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Magnetic properties of Mn_3O_4 and a solution of the canted-spin problem

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The temperature-dependent studies of the low-field magnetization M, the paramagnetic susceptibility χ, and the electron-spin-resonance (ESR) parameters (linewidth ΔH and resonance field H_r) of a polycrystalline natural sample of the ferrimagnet hausmannite (Mn_3O_4) are reported. Since earlier attempts to fit χ and the canted-spin structure of Mn_3O_4 occurring below its $T_C \simeq 42$ K with the use of Lotgering's model have been unsuccessful, special attention has been given to this problem. With the use of an extended Lotgering model, which is equivalent to Néel's two-sublattice model, a set of molecular-field constants, viz. $\lambda_{AB}=54.3$, $\lambda_{BB}=78.9$, and $\lambda_{AA}=26.0$, has been obtained from the fit of χ between 45 and 297 K. With these constants, the calculated values for the canting angle of the B sublattices, the Curie temperature T_C, and the asymptotic Curie-Weiss temperature T_a agree well with the experimental values for these parameters. The M-vs-T data yield anomalies at T_C and 39 K, whereas H_r and ΔH have anomalous changes at T_C, 39 K, and near 32 K. The anomalies near 39 and 32 K are indicative of the known spin reorientation transitions at these temperatures in Mn_3O_4. The ESR parameters indicate a spin-only g value for Mn^{3+} ions at the B sites of Mn_3O_4.

I. INTRODUCTION

The magnetic properties of hausmannite, Mn_3O_4, were first investigated over 20 years ago.[1–3] The temperature dependence of the magnetic susceptibility χ, studied by Borovik-Romanov and Orlova,[1] indicated Mn_3O_4 to be a ferrimagnet with $T_C \simeq 42$ K. Magnetic studies on a powder sample by Jacobs[2] and on a single crystal by Dwight and Menyuk[3] below T_C showed that the magnetic ordering below T_C is not collinear or Néel type,[4] but consists of a canted arrangement of Yafet-Kittel type discussed at length by Lotgering.[5] However, efforts[2,3] to fit the paramagnetic susceptibility χ, as well as the low-temperature canting angle, with the same set of exchange parameters with the use of Lotgering's model[5] were not successful. In particular, the exchange parameters evaluated from χ predicted the canted structure to be energetically unfavorable against the collinear arrangement. Usually, the temperature dependence of χ is fitted to the equation[4]

$$\frac{1}{\chi}=\frac{T}{C}+\frac{1}{\chi_0}-\frac{\sigma}{T-\Theta}\,, \tag{1}$$

where χ_0, C, σ, and Θ are constants to be evaluated from the fit. Since an expression for these constants in terms of the exchange constants and magnetic moments can be derived on different models,[4,5] the evaluation of exchange constants from such a fit is straightforward. Of particular interest is the asymptotic Curie temperature $T_a = C/\chi_0$, which can be determined from $T \gg T_C$, where the contribution of $\sigma/(T-\Theta)$ in Eq. (1) is negligible. The experimental values of T_a are 530 K as used in Refs. 2 and 3 and 640 K as determined in more recent measurements.[6,7] However, as discussed in several publications in the literature,[2,3,7,8] these high magnitudes of T_a are inconsistent with the canted structure using Lotgering's model.[5]

In the meantime, the magnetic structure of Mn_3O_4 has been determined by Jensen and Nielsen[9] using neutron diffraction. The major features of the crystal and magnetic structure of Mn_3O_4 may be summarized as follows. Below 1443 K, Mn_3O_4 has tetragonally distorted spinel structure whereas above 1443 K, it is a cubic spinel. The ionic structure is $Mn^{2+}[Mn_2{}^{3+}]O_4$, so that Mn^{2+} ions occupy the tetrahedral or A sites, where Mn^{3+} are in the octahedral or B sites. As the temperature is lowered through $T_C \simeq 42$ K, the magnetic structure changes as a function of temperature, the structure being different for the regions 42—39 K, 39—33 K, and below 33 K. Below 33 K, the magnetic structure consists of a canted-spin arrangement, as first suggested by Jacobs.[2] According to neutron-diffraction studies,[9] the moments of the Mn^{2+} ions on the A site are directed along the [010] axis and the moments of the Mn^{3+} ions on the B sites, while lying in the (100) plane, subdivide into two sets, each making an angle of 69° with respect to the $[0\bar{1}0]$ axis, so that the resultant B-site moment is antiparallel to the A-site moment. Between 33 and 39 K, the B-site moments form a spiral-spin structure with a propagation vector along [010]. Between 39 K and T_C, the magnetic order is apparently of Néel type. The earlier low-temperature magnetic studies on a single crystal by Dwight and Menyuk[3] correctly showed the [001] axis as being the hard axis. These measurements also showed that the anisotropy in the (001) plane was also considerable, the two anisotropies being $\sim 10^5$ and 10^4 Oe, respectively.[3]

