Principal magnetic susceptibilities and uniaxial stress experiments in CoO

P. S. Silinsky and Mohindar S. Seehra
Physics Department, West Virginia University, Morgantown, West Virginia 26506
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Using a single crystal from which nonstoichiometries have been removed, the principal susceptibilities, \( x_b \) and \( x_d \), of CoO have been determined in the temperature range of 4.2 to 350 K, bracketing \( T_N = 289 \) K. A stress = 210 bars along [001] was applied during measurements and in cooling through \( T_N \) (to remove \( T \) domains), and the initial \( x \) was measured for \( \overline{H} \parallel \{001\} \) and \( \overline{H} \perp \{001\} \) at \( \overline{H} = 250 \) Oe. These measured \( x \)'s are then related to \( x_0 \) and \( x_7 \) using the known magnetic structure of CoO, from which \( x_b \) and \( x_d \) at various temperatures are determined. Then, using the relation \( x_p = (x_0 + 2x_7)/3 \), the calculated \( x_p \) (powder) is found to agree well with the measured \( x_p \) at all temperatures, thus providing a consistency check on the procedures used in this work. For \( T \rightarrow 0 \) K, the experimental \( x_0 \) (0) = \( 39.5 \times 10^{-6} \) cm\(^3\)/g. This value is about 50\% higher than the only available theoretical estimate by Tachiki [although his estimates of \( x_7 \) (0) and \( x(T_N) \) are in good agreement with our measured values]. Various sources for this discrepancy are examined, and it is suggested that further theoretical work is needed to explain this discrepancy as well as the observed temperature dependence of \( x_b \) and \( x_d \). A comparison with the recent results of a similar study in MnO is also made.

I. INTRODUCTION

The accurate determination of the principal susceptibilities, \( x_b \) and \( x_d \), of the transition-metal oxides (CoO, MnO, NiO, and FeO) below their Neél temperatures (\( T_N \)) has long been thwarted by the existence of domains below \( T_N \) (Refs. 1 and 2) and by the presence of nonstoichiometries in the available crystals.\(^3\)\(^-\)\(^6\) Only recently\(^7\) has there been an in-depth study of \( x_b \) and \( x_d \) for one of the oxides, viz., MnO. Here in a companion work we present a determination of \( x_b \) and \( x_d \) for CoO below \( T_N \) (\( = 289 \) K).

CoO has a NaCl structure above \( T_N \).\(^1\) Below \( T_N \), an unstressed crystal undergoes a tetragonal contraction\(^8\) along the cubic [100] directions giving rise to 3-\( T \) domains. The magnetic wave vector is along [111] directions as in MnO; however, unlike MnO, the spins tilt out of the (111) planes making an angle of 27.4\(^\circ\) with the tetragonal axis and lie in the (110) planes.\(^2\) For each contraction axis there are four equivalent [111] directions, allowing a total of 12 domains\(^9\) in the unstressed crystal. Similar to the case in MnO,\(^7\) a stress \( [P] \geq 50 \) bars (Ref. 2) applied along [100] axis defines a preferred contraction axis as the sample is cooled through \( T_N \). A crystal stressed and cooled in this manner contains only a single-\( T \) domain with the four associated \( S \) domains clustered about the stressed axis. The sample used in these experiments was subjected to this stress and cooling with \( P \parallel [001] \).

The determination of \( x_b \) and \( x_d \) from the measured susceptibilities for CoO is more complicated than for MnO (Ref. 1) because of the remaining \( S \) domains. However, this has been carried out here. Particularly noteworthy is the result that \( x_b = 39.5 \times 10^{-6} \) cm\(^3\)/g in the limit \( T \rightarrow 0 \) K, a value about 50\% higher than the only available theoretical estimate.\(^10\) A comparison of our results with the earlier experimental studies\(^11\)-\(^13\) in CoO is also made.

II. EXPERIMENTAL DETAILS

The CoO crystal used in the measurements reported here was cut from a larger boule purchased from Cristal-Tec, Grenoble, France. The \( x \) measurements on the as-obtained crystal indicated the presence of nonstoichiometry,\(^4\) which was eliminated by a special annealing technique, viz., heating the crystal in Co vapor.\(^6\) The annealed sample, measuring about 1.5 \( \times 2 \times 2 \) mm\(^3\), was x-ray-aligned to yield (100), (010), and (001) faces. The magnetic susceptibilities were measured with the Faraday technique employing a Cahn electrobalance and Lewis gradient coils. Some details of this system and the general experimental procedures have been given elsewhere.\(^14\) The \( x \) measurements were done in the temperature range of 4.2 to 350 K with an absolute accuracy of about \( \pm 1\% \) and a relative precision of about 0.3\%.

