^2 pressure along three different [111] directions of the crystal did not cause noticeable changes in the degree of anisotropic susceptibility as plotted in Fig. 2. Reannealing without any applied force, or with a force applied along a [100] direction resulted in an isotropic susceptibility with the same values as shown in Fig. 1.

Figure 3 is a plot of the reciprocal of the susceptibility values found at high temperatures. An extrapolation gives a value of -2000°K for θ, the point at which the extrapolated $1/\chi$-T curve intersects the abscissa. An effective Bohr magneton value per atom of 4.6 is found from the slope.

III. CoO MEASUREMENTS

A CoO single crystal had the susceptibility shown in Fig. 4. Two [100] directions were nearly constant in susceptibility from 273°K down to 77°K, while the third [100] direction has a notable decrease in susceptibility. The increased susceptibility for all directions at liquid helium temperatures is unusual. Stress annealing, with force applied along the [100] axes, did not significantly change the susceptibility.

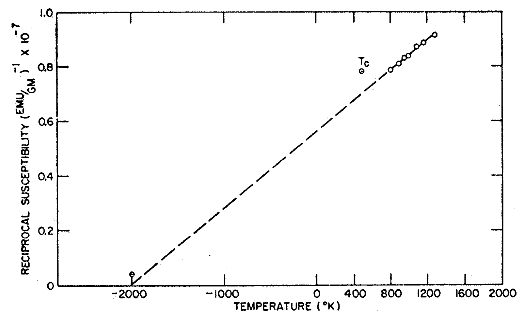

FIG. 3. Reciprocal plot of high-temperature susceptibility of NiO.

A plot of the reciprocal of the susceptibility at high temperatures is shown in Fig. 5. The Curie-Weiss law is satisfied, with $\theta=-330$°, and an effective Bohr magneton value equal to 5.25.

IV. DISCUSSION OF NiO

The theory of antiferromagnetism developed by Van Vleck[6] predicts that below the Curie temperature the susceptibility ($\chi_{\parallel}$) of a single crystal should decrease with decreasing temperature in the direction of electron spin alignment, while perpendicular to the spin axis the susceptibility ($\chi_{\perp}$) should be constant as given by:

$$\chi_{\parallel}=\frac{Ng^2\beta^2S^2B'(y_0)}{k[T+3T_cS(S+1)^{-1}B'(y_0)]}, \tag{1}$$

and

$$\chi_{\perp}=\frac{Ng^2\beta^2S(S+1)}{6kT_c}, \tag{2}$$

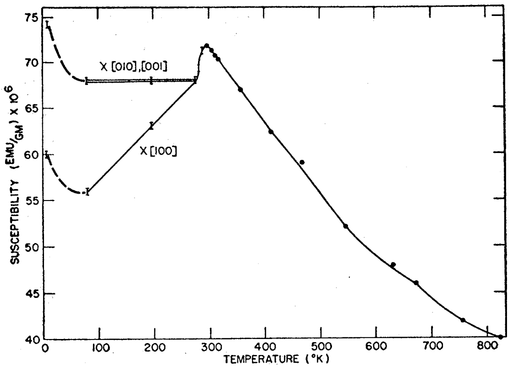

FIG. 4. Susceptibility of CoO.

where $Ng^2\beta S(S+1)/3k$ is the molar Curie constant, $B'(y_0)$ is the derivative of the Brillouin function with respect to its argument, T_c is the Curie temperature, and S is the atomic spin in units of $h/2\pi$. A curve showing the calculated susceptibility using Eqs. (1) and (2) of a set of spins having $S=\frac{3}{2}$ is shown in Fig. 6. The shape of the $\chi_{\parallel}$ curve changes slightly for different S values. The curve labeled $\frac{1}{2}\chi_{\perp}+\frac{1}{2}\chi_{\parallel}$ is applicable to a set of spins randomly oriented in a plane whose susceptibility is measured with the field in that plane. Model 1 in Table I shows the susceptibility of such a set of spins when the maximum susceptibility is taken as the susceptibility found at the Curie temperature.

If only 50% of the spins initially pointing out of the (111) planes are reoriented into that plane by stress annealing then a calculation of the expected susceptibility yields the values shown in Model 2 of Table I. In order to have isotropic susceptibility, $\frac{1}{3}$ of the spins must be directed out of the (111) planes, while a 50% reorientation implies that only $\frac{1}{6}$ of the spins finally point out of the plane. A comparison of the suscepti-

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[6] J. H. Van Vleck, J. Chem. Phys. 9, 85 (1941).

bility of this model and the experimental values found for the NiO crystal indicates excellent agreement as shown in Table I.