According to the above summary, the magnetic structure of Mn_3O_4 is now reasonably well known. However, the inconsistency discussed in the opening paragraph regarding the inability of the Lotgering's model to describe the canted-spin arrangement now confirmed by neutron-diffraction studies, and the temperature dependence of χ with the same set of exchange parameters remains unresolved. Our interest in this Mn_3O_4 problem was focused by our recent observations of Mn_3O_4 clusters (as defects) in available MnO crystals, both by magnetic[10] and electron spin resonance (ESR) methods.[11] Thus the present work was directed towards the following goals: (i) to measure the temperature dependence of χ and fit this to Eq. (1); (ii) to carefully examine the assumption of the Lotgering model in light of the structure of Mn_3O_4 and to extend the validity of this model if necessary; (iii) to carefully measure the temperature dependence of the low-field magnetization M below T_C in order to observe the spin-reorientation transitions at 33 and 39 K seen in the neutron-diffraction work; and (iv) to study the temperature dependence of ESR spectra of Mn_3O_4 both above and below T_C since according to literature, no such study has yet been reported. Here we report the results of these investigations. The important result is that a set of exchange parameters which uses an extension of the Lotgering model has been found which fits both χ and the canted-spin configuration consistently. We also discuss why earlier attempts to solve this problem were unsuccessful. The spin-reorientation transitions at 39 and 33 K are evident from our magnetic and magnetic resonance studies. Details of these and other results are given below.

II. EXPERIMENTAL DETAILS

The polycrystalline sample of natural hausmannite of Swedish origin was obtained from the Smithsonian Institution, Washington, D.C. The magnetic susceptibility studies on the powered Mn_3O_4 were made by the Faraday method using a Cahn microbalance in conjunction with Lewis gradient coils. The absolute precision in χ is about 1.5% whereas the relative precision is about 0.2%. The powered samples were wrapped in high-purity Al foil and the background correction from the Al foil, usually about 1% or less, has been applied to the data presented here in a manner described elsewhere.[12] Some additional details of the Faraday balance have also been given in Ref. 12.

The ESR studies reported here were carried out on a standard reflection-type X-band spectrometer, with the use of a TE_{101} rectangular cavity with a variable Gordon coupler. The Klystron frequency is locked to the sample cavity and the magnetic field is modulated so that only the absorption (first derivative) is recorded. The spectrometer is interfaced to a minicomputer (SCAMP by Spex Industries), which allows easy recording and analysis of the ESR parameters. Measurements were carried out between 22 K and room temperature on thin (~ 1 mm) disks of polycrystalline Mn_3O_4. The temperatures could be stabilized to within 0.1 K with a temperature controller.

III. LOTGERING'S MODEL AND Mn_3O_4

For the purpose of a proper discussion of the experimental results to be presented here, a brief overview of the major results and assumptions of the Lotgering's molecular theory of ferrimagnetism for Mn_3O_4 is first presented. Here we also give results which are an extension of Lotgering's calculations and discuss how these extended results relate to the two-sublattice model.

In the Lotgering model of Mn_3O_4, the A sites are divided into two sublattices (A_1 and A_2) and the B sites into four sublattices with the Weiss constants n, $n\alpha'$, $n\alpha$, $n\beta'$, and $n\beta$ for the exchange interactions A_iB_j, A_iA_i, $A_iA_{j(\neq i)}$, B_iB_i, and $B_iB_{j(\neq i)}$, respectively. The corresponding Weiss fields acting on A_i, and B_i sublattices are

$$\vec{h}_{A_i} = -n[(\alpha'-\alpha)\vec{a}_i + \alpha(\vec{a}_1+\vec{a}_2) + (\vec{b}_1+\vec{b}_2)] \tag{2a}$$

and

$$\vec{h}_{B_i} = -n[(\beta'-\beta)\vec{b}_i/2 + (\vec{a}_1+\vec{a}_2) + \beta(\vec{b}_1+\vec{b}_2)] \ . \tag{2b}$$

