Effect of Pressure on the Néel Temperature of Magnetite*

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The effect of pressure up to \(\approx 45\) kbar on the Néel temperature \(T_N\) of magnetite \((\text{Fe}_3\text{O}_4)\) was measured. \(T_N\) increases linearly over this range with slope \(\delta T_N/\delta p = 2.05 \pm 0.10^0\text{K/kbar}\), or \(\delta nT_N/\delta p = 2.42 \times 10^{-4}\) kbar.\(^{-1}\) To a good approximation, this latter value is a measure of the effect of pressure on the \(A-B\) superexchange interaction, i.e., \(dnJ_{AB}/dp\). On the basis of a model due to Weisz, which assumes that the spin interaction in the inverse spinels is inversely proportional to the interionic distance, the present results, along with the known linear compressibility, indicate that the oxygen parameter \(u\) increases with pressure; the slope is \(dnJ_{AB}/dp = 1.5 \times 10^{-4}\) kbar\(^{-1}\).

INTRODUCTION

The strength of superexchange interactions, which are responsible for the magnetic ordering of ferrites, are proportional to the amount of overlap of the \(3d\) and \(2p\) wave functions on adjacent metal and oxygen ions. This overlap is in turn strongly dependent on the interionic distances. In ferrites, the Néel temperature \(T_N\) is directly related to the superexchange interactions. Thus, the variation of \(T_N\) with pressure provides a measure of the pressure dependence of the exchange forces. This has been well recognized and has led to a number of experimental studies.\(^{1,2}\)

The relationship between the Néel temperature and the various exchange interactions in magnetite \((\text{Fe}_3\text{O}_4)\) or \((\text{FeO} \cdot \text{Fe}_2\text{O}_3)\), has been treated theoretically by several authors;\(^3,4\) however, the variation of \(T_N\) with pressure apparently has not been studied experimentally. We have, therefore, measured the effect of pressure to \(\approx 45\) kbar on \(T_N\) of magnetite, and it is the purpose of this paper to present and discuss the results. It is recalled that magnetite crystallizes in the cubic inverse spinel structure, and its Néel temperature at 1 bar is \(\approx 850^0\text{K}\).

The discussion will center around three points. First, on the basis of earlier theoretical work,\(^5,6\) the observed pressure dependence of \(T_N\) is related to the effect of pressure on the \(A-B\) superexchange interaction [i.e., interaction between iron ions on the tetrahedral \((A)\) and octahedral \((B)\) sites] in \(\text{Fe}_3\text{O}_4\). Secondly, Bloch\(^2\) has recently suggested that in some simple magnetic insulators (including both ferrites and garnets), the superexchange interaction varies as the \(-10/3\) power of volume. The applicability of this relationship to \(\text{Fe}_3\text{O}_4\) will be examined. Finally, on the basis of a model due to Weisz,\(^7\) which assumes that the spin interaction in cubic inverse spinels varies inversely with the interionic distance, the effect of pressure on the crystallographic oxygen parameter \(u\) is determined and discussed.

EXPERIMENT AND RESULTS

The measurements were performed in a large-volume cubic multianvil pressure apparatus. The general experimental techniques including the pressure calibration have been presented elsewhere.\(^7\) The calibration is believed to be accurate to better than \(\pm 5\%\). The sample occupied the center part of the pressure chamber where the pressure gradients were negligible.\(^7\)

The sample assembly consisted of a coil wound on a threaded thin-wall insulating sleeve \((0.03\text{-cm-thick boron nitride})\) enclosing the sample. The low-field self-inductance of the coil, which is related to the initial magnetic susceptibility of the sample, was measured as a function of temperature and pressure.\(^8\) The sample was a compacted powder cylinder prepared from a natural \(\text{Fe}_3\text{O}_4\) crystalline specimen. The cylinder was compacted at a pressure of about 10 kbar and was 0.850 cm long and of 0.640 cm diam.

Several inductance-versus-temperature isobars are shown in Fig. 1. As the sample transforms from the ferrimagnetic to the paramagnetic state with increasing temperature, the inductance drops sharply and then levels off at its air core value. We define the Néel temperature \(T_N\) as the point of intersection of the two linear regions of each isobar as indicated by the dashed lines in Fig. 1. This may not yield a value of \(T_N\) which is exactly the same as that obtained from magnetization-

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versus-temperature measurements, but it does provide an accurate means for measuring the shift of $T_N$ with pressure.