The fact that a force applied along a [100] direction during annealing does not alter the susceptibility indicates that the anisotropic susceptibility, found after annealing with a force in the [111] direction, is not due to the rotation of domains, but is caused by many domains having undergone phase deformation induced by the stress along the [111] axis.

The isotropic susceptibility of the unstressed crystal indicates a twinning or domain structure. One can qualitatively understand that only a fraction of the spins are reoriented by stress annealing since the twinning prohibits exact determination of the direction of applied force relative to the entire crystal.

From least-energy considerations, it is reasonable to assume that the phase contraction takes place along the direction of applied force. In that case spin directions are perpendicular to the contracted axis of the rhombohedral form. This assignment agrees with Roth[7] who found that the spins are probably in (111) planes of the cubic phase.

TABLE I. Calculated susceptibility of antiferromagnetic spins randomly oriented in the (111) plane measured with the magnetic field along and perpendicular to this plane, and compared with the experimental values. Susceptibilities are in emu/gram at 0°K (extrapolated).

	Measured parallel to the (111) plane	Measured perpendicular to the (111) plane
Model 1 All spins in (111) planes	6.5×10^{-6}	13.0×10^{-6}
Model 2 $\frac{5}{6}$ of spins in (111) planes, $\frac{1}{6}$ of spins perpendicular to (111) plane	7.6×10^{-6}	10.8×10^{-6}
Experimental values for NiO	7.7×10^{-6}	10.8×10^{-6}

The value of θ $|2000°\mathrm{K}|$ found here is approximately three times the Curie temperature (640°K); this is consistent with the assumption of lattice ordering of the second kind or antiparallel next nearest neighbors as was pointed out by Smart[8] and confirmed by Shull.[2]

V. DISCUSSION OF CoO

Roth[7] has pointed out that paramagnetic islands occur in antiferromagnets in the region of a lattice vacancy or impurity. If there are large amounts of such islands in our CoO crystal, they would tend to cause increased susceptibility at very low temperatures as we found. Due to these increased values no definite spin direction can be assigned to CoO, but if the higher susceptibilities can be attributed to lattice defects, the spin direction of CoO is probably in one of the [100] directions of the cubic form.

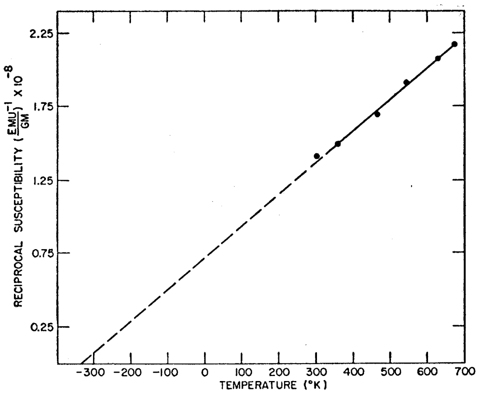

FIG. 5. Reciprocal high-temperature susceptibility of CoO.

VI. SUMMARY

We summarize the principal results of this paper as follows:

1. NiO single crystals exhibit isotropic susceptibility similar to powdered materials.
2. Stress annealing of NiO with the force applied along the [111] axis results in an increased susceptibility along the stressed direction, and a decreased susceptibility in the perpendicular direction.
3. If 50% of the NiO spins are rotated from the [111] direction of applied force to the perpendicular (111) planes, then one can account for the susceptibility values found after stress annealing.
4. An assignment of spin directions to the (111) planes perpendicular to the shortened [111] axis of the NiO rhombohedral is consistent with the susceptibility data.
5. The susceptibility of CoO increases at liquid

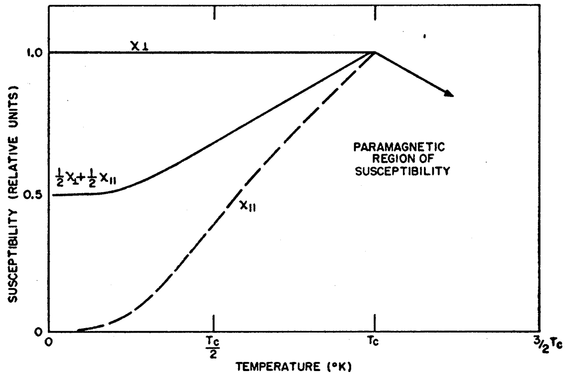

FIG. 6. Theoretical curves for susceptibility measured perpendicular and parallel to the spin axis.

