Magnetic Resonance and Susceptibility of Several Ilmenite Powders

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Magnetic susceptibility, paramagnetic resonance, and antiferromagnetic resonance have been measured in $MnTiO_3$, $FeTiO_3$, $CoTiO_3$, and $NiTiO_3$. Néel temperatures T_N of 65, 56, 37, and $23\pm2°K$, respectively, have been measured. The molar susceptibilities appear to obey a Curie-Weiss law with $C_m = 4.36, 3.37, 3.72$, and $1.24°K$, and with paramagnetic Curie temperatures $\Theta_p = -219, +32, -9.3$, and $-11°K$, respectively. The effective spectroscopic splitting factors consistent with this law and with paramagnetic resonance are $g_{eff} = 2.01, 2.13, 2.83, 2.22 \pm 0.01$. The susceptibility of $MnTiO_3$ exhibits a broad peak near $100°K$ rather than a well-defined peak at T_N. No antiferromagnetic resonance was observed in $FeTiO_3$, and no paramagnetic resonance was observed in $FeTiO_3$ or $CoTiO_3$. The antiferromagnetic resonant frequencies, extrapolated to $0°K$, are 156, 145, and 187 kMc/sec for $MnTiO_3$, $CoTiO_3$, and $NiTiO_3$, respectively. A low-frequency mode of 19.1 kMc/sec was also detected in $NiTiO_3$. In the system $Mn_{1-x}Mg_xTiO_3$, both ω_R and T_N decrease roughly linearly with x in the range $0 < x < 0.075$.

I. INTRODUCTION

THE purpose of this study is to provide careful susceptibility and resonance data for powder samples of the ilmenites $MTiO_3$, where $M = $ Mn, Fe, Co, and Ni. It has been shown that uniaxial antiferromagnetic powdered materials exhibit an absorption edge as the applied magnetic field is varied.[1,2] A preliminary report on this data has already appeared.[1,3] Neutron-diffraction and Mössbauer studies are also available for these materials.[4–8] Independent susceptibility data are available for $MnTiO_3$,[9] $CoTiO_3$,[4,10] and $NiTiO_3$.[10] In the companion paper,[11] these are used to determine various phenomenological constants that enter the molecular-field description of these antiferromagnetic, layer compounds. They provide an over-determined set of numbers that permit a check of the self-consistency of the theory.

II. SAMPLE PREPARATION

1. MnTiO₃. Spectroscopic-grade TiO_2 was dried at 560°C and spectroscopic-grade Mn_3O_4 was reduced to

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MnO with hydrogen at 1000°C for 20 h. They were weighed out in the mole ratio of 1:1 and ground thoroughly in air with agate mortar and pestle. The mixture was heated at 950°C for 21 h in CO_2 and allowed to cool under CO_2 to room temperature. It was then reground and fired at 1150°C in $CO-CO_2$ (1:10) for 33 h and 1000°C for 6 h under the same gas atmosphere. The $MnTiO_3$ was quenched from 1000°C and was yellow-green in color. The final product was annealed in a sealed, evacuated silicon tube at 800°C for two weeks, and cooled at 50°/h. X-ray and chemical analysis indicated a single $MnTiO_3$ phase.

TABLE I. Néel temperature T_N, molar Curie constant C_m, paramagnetic Curie temperature Θ_p, effective number of Bohr magnetons per atom $n_{eff} = \mu_{eff}/\mu_B$, and effective spectroscopic splitting factor g_{eff} for several ilmenites from dc susceptibility measurements. ($\mu_{eff} = g_{eff}[S(S+1)]^{1/2}$.)