The shift of $T_N$ with pressure is shown in Fig. 2. The open circles represent the experimental data, whereas the closed circles represent the data corrected for the effect of pressure on the emf of the thermocouple. The correction is based on the results of Hanneman and Strong.9 The data can be fitted by a straight line with slope $\partial T_N/\partial p = 2.05 \pm 0.10$ K/kbar. Table I compares values of $T_N$ and its logarithmic pressure derivative for Fe$_3$O$_4$ and a number of other ferrites and garnets. It is seen that the pressure derivatives are all of the same magnitude.

DISCUSSION

The increase in the Néel temperature of magnetite, as well as those of other cubic ferrites, with increasing pressure can be qualitatively explained quite simply. When hydrostatic pressure is applied to a cubic crystal, the unit cell will remain cubic (barring any phase transformations, and there is no indication of any such transformations in ferrites), and, to a first approximation, the interionic distances will be reduced in proportion to the linear compressibility. As a result, the superexchange interaction would be expected to increase. Thus $T_N$ should increase, as is observed experimentally.

Table I. Values of the Néel temperature $T_N$ and its logarithmic pressure derivative for a number of ferrites and garnets.

<table>
<thead>
<tr>
<th>Ferrite</th>
<th>$T_N$ (°K)</th>
<th>$\frac{\partial \ln T_N}{\partial p}$ (10$^{-6}$ kbar$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$O$_4$</td>
<td>850</td>
<td>2.42</td>
<td>Present work</td>
</tr>
<tr>
<td>Ni$<em>{60}$Zn$</em>{40}$Fe$_{3}$O$_4$</td>
<td>318$^a$</td>
<td>2.51</td>
<td>Werner (Ref. 2)</td>
</tr>
<tr>
<td>Ni$<em>{60}$Zn$</em>{40}$Fe$_{5}$O$_4$</td>
<td>481$^a$</td>
<td>1.73</td>
<td>Foiles and Tomizuka (Ref. 1)</td>
</tr>
<tr>
<td>Mn$<em>{60}$Zn$</em>{40}$Fe$_{3}$O$_4$</td>
<td>363</td>
<td>2.48</td>
<td>Patrick (Ref. 1)</td>
</tr>
<tr>
<td>NiFe$<em>{2}$O$</em>{4}$</td>
<td>889</td>
<td>1.30</td>
<td>Foiles and Tomizuka (Ref. 1)</td>
</tr>
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<td>NiFe$<em>{2}$O$</em>{4}$</td>
<td>889</td>
<td>1.30</td>
<td>Foiles and Tomizuka (Ref. 1)</td>
</tr>
<tr>
<td>Ni$<em>{60}$Fe$</em>{30}$</td>
<td>363</td>
<td>2.23</td>
<td>VIG</td>
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<td>VIG</td>
</tr>
</tbody>
</table>

$^a$ The large difference in the value of $T_N$ for Ni$_{60}$Zn$_{40}$Fe$_{3}$O$_4$ reported in Ref. 1 and by Werner (Ref. 2) is surprising and no explanation for it has been given.

The quantitative interrelationship between $T_N$ and the various exchange interactions in Fe$_3$O$_4$ has been the subject of many theoretical treatments. From a spin-wave analysis of the Fe$_3$O$_4$ structure, Kouvel found that $T_N$ is related to the absolute magnitudes of the different exchange interactions $J_{ij}$ between nearest-neighborin spins by

$$kT_N = 4\sqrt{2}J_{AB} \sigma_A \sigma_B - \frac{3}{2}J_{AA} \sigma_A^2 - 2J_{BB} \sigma_B^2,$$

where

$$\sigma_i^2 = S_i(S_i+1), \quad i = A \text{ or } B.$$  

Here $S_A$ and $S_B$ are the average electronic spins associated with the iron moments on tetrahedral (A) and octahedral (B) sites, respectively (see Fig. 3). It is considered that at temperatures greater than the 120°K electronic ordering transition temperature, the electron exchange between ferric and ferrous ions on B sites is so rapid that those sites are effectively occupied by a single-ionic species of spin

$$S_B = \frac{1}{2}(S_{Fe^3} + S_{Fe^2}) = \frac{1}{2}(4/2 + 5/2) = 2.25.$$  

Mills et al.,$^5$ on both experimental and theoretical grounds, have shown that in magnetite $J_{BB} \approx -0.1J_{AB},$
and $J_{AA}$ is expected to be considerably smaller. (The $A-O-A$ distance is large and the angle is small $\approx 80^\circ$; both conditions are unfavorable for superexchange.) This is consistent with Watanabe and Brockhouse's experimental study of the dispersion relation for the spin waves in magnetite which showed that $J_{BB}$ and $J_{AA}$ are negligible compared with $J_{AB}$. Thus, as a good approximation, the terms in $J_{BB}$ and $J_{AA}$ may be neglected, and Eq. (1) reduces to

$$kT_N \approx 4\sqrt{2}J_{AB} A^0_B A^0_B.$$  

(4)