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[7] W. L. Roth, Annual Meeting, American Crystallographic Association, June, 1956 (unpublished).

[8] J. S. Smart, Phys. Rev. **86**, 986 (1952).

helium temperatures. This is probably due to paramagnetic islands in the regions about lattice defects.

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Nuclear Quadrupole Interactions in Two Tutton's Salts[*]

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This paper reports results of nuclear induction experiments on two isomorphic single crystals of Tutton's salts, $Rb_2Mg(SO_4)_2\cdot 6H_2O$ and $Cs_2Mg(SO_4)_2\cdot 6H_2O$, belonging to crystal class $P2_1/a$. The splittings, due to nuclear electric quadrupole interactions, of the nuclear magnetic resonance spectra of Rb^{87} and Cs^{133} observed in these experiments are analyzed by using perturbation theory. Analysis of the data yields a quadrupole coupling constant for Rb^{87} of $|eQq/h| = 3141\pm 35$ kc/sec, and the asymmetry of the field gradient at the nuclear site is $\eta = (\phi_{xx}-\phi_{yy})/\phi_{zz} = 0.47\pm 0.01$. The principal axis of the field gradient is directed toward the nearest sulfate ion but no correlation of asymmetry and near neighbor locations is observed.

Comparison of the magnitudes of the field gradient at the nuclear sites of Rb and Cs were obtained by comparing the observed line patterns for the symmetry axis rotations, using the known moments of Cs and Rb. The complexity of the Cs spectra precluded a more complete comparison of the electric field symmetry.

INTRODUCTION

THE first investigations on the effect of nuclear electric quadrupole interactions on the nuclear magnetic resonance spectrum from solids were reported by Pound.[1] His paper was concerned with the removal of the transition degeneracy between the magnetic sublevels of the nuclear ground state in the presence of a large magnetic field. An orientational effect results from the electric quadrupole interacting with an electric environment of symmetry lower than cubic. The data obtainable in an experiment of this type are the directions of the principal axes of the electric field gradient tensor at the nuclear site, the magnitude of the interaction between quadrupole moment and field gradient $|eQq|$, where q is the largest of the eigenvalues of the tensor ∇E and Q is the nuclear quadrupole moment, and the asymmetry parameter defined as $\eta = (\phi_{xx}-\phi_{yy})/Q_{zz}$. Such experiments will also unambiguously determine the nuclear spin and give accurate quadrupole moment ratios of isotopes. Subsequent papers have been more detailed in the treatment of the theory,[2–4] and particular reference should be made to Volkoff[5] who describes in great detail most of the information which may be obtained by studying the electric quadrupole interaction as a perturbation on the nuclear magnetic resonance spectrum. Volkoff and co-workers[6,7] have applied his analysis to the study of Li^7 and Al^{27} in spodumene. Recently, the same theory has been applied to a more complex spectrum by Blood and Proctor,[8] and by Waterman and Volkoff[9] in their analysis of the B^{11} and Na^{23} interactions in kernite. We have again used Volkoff's theory in analyzing the data from resonance experiments on two isomorphic single crystals, which differ in the respect that the Rb^{87} ions in one crystal are replaced by Cs^{133} ions in the other.

The purpose of such a substitution is twofold.[7] One may observe differences in the spectra arising from the slight difference in structure due to size of the ions in the two cases. These differences may lead to useful information about the relation between the electric field gradient tensor and the crystal structure. Secondly, if the quadrupole moment of either nucleus is known, the experiment may provide information for estimating the other quadrupole moment.

The choice of crystal for the experiment was determined by a desire for a rather simple structure which would remain unchanged upon substitution of ions. The

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[1] R. V. Pound, Phys. Rev. **79**, 685 (1950).

[2] R. Bersohn, J. Chem. Phys. **20**, 1505 (1952).

[3] G. Becker, Z. Physik **130**, 457 (1951).

[4] E. F. Carr and C. Kikuchi, Phys. Rev. **78**, 1470 (1950).

[5] G. M. Volkoff, Can. J. Phys. **31**, 820 (1953).

[6] Volkoff, Petch, and Cranna, Can. J. Phys. **31**, 837 (1953).

[7] Volkoff, Petch, and Smellie, Can. J. Phys. **30**, 270 (1952).

[8] H. L. Blood and W. G. Proctor (to be published).

[9] H. H. Waterman and G. M. Volkoff, Can J. Phys. **33**, 156 (1955).