Measurements were made on the sample under both unstressed and stressed conditions with stress applied along [001] to remove \( T \) domains. The stress was applied by placing the sample in an aluminum fixture containing a set screw at one end. Strain gauge calibration indicated the stress along [001] to be about 210 bars. The sample and fixture were mounted in the Faraday balance and magnetic susceptibilities were measured along principal axes.
parallel and perpendicular to the stressed direction. The measured values were later adjusted for the background due to the aluminum fixture with corrections determined in a separate experiment.  \(^{14}\)

**III. RELATIONSHIPS BETWEEN MEASURED AND PRINCIPAL SUSCEPTIBILITIES**

In the experiments reported here, \(\chi\) was measured with the stress \(P\) applied along the [001] direction and the magnetic field \(H\) applied either parallel to [001] or perpendicular to [001]. (In the latter case \(H\) was parallel to one of the other two cubic directions [100] or [010].) These susceptibilities are, respectively, termed as \(X_h\) and \(X_t\). As pointed out in the Introduction, neither \(X_h\) nor \(X_t\) is equal to either \(X_{III}\) (measured parallel to the easy axis) or \(X_{II}\) (measured perpendicular to the easy axis). Here we derive the relationships among \(X_h\), \(X_t\), \(X_\parallel\), and \(X_\perp\) based on the known magnetic structure of CoO.  \(^2\)

It has been established  \(^2\) that \(P = 50\) bars applied along [001], during cooling through \(T_N\), is sufficient to "select" one preferred \(T\) domain to the exclusion of the other two. Thus in our experiment with \(P = 210\) bars, we only need to concern ourselves with four \(S\) domains, with their easy axis tilted at \(\phi = 27.4^\circ\) away from [001] in the four [110] planes. For \(H\parallel [001]\), the easy direction, it is easy to see that all four \(S\) domains yield the same magnetization and the measured \(\chi\) along [001] is given by

\[
\chi = \chi_h \cos^2 \phi + \chi_t \sin^2 \phi \tag{1a}
\]

or

\[
\chi = 0.7882 \chi_h + 0.2118 \chi_t \tag{1b}
\]

For \(H \perp [001]\), the measured \(\chi\) is likewise given by

\[
\chi = \frac{1}{2} [\chi_h \sin \phi \cos \phi + \chi_t (1 + \cos^2 \phi)] \tag{2a}
\]

or

\[
\chi = 0.1059 \chi_h + 0.8941 \chi_t \tag{2b}
\]

In the above we have used \(\phi = 27.4^\circ\) as determined from neutron-diffraction measurements.  \(^2\) Solving Eqs. (1b) and (2b) yields

\[
\chi_h \approx 1.3103 \chi_t - 0.3103 \chi_t \tag{3a}
\]

and

\[
\chi_t \approx 1.1552 \chi_t - 0.1552 \chi_t \tag{3b}
\]

For a powdered material, one gets \(\chi_p = (\chi_h + 2\chi_t)/3\), which in the present case is given by \([\text{using Eqs. (3a) and (3b)}]\)

\[
\chi_p = (\chi_h + 2\chi_t)/3 \tag{4}
\]

For comparison, we note that in MnO, where the spins (and the \(S\) domains) are confined to the \((111)\) plane, the measured \(\chi\) in the \((111)\) plane equals \((\chi_0 + \chi_1)/2\). It should be noted that the above relations hold only if \(X_h\) and \(X_t\) are the initial susceptibilities. This is an important consideration in MnO (Ref. 7) as well as in CoO, as the experimental results below will demonstrate.