Here $i=1,2$ and $\vec{a}_i$ and $\vec{b}_i$ are the magnetization vectors for the A_i and B_i sublattices, respectively. Considering the Mn_3O_4 lattice, the Lotgering assumption $a_1=a_2=a$ and $b_1=b_2=b$ is considered to be valid. The magnetic energy E of the system is

$$E = -\tfrac{1}{2}\sum_{i=1}^{2}(\vec{h}_{Ai}\cdot\vec{a}_i + \vec{h}_{Bi}\cdot\vec{b}_i) \ . \tag{3}$$

The magnetic energy for the different spin configurations considered by Lotgering can be calculated from Eq. (3). However, unlike Lotgering, who assumed $\alpha'=\beta'=0$ for Mn_3O_4, we retain these parameters for reasons to become clear later on. For the triangular arrangement $\triangleright$ in which spins of the A sublattices are parallel and those on the two sublattices of B are canted at angle ψ with respect to the direction of the A spins, the following expression for E is obtained:

$$E = n[(\alpha+\alpha')a^2 + (\beta'+\beta)b^2/2 - 4ab\cos\psi + \beta b^2\cos 2\psi] \ . \tag{4}$$

Minimizing E with respect to ψ yields two conditions: (i) $\sin\psi=0$ (no canting) and (ii) $\cos\psi = a/\beta b$ (canting). Energy for the collinear state ($\uparrow\downarrow$) for $\psi=0$ and the canted state ($\triangleright$) with $\cos\psi=a/\beta b$ are

$$E_{\uparrow\downarrow} = n[(\alpha+\alpha')a^2 + (\beta'+3\beta)b^2/2 - 4ab] \tag{5}$$

and

$$E_{\triangleright} = n[(\alpha+\alpha'-2/\beta)a^2 + (\beta'-\beta)b^2/2] \ . \tag{6}$$

Another configuration discussed by Lotgering is the case where A_1 and A_2 are antiparallel and so are B_1 and B_2. From Eq. (3), energy of this state ($\updownarrow\updownarrow$) is

$$E_{(\updownarrow\updownarrow)} = n[(\alpha'-\alpha)a^2 + (\beta'-\beta)b^2/2] \ . \tag{7}$$

It is noted that with Lotgering's assumption of $\alpha'=\beta'=0$, Eqs. (5)—(7) reduce to the expressions given in his paper.[5] However, this assumption is not necessary to derive the condition for canting. If the canted arrangement ($\triangleright$) must have the lowest energy, then $E_{\triangleright}$ should be less than

$E_{\updownarrow\updownarrow}$ and $E_{\uparrow\uparrow}$. The condition $E_{\triangleright} < E_{\uparrow\downarrow}$ yields the obvious result $a/\beta b(=\cos\psi) < 1$, whereas the condition $E_{\triangleright} < E_{\updownarrow\updownarrow}$ yields the inequality

$$\alpha\beta < 1 \,, \tag{8}$$

the same as derived by Lotgering. It is important to note that $\alpha\beta < 1$ has been obtained without conditions on α' and β'. So although α' and β' affect the Weiss fields (Eqs. (2)] and energies [Eq. (4)], the famous condition for the stability of the canted arrangement, viz., $\alpha\beta < 1$, is independent of α' and β'. This is a new result of our calculations.

Above T_C, where the spins are not ordered, the expressions for σ, Θ, and $1/\chi_0 = T_a/C$ are dependent on α' and β', as is evident from Eq. (2). Following Lotgering, if $\alpha' = \beta' = 0$, then

$$T_a = \frac{3n}{C}\left(\tfrac{1}{6}\alpha C_A^2 + \beta C_B^2 + \tfrac{4}{3} C_A C_B\right) \tag{9}$$

with expressions for σ and Θ given in Ref. 5. Here

$$C_i = N_i g_i \mu_B^2 S_i(S_i+1)/3k_B$$

are the Curie constants for $i = A$ and B sublattices with the usual notations[13] and $C = C_A + 2C_B$. Equation (9) for T_a (and Lotgering's expressions for σ and Θ in Ref. 5) has been used by all previous investigators[2,3,7,8] to evaluate α and β from the experimental T_a and they found that α and β so evaluated violate condition (8), i.e., they found $\alpha\beta > 1$. If, on the other hand, we assume $\alpha' = \alpha$ and $\beta' = \beta$, then it is easily seen that Eq. (2) for the Weiss field become exactly equal to those for the two sublattice model[13] of ferrimagnetism. In this case, the expressions for T_a, σ, and Θ become

