# Nature of magnetic transitions in MnO, $Fe_zO$, CoO, and NiO

G. Srinivasan and Mohindar S. Seehra
*Physics Department, West Virginia University, P. O. Box 6023, Morgantown, West Virginia 26506-6023*
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High-resolution measurements of the magnetic susceptibility $\chi$ in polycrystalline MnO, $Fe_zO$ ($z=0.938$), CoO, and NiO, and in stressed (along [111]) NiO crystals near their respective $T_N$'s are reported. From the behavior of $\chi$ and $\partial(\chi T)/\partial T$ vs $\epsilon=(T-T_N)/T_N$ for $|\epsilon|<0.03$, it is found that the transitions to the magnetic state in MnO and $Fe_zO$ are first order, whereas those in CoO and NiO are continuous.

The four transition-metal oxides, viz., MnO, FeO, CoO, and NiO, with fcc structure, are type-II antiferromagnets[1] characterized by a propagation vector $\vec{k}=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. In MnO and NiO, the sublattice mangetization vector $\vec{m}\perp\vec{k}$ and the order parameter are characterized by eight components ($n=8$). In $Fe_zO$ ($z=0.89$ to 0.95), $\vec{m}\parallel\vec{k}$ and $n=4$,[2] whereas, in CoO, $\vec{m}$ makes an angle of 82° with $\vec{k}$ (Ref. 3) and $n=12$. Based on the arguments of the renormalization-group analyses in $(4-\epsilon)$ dimensions it has been suggested[4,5] that the paramagnetic to antiferromagnetic (PM → AF) transition in all the four oxides should have a first-order character. Experimentally, the transition in MnO has been established to be of first order,[6] whereas specific-heat measurements near the Néel temperature $T_N$ show the transition in CoO to be of second order.[7] In NiO, the measurements of LMB (linear magnetic birefringence) by Germann, Maier, and Straub,[8] and of the sublattice magnetization by neutron diffraction[9] near its $T_N\simeq 524$ K, indicate the PM → AF transition to be a continuous one or of second order. Since NiO and MnO have exactly the same symmetries in crystal and magnetic structure, and since MnO appears to follow the major predictions of the renormalization-group calculations (e.g., the change of the transition to second order under a symmetry breaking [111] stress[10,11]), it is of great theoretical interest to establish beyond doubt the nature of the transition in NiO. In $Fe_zO$, a careful study of the nature of the PM → AF transition has not yet been reported.

The nature of the transition in AF can be established by measuring the temperature variation of the sublattice magnetization $\vec{m}$ or that of $C_p$, the specific heat near $T_N$. Fisher[12] showed that in antiferromagnets near $T_N$, the magnetic susceptibility $\chi$ and $C_p$ are related as $C_p\propto\partial(\chi T)/\partial T$ so that the temperature variation of $(\chi T)'\equiv\partial(\chi T)/\partial T$ should resemble $C_p$. This relationship has been verified in a number of antiferromagnets.[13]

In this paper we report high-resolution $\chi$ measurements in MnO, CoO, $Fe_zO$ ($z=0.938$), and NiO near their respective $T_N$'s, and the quantity $(\chi T)'$ has been computed from this data. Since the nature of the transitions in MnO and CoO are reasonably well established, we have used the results on these systems as a test for our procedure. Our measurements show that in NiO, PM → AF transition is continuous, in agreement with the experimental results reported by other groups,[8,9] but in conflict with the predictions of the renormalization-group calculations.[4,5] On the other hand, the transition in $Fe_zO$ appears to be first order. Details of these results are given below.

The measurements of the static magnetic susceptibility $\chi$ were carried out with a Faraday balance apparatus[14] on polycrystalline samples and a stressed NiO crystal. The samples of MnO, CoO, and NiO were obtained from single-crystal specimens (purchased from Cristal-Tec, Grenoble, France) and the sample of $Fe_zO$ ($z=0.938$) was prepared by heating appropriate amounts of $\alpha$-$Fe_2O_3$ and Fe in an evacuated-sealed quartz ampoule for 24 h at 1100 K, followed by quenching the sample in liquid nitrogen.