**IV. EXPERIMENTAL RESULTS**

The magnetic field dependence of the magnetization \(M\) at 5.5 K is shown in Fig. 1. It is seen that for \(H \parallel [001]\) (i.e., parallel to the direction of the applied stress), \(\bar{M}\) varies nonlinearly with field for \(H < 1\) kOe, whereas for \(H \perp [001]\) (i.e., perpendicular to the applied stress), \(\bar{M}\) varies linearly with \(H\). Therefore, it is essential that in order to determine the initial susceptibilities, \(\chi_h(\bar{H} \parallel [001])\) be measured at the smallest possible \(H\). In our experiments we used \(H = 250\) Oe for measuring both \(X_h\) and \(X_t\). Qualitatively, the variations of \(\bar{M}\) with \(H\) in Fig. 1 are similar to those seen in MnO (Ref. 7). We will return to the discussion of this point later.

The temperature dependence of \(X_h\) and \(X_t\) is shown in Fig. 2. It is seen that below \(T_N = 289\) K, \(X\) becomes anisotropic due to the onset of the magnetic order. The transition is not of first order even in applied stress, since there is no discontinuous change in \(X\) at \(T_N\), as in MnO (Ref. 7). Below \(T_N\), \(X_h\) is essentially temperature independent; however, \(X_t\) decreases considerably, reaching a minimum around 70 K, and then increases by about 2% as the temperature is lowered to 4.2 K.

Using Eqs. (3a) and (3b) and the data of Fig. 2, we have determined \(X_h\) and \(X_t\) and the results are shown in Fig. 3. The temperature dependence of \(X_h\) below \(T_N\) and that of \(X_\parallel\) below about 100 K is quite negligi-
The estimated values at 0 K and $T_N$ (in units of $10^{-6} \text{ cm}^3/\text{g}$) are $\chi_\parallel(0) = 39.5$, $\chi_\perp(0) = 67.5$, $\chi_p(0) = 58.2$, and $\chi_\perp(T_N) = 66.5$.

The effect of stress on the measured $\chi_1$ is shown in Fig. 4. It is evident that below $T_N$, the applied stress considerably lowers the measured $\chi$ compared to the unstressed value due to the elimination of $T$ domains. It is to be noted that the stress applied was during the cooling of the sample through $T_N$ and during the measurements. For $\chi_1$, a similar behavior was observed with varying stress, although the decrease in $\chi$ below $T_N$ was not as large.

V. DISCUSSION

We begin this section by comparing the results of the preceding section with the measurements of $\chi$ reported by others. Using a powdered specimen, Le Blanchetais$^{15}$ measured $\chi_p$ from about 80 to 750 K. Measurements of $\chi$ on a single crystal of CoO have been reported by Singer$^{12}$ and Uchida et al.$^{13}$ at a few selected temperatures below $T_N$. In Ref. 11, the absolute values of $\chi_p$ above $T_N$ are in excellent agreement with the results of Fig. 2. We believe that the data on a single crystal by Singer$^{12}$ were strongly influenced by the nonstoichiometry of the sample since the magnitudes of $\chi_3$ and $\chi_1$ were larger at 4.2 K (by about 10%) than the values at 77 K. This is consistent with our observations in a nonstoichiometric crystal.$^{4,6}$ The anisotropy between $\chi_3$ and $\chi_1$ observed by Singer at 77 K is about half the value shown in Fig. 2. This may be partly due to multiple $T$ domains, since the sample was only stress annealed and not stressed during $\chi$ measurement as done in the present experiments. In the measurements of Uchida et al.$^{13}$ the single crystal was subjected to a temperature gradient along [001] in an effort to obtain a single $T$-domain crystal. The torque measurements indicated that the method had some success; although these authors were unsure of complete success. Consequently, $\chi_3$ and $\chi_1$ were not determined.$^{15}$

Also, the measurements in this work were limited to temperatures above 90 K. Therefore, to the best of our knowledge, the results of Figs. 2 and 3 provide the first determination of the complete temperature dependence of $\chi_1$ and $\chi_3$ and, more importantly, $\chi_\parallel$ and $\chi_\perp$ in CoO.

In an unstressed crystal, the presence of three $T$ domains and the associated randomness of the easy axis makes the measured $\chi_3$ larger than that measured in a single $T$-domain crystal because of the larger contributions from $\chi_3$. The decrease of $\chi_1$ with stress, as observed in Fig. 4, is consistent with this interpretation. A similar effect was observed in MnO.$^7$ Note that the stress applied in our experiments ($\approx 210$ bars) is several times larger than the minimum stress ($\approx 50$ bars) required to eliminate $T$
domains in CoO (as determined by neutron-diffraction experiments) so that a mono-T-domain crystal is assured. The analysis of Sec. III is, therefore, applicable to the results of Fig. 2 and one can be confident of the values of $X_0$ and $X_1$ as shown in Fig. 3.