$$T_a = (n/C)(\alpha C_A^2 + \beta C_B^2 + 2C_A C_B) \,, \tag{10a}$$

$$\sigma = \frac{n^2 C_A C_B}{C^3}[C_A(1-\alpha) - C_B(1-\beta)]^2 \,, \tag{10b}$$

and

$$\Theta = \frac{n C_A C_B}{C}(2-\alpha-\beta) \,. \tag{10c}$$

It is obvious that α and β will be different depending on whether Eq. (9) obtained under $\alpha' = \beta' = 0$ or Eq. (10) obtained under $\alpha = \alpha'$, $\beta = \beta'$ is used to evaluate α and β. As discussed in the following sections, it is our belief that the conditions $\alpha = \alpha'$, $\beta = \beta'$ are more appropriate for Mn_3O_4. Moreover, α and β so evaluated from χ do satisfy the canting condition $\alpha\beta < 1$ and give the correct ψ in $\cos\psi = a/\beta b$. On the other hand, our analysis of χ using Eq. (9) yields $\alpha\beta > 1$, a problem encountered by previous investigators.[2,3,7,8] Now we present details of our results and analysis.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. Paramagnetic susceptibility

The temperature dependence of the paramagnetic susceptibility, χ, measured in a field of 200 Oe, is shown in Fig. 1 as a plot of $1/\chi$ and χ versus temperature. Our measured values are in excellent agreement with those reported in Refs. 6 and 7, but differ substantially with the earlier data of Ref. 1. These somewhat different values reported in Ref. 1 might be the result of a somewhat lower quality of the sample.

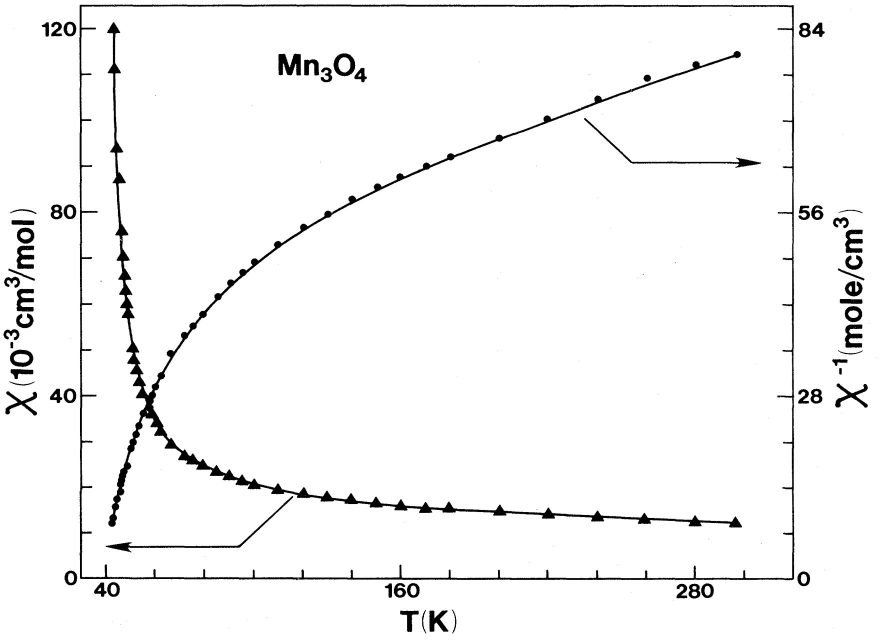

FIG. 1. Temperature variation of χ and $1/\chi$. The solid lines are fits to Eq. (1) with parameters given in the text.

The fit of χ to Eq. (1) is also shown in Fig. 1 as the solid line with the following parameters: $\Theta=10.2$ K, $\sigma=1700$, $1/\chi_0=57.5$, and $C=10.43$ In making this fit σ, Θ, and $1/\chi_0$ were treated as adjustable parameters, where the Curie constant $C=C_A+2C_B=4.37+2(3.03)=10.43$ corresponds to $g=2$ for Mn^{2+} (A sites) and $g=2.01$ for Mn^{3+} (B sites) as determined from our ESR experiments discussed later. (The diamagnetic contribution to χ is estimated to be 1% near 295 K and ~0.5% near 60 K, and hence it is ignored in this analysis.) The next step is to determine n, α, and β using the above parameters and Eqs. (10). Because of the quadratic nature of Eq. (10b), two sets of values for n, α, and β fit the evaluated parameters σ, Θ, and $1/\chi_0$. These are as follows: In set 1, $n=54.3$, $\alpha=0.479$, $\beta=1.454$, and in set 2, $n=62.7$, $\alpha=1.375$, $\beta=0.560$. With the use of both sets, the calculated value of $T_a=C/\chi_0=600$ K is in good agreement with the experimental estimates which range from 540 K (Refs. 2 and 3) to 640 K.[6,7]