In Fig. 1, the initial susceptibility $\chi$ measured at 200 Oe with increasing temperatures is plotted against $\epsilon=(T-T_N)/T_N$ for the four oxides. The Néel temperatures $T_N$'s are determined from the peak positions of $(\chi T)'$ vs $\epsilon$ shown in Fig. 2. The measured values of $T_N$ for MnO, $Fe_zO$, CoO, and NiO are, respectively, 118.9, 195.7, 288.5, and 524.5 K, in good agreement with the values quoted in

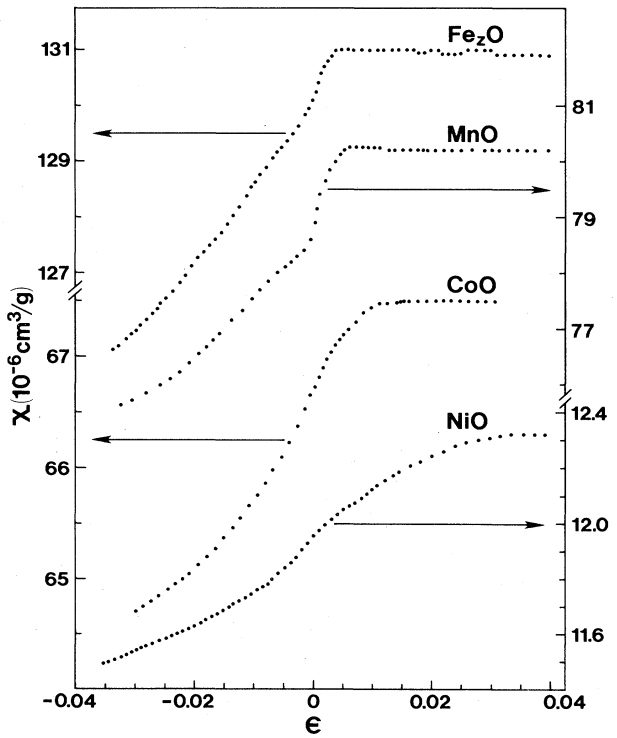


FIG. 1. Variation of $\chi$ vs $\epsilon=(T-T_N)/T_N$ for polycrystalline samples, with $T_N$ values given in the text. Note the different scales for $\chi$ for the four oxides.

 

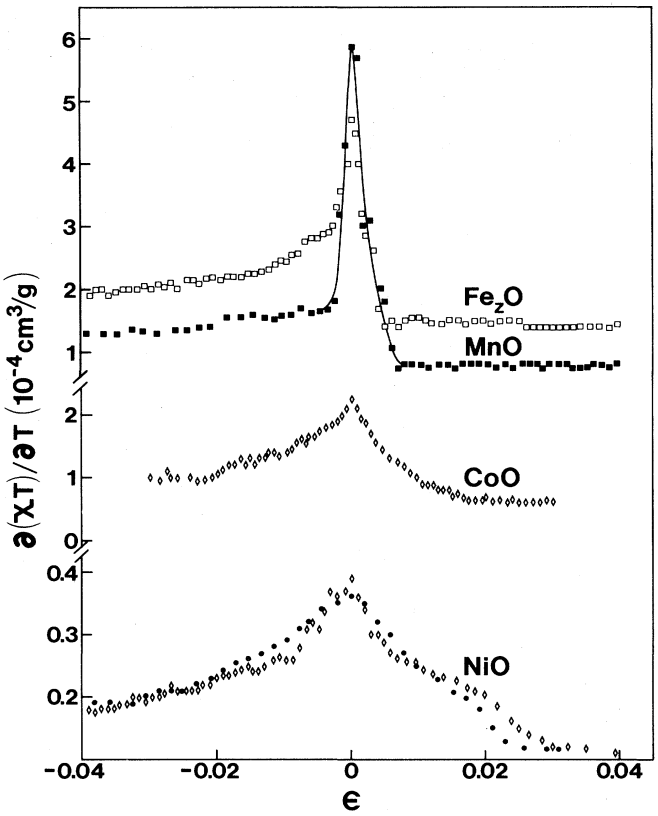


FIG. 2. Variation of $\partial(\chi T)/\partial T$ vs $\epsilon=(T-T_N)/T_N$ for the four oxides. For NiO, data for polycrystalline sample (solid circles) as well as a stressed single crystal ($\diamond$) along [111] are shown. For MnO, the solid line is drawn through points for visual aid.

literature. We note that any temperature-independent contributions to $\chi$, such as the diamagnetic and Van Vleck susceptibilities, only add a constant background to $(\chi T)'$ in Fig. 2 and therefore do not affect the character of the transitions.

From the behavior of $\chi$ against $\epsilon$ for $|\epsilon|<0.03$ in Fig. 1, it is evident that the PM $\rightarrow$ AF transitions in NiO and CoO are of continuous type, whereas more abrupt changes are noticed for MnO and $Fe_zO$. This is more clearly evident in Fig. 2 in the plots of $(\chi T)'$ against $\epsilon$. In MnO and $Fe_zO$, most of the variation in $(\chi T)'$ occurs in the region $|\epsilon|<0.005$, whereas in CoO and NiO, changes in $(\chi T)'$ are gradual, which are characteristic of second-order transitions. Experiments on all four systems were done under similar conditions, so as to make the comparison more meaningful. Since the transition in MnO is known to be of first order,[6] we infer from Figs. 1 and 2 that PM $\rightarrow$ AF transition in $Fe_zO$ also has a dominant first-order character. This is a major new result of this work. It is noted that no evidence of noticeable hysteresis could be found in $Fe_zO$. However, in MnO, hysteresis at its first-order transition has not been observed either.