An additional check on the accuracy of the magnitudes of $X_0$ and $X_1$ can be obtained from the use of Eq. (4) giving $X_p$ in terms of $X_0$ and $X_1$ (or equivalently $X_p = (X_0 + 2X_1)/3$) and comparing it with the measured $X_p$. This comparison is shown in Fig. 5, where the solid curve is Eq. (4) using $X_0$ and $X_1$ values from Fig. 2 and the circles are the data on an independently prepared powder sample (sample B, Ref. 4). The behavior of $X_p$ vs $T$ for the two sets of values is very similar and the absolute magnitudes differ by about the experimental error only, signifying the accuracy of our analysis.

A spin-flop field of about 120 kOe for CoO has been determined by Inagawa et al. Therefore, the magnetic field dependence of the magnetization for $H || [001]$ and the associated critical field of only about 1 kOe (Fig. 1) cannot be due to the same spin-flop process. In MnO, where a similar critical field of about 2 kOe was observed, this field was related to the in-plane anisotropy. Unlike CoO, the spins in MnO are confined to a single (111) plane in a stressed crystal so that the application of 2 kOe is believed to flop the spins perpendicular to $H$, but they remain within the (111) plane. In CoO, the spins are confined to two mutually perpendicular (110)-type planes. It is possible that the critical field of 1 kOe (Fig. 1) is in some way related to the anisotropy within the (110)-type planes. However, we are not aware of any other study with which this result could be compared. The critical field of 120 (Ref. 16) probably corresponds to the case when all the spins flop to a direction perpendicular to $H$. In any case, the importance of using only the initial susceptibilities in Eqs. (1) through (3) (as done in this work) is quite evident since there is usually a field-dependent contribution to $X$ at higher fields.

Now we consider the magnitudes and the temperature dependence of $X_0$ and $X_1$ as shown in Fig. 3. Below $T_N$, $X_1$ is essentially temperature independent; whereas $X_0$ decreases by about 40% between $T_N$ and $T_N/3$ and then remains nearly temperature independent at lower temperatures. It is very likely that this temperature independence of $X_0$ (and consequently, of the $X_p$ in Fig. 5) below that $T_N/3$ is an intrinsic property of CoO rather than being due to any remnant nonstoichiometry in the sample as was suggested in an earlier communication. There are several low-lying levels at energies $-k_B T_N$ above the ground state of Co$^{2+}$ in CoO so that varying contributions with temperature from these levels are likely to be very important in characterizing the temperature dependence of $X_0$ and $X_1$ in CoO. To our knowledge, such a theory for CoO is yet to be advanced. The only known relevant theoretical study is by Tachiki, which was based on the earlier work by Kanamori. However, this calculation was limited to the evaluation of $X_0(0)$ and $X_1(0)$, the values of $X_0$ and $X_1$ in the limit $T \to 0$ K, and the evaluation of $X(T_N)$. These estimates (in units of $10^{-6}$ cm$^3$/g) are $X_0(0) = 25.9$, $X_1(0) = 66.6$ and $X(T_N) = 68.7$, to be compared with our experimental values (within $\pm 1\%$) of 39.5, 67.5, and 66.5, respectively. The only significant discrepancy is in $X_0(0)$, where the experimental value is about 50% larger than the theoretical estimate. It is noted that the nonzero value of $X_0(0)$ in CoO is due to the unquenched orbital moment of Co$^{2+}$ in CoO, as first suggested by Kanamori.

The discrepancy between the measured and the calculated $X_0(0)$ is now examined. In the calculations of Tachiki, $X_0(0)$ is given by

$$X_0(0) = 2N \mu_B \left\{ g_\alpha^2 \alpha^2 + g_\beta^2 \beta^2 + 2g_\alpha g_\beta \gamma^2 + 2(2J_1 z_1 + 2J_2 z_2) \gamma^2 (\alpha^2 - 2) \right\}$$