Next we consider the validity of the two sets of molecular field constants evaluated above and apply these in explaining the low-temperature canted-spin structure. The stability of the canted structure requires that $\alpha\beta<1$ [inequality (8)]. For set 1, $\alpha\beta=0.696$, and for set 2, $\alpha\beta=0.77$. So both sets are consistent with $\alpha\beta<1$. Which set is the correct one? To determine this, we use the condition $\cos\psi=a/\beta b$, knowing that the experimental $\psi\simeq 69°$.[9] Note that a and b are, respectively, the A and B sublattice magnetizations and can be calculated from $|a|=g_A S_A \mu_B$ and $|b|=2g_B S_B \mu_B$ with $g_A(Mn^{2+})=2$, $g_B(Mn^{3+})=2.01$, $S_A=\frac{5}{2}$, and $S_B=2$. This yields $\cos\psi=0.428$ or $\psi=64.7°$ for set 1 with $\beta=1.454$ and $\cos\psi>1$ for set 2 with $\beta=0.56$. Thus the exchange parameters of set 2 cannot explain the observed canting of the B moments in Mn_3O_4. The calculated value of $\psi=64.7°$ using set 1 agrees very well with the experimental value of $\psi=69°$.[9] It is noted that if we use $|a|=4.34\mu_B$ and $|b|=6.89\mu_B$, the values determined by the neutron-diffraction measurements,[9] then $\cos\psi=a/b\beta$ with $\beta=1.454$ yields $\psi=64.3°$, a value essentially identical to one calculated above (the reduced value of $|a|$ and $|b|$ as compared to free-spin moments are probably due to the large anisotropy of Mn_3O_4). Thus set 1 with $n=54.3$, $\alpha=0.479$, and $\beta=1.454$ gives the correct description of the low-temperature canted magnetic structure as well as that of the temperature dependence of the paramagnetic χ in Mn_3O_4.

It is noted that if we use Lotgering's model (with $\alpha'=\beta'=0$) and Eq. (9) to calculate the exchange constants from our measured χ, we obtain two sets with $n=54.3$, $\alpha=0.97$, and $\beta=1.92$, and $n=62.5$, $\alpha=2.75$, and $\beta=0.75$. For both sets the canting condition $\alpha\beta<1$ is violated, a problem encountered by the earlier investigators.[2,3,7,8] Thus it is the use of the Lotgering model with $\alpha'=\beta'=0$ which is the source of discrepancy. Now the assumption $\alpha'=\beta'=0$ means that some AA and BB interaction are of zero strength. This is clearly a drastic assumption, one that is not consistent with the magnetic structure of Mn_3O_4 involving the lengths and the distances of various interactions.[5] Our assumption that all AA and all BB interactions are of the same strength, but each different from the AB interaction, fits the experimental facts very well. The small difference between the calculated canted angle ψ and the experimental value of 69° might be due to the fact that our assumption that $\alpha=\alpha'$ and $\beta=\beta'$ is probably correct only to a good approximation.

B. Spin-reorientation transitions

The temperature dependence of the low-field magnetization M, carried out under several different cooling conditions of the sample and in different magnetic fields, is shown in Fig. 2. In all cases, the sample was first cooled to 4.2 from 77 K and then the temperature-dependent data was taken with increasing temperatures. The four curves in Fig. 2 correspond to the following conditions: curve 1—sample cooled in the residual field (~77 Oe) of the electromagnet followed by M measured at 200 Oe; curve 2—sample cooled in 77 Oe, field increased to 5 kOe at 4.2 K, then lowered to 100 Oe and then M measured at 100 Oe; curve 3—sample cooled in zero field and M measured at 100 Oe; curve 4—sample cooled in zero field and M measured at 200 Oe. In addition to the expected observation of T_C near 42 K in all four cases (apparent shift of T_C with higher fields is expected), a distinct anomaly near 39 K is also observed in the M vs T curves, although the anomaly is the sharpest in curve 3. However, only in curve 4 is there any indication of the transition near 33 K. In the earlier magnetic work by Dwight and Menyuk[3] on a single crystal, there was a hint of the 39-K transition only