The logarithmic derivative of $T_N$ with respect to pressure is then given by

$$\frac{\partial \ln T_N}{\partial \rho} = \frac{\partial \ln J_{AB}}{\partial \rho},$$  

(5)

where we have assumed that $\sigma_A$ and $\sigma_B$ are independent of pressure. This assumption is quite reasonable since in magnetite the magnetic moment has the spin-only value of $4\mu_B$, and it is further justified by our recent results on the effect of hydrostatic pressure on the saturation magnetization $M_s$. These results show that at $20^\circ C$, $M_s$ increases by $<0.1\%$ kbar$^{-1}$, and that this increase can be accounted for on the basis of the displacement of $T_N$ (and thereby the $M_s$-versus-$T$ curve) to higher temperatures. Thus, in the above approximations, the change in $T_N$ with pressure is a direct measure of the corresponding change in $J_{AB}$. Our experimental results yield $\frac{\partial \ln J_{AB}}{\partial \rho} = 2.4 \times 10^{-4}$ kbar$^{-1}$.

Using the fact that the pressure derivative of $J_{AB}$ can be obtained, a comparison with Bloch's $-10/3$-power relationship can be made. Bloch has recently suggested empirically that in some ferrites and garnets the superexchange interaction varies as the $-10/3$ power of the volume. Thus, according to Bloch,

$$\frac{\partial \ln J_{AB}}{\partial \ln V} = \gamma,$$  

(6)

where $\gamma$ is determined to be $-10/3$. From Eq. (4) we also have

$$\frac{\partial \ln J_{AB}}{\partial \ln V} \approx \frac{\partial \ln T_N}{\partial \ln V}.$$  

(7)

Equations (6) and (7) yield

$$1/\beta = \frac{\partial \ln T_N}{\partial \rho} = -\gamma.$$  

(8)

Here $\beta = -\frac{\partial \ln V}{\partial \rho}$ is the isothermal volume compressibility.

The appropriate value of $\beta$ to use in Eq. (8) is that measured at temperatures near $T_N$, but this value is not available. However, Bridgman and, more recently, Mao have measured $\beta$ for magnetite at $25^\circ C$, and they reported values $(5.50 \pm 0.30) \times 10^{-4}$ and $(5.40 \pm 0.30) \times 10^{-4}$ kbar$^{-1}$, respectively. In addition, Bridgman reported that $\beta$ decreases slightly (from 5.50 to $5.48 \times 10^{-4}$ kbar$^{-1}$) on heating from 30 to $75^\circ C$. Thus $\beta$ is only weakly temperature-dependent, and for the present purposes it is adequate to take $\beta = 5.5 \times 10^{-4}$ kbar$^{-1}$.

Using this value of $\beta$ and our measured value of $\frac{\partial \ln T_N}{\partial \rho} = 2.42 \times 10^{-3}$ kbar$^{-1}$, Eq. (8) yields $\gamma = -10/2.3$. This value of $\gamma$ is about 30% larger in magnitude than the $-10/3$ value suggested by Bloch.

As was mentioned earlier, the strength of the superexchange interaction in ferrites is directly proportional to the amount of overlap of the $3d$ and $2p$ wave functions on adjacent metal and oxygen ions, and this in turn is proportional to the interionic distances. Thus, quantitative comparison between theory and experiment should involve the $A-O-B$ distance rather than volume.

On the hypothesis that the spin interaction in the inverse spinels is inversely proportional to the distance from a metal ion to a nearest neighbor (i.e., to an oxygen ion, and thence to another metal ion), Weiss derived a quantitative semiempirical relationship between the spin-exchange energy, as measured by $kT_N$, and the pertinent variables. The relationship is

$$kT_N = c_1 S_A S_B e^{-\epsilon_0 D},$$  

(9)

where $D$ is the $A-O-B$ distance in Å and equals $0.470 a_0$ for Fe$_3$O$_4$, at atmospheric pressure and temperature ($a_0$ is the lattice constant), $c_1 = 5.04 \times 10^{-3}$ erg, and $c_2 = 7$ Å$^{-1}$. Both $c_1$ and $c_2$ are determined empirically and are

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crystal-structure-dependent. The hypothesis is based on a molecular-field model and on empirical observations concerning the various cation-oxygen-cation distances in the spinels.