In MnO, application of a small ($\sim 20$ bars) stress along a [111] axis (the direction of lattice contraction below $T_N$) brings out the true first-order character of its transition by elimination of twin domains.[15] Therefore a similar experiment was tried in NiO. A single crystal of NiO was stressed along a [111] axis with a stress $\simeq 10$ bars, and the temperature was then raised to above its $T_N$, followed by measurements of $\chi$ for applied field $\vec{H}\perp[111]$ axis with lowering temperature at $\vec{H}=200$ Oe [for a single domain crystal, this arrangement measures $\chi_{\parallel}^{*}=(\chi_{\parallel}+\chi_{\perp})/2$ (Ref. 15)]. The data of $(\chi T)'$ vs $\epsilon$ for the stressed crystal is also shown in Fig. 2. It is clear that no significant difference is observed from the data on a polycrystalline sample near $T_N$, although, as $T$ is lowered toward room temperature, $\chi_{\parallel}^{*}<\chi$ (polycrystalline) as expected.[15] In a later experiment, even a stress $\simeq 50$ bars produced no significant differences from the data shown in Fig. 2. Our data near $T_N$ on the stressed crystal are significant in that in the earlier experiments on NiO, where a continuous transition was reported,[8,9] the measurements were carried out without any applied stress. From the observations reported in Fig. 2, it is safe to infer that the PM $\rightarrow$ AF transition in NiO is indeed continuous. It is also appropriate to note here that even in CoO, a [001] stress (along the contraction axis) on cooling the sample through $T_N$ does not alter the character of the PM $\rightarrow$ AF transition.[16]

In summary, the observations reported here suggest that the PM $\rightarrow$ AF transitions in MnO and $Fe_zO$ are first order and those in NiO and CoO are continuous. The suggestion of a first-order transition in $Fe_zO$ is a new result which should be confirmed by additional experiments such as the measurements of the temperature dependence of the sublattice magnetization by neutron scattering experiments. Additional support for a continuous transition in NiO is provided here by making measurements on a single crystal of NiO under a [111] stress. The predictions of the renormalization-group calculations are thus found not to be entirely correct, and there still remains the question whether the first-order transitions in MnO and in $Fe_zO$ (which carry larger moments than CoO and NiO) are driven by other mechanisms such as the magnetoelastic interactions.

## ACKNOWLEDGMENTS

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[1]W. L. Roth, Phys. Rev. 110, 1333 (1958).
[2]P. D. Battle and A. K. Cheetham, J. Phys. C 12, 337 (1979).
[3]D. Hermann-Ronzaud, P. Burlet, and J. Rassat-Mignod, J. Phys. C 11, 2123 (1978).
[4]S. A. Brazovskii and I. E. Dzyaloshinskii, Pis'ma Zh. Eksp. Teor. Fiz. 21, 360 (1975) [JETP Lett. 21, 164 (1975)].
[5]P. Bak, S. Krinsky, and D. Mukamel, Phys. Rev. Lett. 36, 52 (1976).
[6]D. Bloch, R. Maury, C. Vettier, and W. B. Yelon, Phys. Lett. 49A, 354 (1974).
[7]M. B. Salamon, Phys. Rev. B 2, 214 (1970).
[8]K. H. Germann, K. Maier, and E. Straub, Solid State Commun.

14, 1309 (1974).
[9]C. F. Van Doorn and P. de V. Duplessis, Phys. Lett. 66A, 141 (1978).
[10]D. Bloch, D. Hermann-Ronzaud, C. Vettier, W. B. Yelon, and R. Alben, Phys. Rev. Lett. 35, 963 (1975).
[11]M. Kerszberg and D. Mukamel, Phys. Rev. Lett. 43, 293 (1979).
[12]M. E. Fisher, Philos. Mag. 7, 1731 (1962).
[13]E. E. Bragg and M. S. Seehra, Phys. Rev. B 7, 4197 (1973), and references therein.
[14]M. S. Seehra and M. S. Jagadeesh, Phys. Rev. B 20, 3897 (1979).
[15]M. S. Jagadeesh and M. S. Seehra, Phys. Rev. B 23, 1185 (1981).
[16]P. S. Silinsky and M. S. Seehra, Phys. Rev. B 24, 419 (1981).