(5)

where $\alpha, \beta, \gamma$ are, respectively, the matrix elements of $s_z$, $l_z$, and $s_z l_z$ between the ground state and excited states while the other symbols have their usual meanings. Tachiki's calculations are based on the assumption that the magnetic moments in CoO are parallel to [001], the direction of crystal distortion, so that $s_z$ and $l_z$ are simul-
taneously diagonalizable. This yields \( \alpha' = \beta' = -\gamma' \) and the off-diagonal term in Eq. (5) vanishes, leading to

\[
\chi_n(0) = 2N\mu^2 \left( \frac{g_1 - g_2)^2 \alpha'}{1 + 2\alpha'(2J_1z_1 + 2J_2z_2)} \right).
\]

In his calculations,\(^{10}\) Tachiki uses \( g_\parallel = 2.16 \) (obtained by fit to \( T > T_N \)), \( g_\perp = -1.415 \) (calculated value), \( J_1 = 4.80 \text{ cm}^{-1} \), \( J_2 = 15.0 \text{ cm}^{-1} \), and, of course, \( z_1 = 6 \) and \( z_2 = 12 \) for \( \text{CoO} \). From spin-wave dispersion curves obtained by neutron-diffraction experiments, Rechtin and Averbach\(^{19}\) have recently determined \( J_1 = 3.82 \text{ cm}^{-1} \) and \( J_2 = 19.03 \text{ cm}^{-1} \). Using these values in Eq. (6) reduced the value of \( \chi_n(0) \) by about 1.5% from Tachiki’s estimate so that this cannot be the source of the discrepancy. The values of \( g_\parallel \) and \( g_\perp \) cannot be readjusted without affecting \( \chi_n(0) \) and \( \chi(T_N) \), the quantities which at present are in good agreement with the experiment. A 50% increase in the value of \( \alpha' \) in Eq. (6) would increase \( \chi_n(0) \) by about 38%, a value more in line with the experiment. But such as \( \text{ad hoc} \) change is not justified at present. However, the magnitudes of \( \alpha', \beta', \gamma' \) depend on the energy splittings between the ground state and excited states. Their magnitudes as well as the status of the off-diagonal term in Eq. (5) are dependent on Tachiki’s assumption that the magnetic moments are parallel to [001]. In actuality, the moments are tilted 27.4° away from [001]. Therefore, in our view, the effect of this assumption on the calculated magnetic susceptibilities needs to be reexamined.

VI. CONCLUDING REMARKS

The temperature dependence of the principal magnetic susceptibilities in a single crystal of \( \text{CoO} \) from which nonstoichiometries and \( T \) domains have been eliminated has been presented in this paper. To our knowledge, this is the first successful experiment in which the temperature dependence of \( \chi_n \) and \( \chi_\parallel \) in \( \text{CoO} \) has been determined. Although the measured \( \chi_n(0) \) and \( \chi(T_N) \) agree with the calculations of Tachiki, his estimate of \( \chi_n(0) \) is lower by about 50% from our experimental value.\(^{20}\) An examination of the various possible sources for this discrepancy suggests that the assumption that the magnetic moments are parallel to [001] should be reconsidered. Also, further theoretical work is necessary to explain the observed temperature dependence of \( \chi_n \) and \( \chi_\parallel \). On another matter, the transition in \( \text{CoO} \) at \( T_N \) does not have a first-order character, in contrast to \( \text{MnO} \), where the nature of the first-order transition becomes quite evident with a small stress.\(^{7}\)

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1W. L. Roth, Phys. Rev. 110, 1333 (1958); 111, 772 (1958).
9Here we follow the nomenclature of Refs. 1 and 7, rather than that of Ref. 2, in which the \( T \) and \( S \) domains are, respectively, referred to as \( S \) and \( K \) domains.
15In Ref. 13, expressions for \( \chi_n \) and \( \chi_\parallel \) in terms of \( \chi_{\parallel \parallel} \), \( \chi_{\parallel \perp} \), the tilt angle \( \phi \) and the mixing parameter \( p \) of the various \( T \) domains are derived. These expressions agree with our Eqs. (1a) and (2a) in the limit of a single \( T \) domain.
17For example, see F. Keffer and W. O'Sullivan, Phys. Rev. 108, 637 (1957).
20A diamagnetic contribution, estimated to be about \(-0.5 \times 10^{-6} \text{ cm}^3/\text{g} \) for \( \text{CoO} \) (about the same as for \( \text{MnO} \) in Ref. 7), though relatively negligible here, should be included for accuracy.