Weisz checked the applicability of Eq. (9) for several ferrites and found good agreement between the experimental and the calculated exchange energies. The agreement is particularly good for Fe$_3$O$_4$, where $(kT_N)_{mol}=1.17 \times 10^{-18}$ erg and $(kT_N)_{exp}=1.19 \times 10^{-18}$ erg.

In Eq. (9) it is again appropriate to consider $S_A$ and $S_B$ independent of pressure. If it is further assumed that $C_1$ and $C_2$ are also independent of pressure, then it follows directly that

$$\frac{\partial \ln T_N}{\partial p} = -C_2 \frac{\partial D}{\partial p} = -0.470 C_2 \frac{\partial a_0}{\partial p}. \quad (10)$$

From our measured value of $\partial \ln T_N / \partial p$ and Weisz's value of $C_2=7$ Å$^{-1}$, we obtain

$$\frac{\partial a_0}{\partial p} = -0.74 \times 10^{-3} \text{Å/kbar}.$$ 

This is a factor of 2 smaller than the value of $-1.5 \times 10^{-3}$ Å/kbar measured by Mao.\textsuperscript{13}

What is the cause(s) of this discrepancy? Our assumption concerning the constancy of $C_1$ and $C_2$ is probably not bad since there is no structural change, but the assumption concerning the scaling of $D$ with the linear compressibility warrants further consideration.

As mentioned earlier, $D$ is the distance between the $A$ and $B$ sites via the intermediate oxygen. With reference to Fig. 3, it is seen that $D = p + q$. For the spinel structure, $p$ and $q$ can be expressed in terms of the lattice parameter $a_0$ and the oxygen parameter $u$. The relationships are\textsuperscript{14}

$$p = (\frac{2}{3} - u) a_0,$$

and

$$q = \sqrt{3} (u - \frac{1}{2}) a_0.$$ 

For magnetite at normal conditions $u=0.379$. The corresponding $A$-$O$-$B$ angle is $\phi=126^\circ$.

The oxygen parameter $u$ arises in the following way.\textsuperscript{15} In the spinel lattice (Fig. 3) the tetrahedral $A$ sites, which are smaller than the octahedral $B$ sites, are too small to contain a transition metal ion (Fe$^{3+}$ in the present case), if all ions are regarded as solid spheres. As a consequence, all $A$ sites are expanded by equal displacements of the four O$^{2-}$ ions outwards along the body diagonals of the cube. This then reduces the size of the $B$ sites and thus tends to make the sizes of the $A$ and $B$ sites more nearly equal. The parameter $u$ (or $a_0$) provides a quantitative measure of the displacement of the oxygen ions.

In terms of $a_0$ and $u$ we then have

$$D = (0.192 + 0.732 u) a_0, \quad (11)$$

and Eq. (10) becomes

$$\frac{\partial \ln T_N}{\partial p} = -C_2 \left[ (0.192 + 0.732 u) \frac{\partial a_0}{\partial p} + 0.732 a_0 \left( \frac{\partial u}{\partial p} \right) \right]. \quad (12)$$

Substituting the appropriate values for the various quantities with $u=0.379$ and $a_0=8.390$ Å, Eq. (12) yields

$$\frac{\partial u}{\partial p} = 5.8 \times 10^{-5} / \text{kbar}$$

and

$$\frac{\partial \ln u}{\partial p} = 1.5 \times 10^{-4} / \text{kbar}.$$ 

This is to be compared with $\frac{\partial \ln a_0}{\partial p} = -1.78 \times 10^{-3} / \text{kbar}$.

Thus it is seen that, unlike the lattice parameter $a_0$, the oxygen parameter $u$ increases with increasing pressure.\textsuperscript{16} This may not be unreasonable if one considers the manner in which $u$ is defined. An increase in $u$ can result from an increase in the size of the tetrahedral site relative to that of the octahedral site. The large octahedral site can be expected to be more compressible than the smaller tetrahedral site and thus yield the indicated effect.

It would be very desirable to do a detailed x-ray and/or neutron diffraction study of Fe$_3$O$_4$ under pressure in order to check this indicated increase in $u$.


\textsuperscript{15} See, e.g., Ref. 14, p. 139.

\textsuperscript{16} Small changes in the $A$-$O$-$B$ angle $\phi$ are lumped into the change in $u$.\textsuperscript{18}