Sample	$T_N(°K)$	C_m(emu)	$\Theta_p(°K)$	n_{eff}	g_{eff}
$MnTiO_3$	66++ 63.5+	4.36	−219	5.93	2.01++
$FeTiO_3$	56	3.40	+59	5.23	2.14
$CoTiO_3$	36+ 38	3.61	−3	5.46	2.79
$NiTiO_3$	22+ 23	1.26	−13	3.16	2.21++ 2.23

2. FeTiO₃. Spectroscopic-grade Fe_2O_3 and TiO_2 were ground under acetone and allowed to air dry. The mixture was heated in air for 24 h at 1000°C. The sample was reground and heated under a $CO:CO_2$ atmosphere (1:3) at 1000°C for 6 h and quenched under the same atmosphere. The sample was annealed in an evacuated silicon tube at 800°C for two weeks and slow cooled at 50°/h. X-ray and chemical analysis indicated a single $FeTiO_3$ phase.

3. CoTiO₃. Spectroscopic-grade CoO and TiO_2 were weighed in the ratio 1:1, ground in air, and heated under a nitrogen atmosphere at 1000°C for 24 h. The sample was reground and reheated under nitrogen at 1150°C
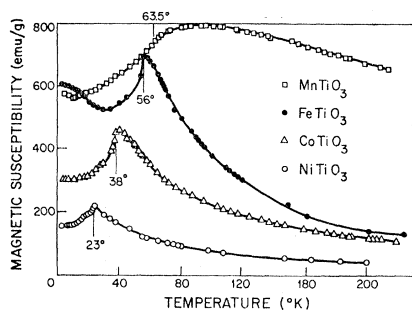
FIG. 1. Magnetic susceptibilities versus temperature of the antiferromagnetic ilmenites $M^{2+}TiO_3$. The susceptibility of $MnTiO_3$ has been multiplied by 10.

for 24 h. The resulting product was slow-cooled under nitrogen at the rate of $50°/h$. X-ray and chemical analysis indicated a single phase corresponding to $CoTiO_3$.

4. $NiTiO_3$. Spectroscopic-grade NiO and TiO_2 were prepared by the thermal decomposition of the oxalates $NiC_2O_4 \cdot M_2O$ and $(NH_4)_2$ $TiO(C_2O_4)_2 \cdot 2H_2O$. A 1:1 mixture of the finely divided, reactive oxides NiO and TiO_2 was ground intimately under acetone and air dried. The resulting mixture was heated in a platinum crucible at 1150°C for 48 h and then reground. The produce was reheated at 1300°C for 24 h and cooled slowly to room temperature. X-ray and chemical analysis indicated the presence of a single phase corresponding to the formula $NiTiO_3$.

III. MAGNETIC SUSCEPTIBILITY

Magnetic susceptibilities were measured with a vibrating-sample magnetometer from 4.2 to 300°K at a field of 7320 G. In the case of $MnTiO_3$, measurements were extended to 600°K to permit a more accurate determination of the Curie-Weiss temperature Θ_p. Temperature was monitored with a copper-constantan thermocouple and was accurate to 0.5°K, according to susceptibility measurements on samples with known temperature characteristics.

Measured susceptibilities versus temperature are shown in Fig. 1. In the high-temperature $(T > T_N)$ region, the molar susceptibilities appear to obey a Curie-Weiss law:

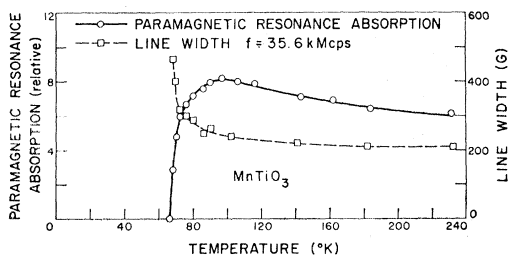$$\chi_m = C_m/(T - \Theta_p); \qquad C_m = N(g_{eff}\mu_B)^2 S(S+1)/3k. \quad (1)$$

FIG. 2. Paramagnetic resonance absorption versus temperature for $MnTiO_3$.

The empirical values of C_m, Θ_p, and g_{eff}, consistent with this law and measured values of T_N, are given in Table I for $S = \frac{5}{2}$, 2, $\frac{3}{2}$, and 1 for $MnTiO_3$, $FeTiO_3$, $CoTiO_3$ and $NiTiO_3$, respectively. N is Avogadro's number.

The susceptibility of $MnTiO_3$ exhibits a broad peak near 100°K rather than a well-defined peak at T_N, and $T_N = 63.5°K$ was obtained from resonance and specific-heat[12] data.

IV. PARAMAGNETIC RESONANCE

Paramagnetic-resonance absorption was observed on powder samples at 35 kMc/sec from 4.2 to 300°K. In the region of the Néel temperature, where the resonance peak absorption and linewidth depend critically on temperature, care was taken to ensure that the
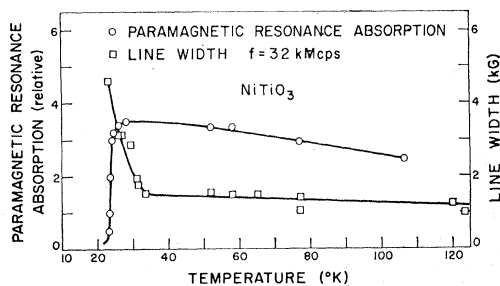

FIG. 3. Paramagnetic resonance absorption and linewidth versus temperature for $NiTiO_3$.

sample was at temperature equilibrium. Temperature was raised either by allowing the sample waveguide to warm up or by using helium exchange gas in conjunction with a carbon resistor heater so as to cycle the sample temperature. Resonance absorption was observed by means of a waveguide reflection-type spectrometer.

Paramagnetic resonance could only be observed in $MnTiO_3$ and $NiTiO_3$, where spin-lattice coupling via spin-orbit interactions is minimal. The resonance absorption vanished rapidly on decreasing the temperature through T_N, as shown in Figs. 2 and 3, reaching a tenth of their paramagnetic intensity at 66°K in $MnTiO_3$ and at 22°K in $NiTiO_3$.

V. ANTIFERROMAGNETIC RESONANCE

Antiferromagnetic (AFM)-resonance studies were made at selected frequencies from 35 to 200 kMc/sec and at temperatures ranging from 4.2 to 300°K. Because the sample materials were in the form of powders, it was more convenient to use waveguide transmission and reflection spectrometers than the more conventional cavity spectrometer. Klystrons and carcinatrons served as millimeter-wave sources, except at frequencies above 140 kMc/sec where crystal harmonic generators were

[12] D. Smith, thesis, Department of Chemistry, MIT, 1965 (unpublished).

used. Frequencies were measured with calibrated wave meters, and the final frequency uncertainty was about 0.2 kMc/sec. To facilitate the measurement of powders, the sample material was pressed into thin, plastic cylindrical containers tapered at both ends to reduce sample reflections and to minimize particle movement with applied fields. A uniform sample temperature was maintained by placing the sample inside a waveguide section made of thick-walled copper. The transmission and reflection waveguide sections extending into the cryostat were enclosed in an evacuated, stainless-steel jacket, which prevented liquid helium from entering the sample waveguide and producing noise. To permit heat exchange between the sample and the surrounding helium bath, controlled amounts of helium gas were introduced inside the steel jacket. A 0.1-W, 82-Ω carbon resistor, secured to the sample waveguide with thermal cement, measured temperatures below 20°K, while gold-cobalt and copper-constantan thermocouples were used at higher temperatures. The error in the temperature measurement, as determined from data taken on warming and cooling cycles, amounted to 0.5°K.

AFM resonance was observed in $MnTiO_3$, $CoTiO_3$, and $NiTiO_3$. The resonant frequencies versus temperature are shown in Fig. 4. No AFM resonance was observed in $FeTiO_3$. The data were obtained by noting the temperature at which the resonance absorption reached a maximum with zero applied field and fixed frequency. The resonant frequency was not obtained by varying an applied magnetic field H_a because of the dependence of resonant frequency on the net internal magnetic field, which varies with particle orientation in powder samples if $H_a \neq 0$. The values of the AFM resonant frequencies obtained by extrapolation to $T=0$°K are
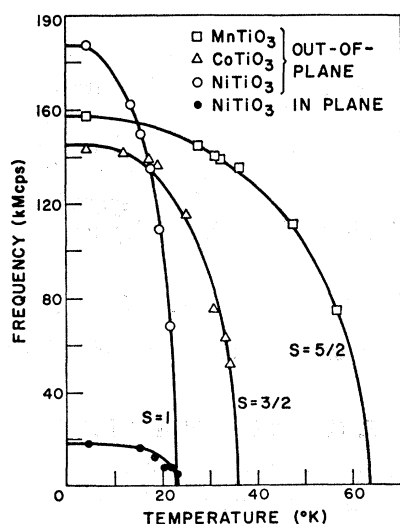

FIG. 4. Zero-field antiferromagnetic-resonance frequency of the ilmenites $M^{2+}TiO_3$ as a function of temperature. The solid curves represent Brillouin functions with $S=1$, $\frac{3}{2}$, $\frac{5}{2}$ for $NiTiO_3$, $CoTiO_3$, and $MnTiO_3$, respectively.
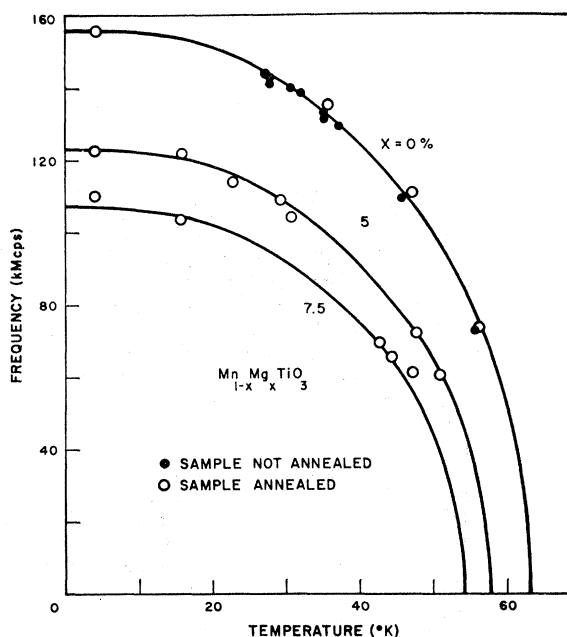

FIG. 5. Zero-field antiferromagnetic-resonance frequency versus temperature for three members of the system $Mg_xMn_{1-x}TiO_3$.

156, 145, and 187 kMc/sec for $MnTiO_3$, $CoTiO_3$, and $NiTiO_3$, respectively.

A low-frequency $[\omega_R(0)=19.1$ kMc/sec at $T=0$°K and applied field $H_a=0]$ AFM resonant mode was detected in $NiTiO_3$. This resonant-frequency branch (see Fig. 4) is associated with oscillations within the basal planes; the higher-frequency branch is due to out-of-plane oscillations. The small in-plane anisotropy is reflected in the low value of "spin-flop" critical field, which is given by the internal field H_c at $T=0$°K. $[H_c=\omega_R(0)/\gamma=6.1$ kG, where $\gamma=ge/2mc$ and $g_{Ni}=2.22.]$ This is about one-tenth the critical field for the out-of-plane modes. Since the frequency of measurement was $\omega=34.5$ kMc/sec$>\omega_R(0)=19.1$ kMc/sec, the measured low-frequency resonance was for the spin-flopped configuration in which the spins lie in the basal plane and are perpendicular to an applied field. In this case it was necessary to calculate the zero-field resonance frequencies given in Fig. 4 from the relation[13]

$$\omega/\gamma=[H_c^2+H_a^2]^{1/2}.$$

Measurements of resonant frequency versus temperature for the system $Mn_{1-x}Mg_xTiO_3$ are shown in Fig. 5; both ω_R and T_N decrease roughly linearly with increasing x in the range $0<x<0.075$.

ACKNOWLEDGMENTS

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