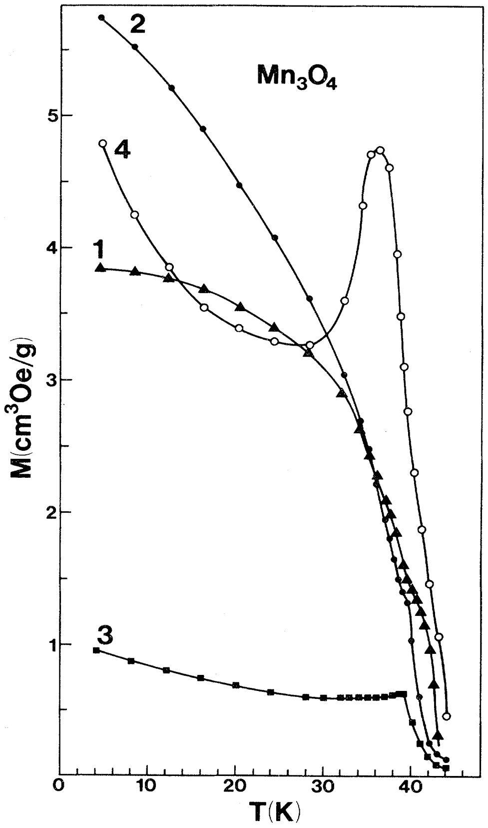

FIG. 2. Measured magnetization M vs temperature for various cooling conditions and measuring fields as explained in the text.

when M was measured at 250 Oe. For higher field values (1 and 10 kOe), their measurements of M vs T did not reveal the 39-K transition. This was the primary reason for our carrying out the studies at lower fields[14] and it appears that the zero-field cooling combined with measurements at low fields is able to bring out the major features, at least those of the 39-K transition.

During the initial cooling of the virgin sample, we also observed a time dependence of magnetization at a constant field at 4.2 K. For example, at 4.2 K, in a field of 200 Oe, M increased from an initial value of 1.25 cm^3Oe/g to the final constant value of 3.89 cm^3Oe/g in 60 min. However, in the subsequent cooling of the sample through T_C, this time dependence was not observed. Somewhat similar time dependence in Mn_3O_4 was reported by Dwight and Menyuk.[3]

The Curie temperature T_C, with $\alpha=\alpha'$ and $\beta=\beta'$, is given by

$$T_C=\frac{n}{2}\{-(\alpha C_A+\beta C_B)+[(\alpha C_A-\beta C_B)^2+4C_AC_B]^{1/2}\} . \tag{11}$$

The use of our evaluated values of $n=54.3$, $\alpha=0.479$, $\beta=1.454$, $C_A=4.37$, and $C_B=6.06$ gives $T_C=37.6$ K. This compares favorably with the experimental value of 42 K. The small discrepancy is most likely due to the expected failure of the molecular field model close to T_C.

The temperature dependence of the ESR parameters (peak-to-peak linewidth ΔH and the resonance field H_r) of Mn_3O_4 is shown in Fig. 3. Above T_C, only a single line with $g=2.01$ and $\Delta H=405\pm10$ Oe is observed, with no temperature dependence of ΔH or H_r down to 55 K. Below 55 K, ΔH begins to increase reaching a maximum at 43 K, and then decreases. A minimum in ΔH is observed at 39 K, followed by the sharpest rate of increase near 32 K. The resonance field H_r shows anomalies at similar temperatures, as also shown in Fig. 3. Thus the location of the anomalies in H_r and ΔH near 43, 39, and 32 K coincide with the various spin-orientation transitions discussed already in connection with the magnetization studies. For temperatures below 43 K a second broader line, on the lower-field side of the main line, was also observed. This line shifted towards zero field for lower temperatures and only a part of this line was observed for most temperatures above zero field. Consequently, its ΔH and H_r could not be measured accurately.

The appearance of two resonance lines below T_C and the shifts of their H_r is now considered. First, it is straightforward to show that in the presence of an anisotropy field H_a for a ferromagnet, the resonance condition at frequency ν becomes $H_r=(h\nu/g\mu_B)-H_a$. Second, in a powdered sample of Mn_3O_4 below T_C, some of the domains are expected to be oriented favorably to the applied field, for which the saturation field is approximately equal to H_r at $\nu\simeq9$ GHz, whereas the remaining domains are at various orientations with respect to the field. Now the main line, for which the data is shown in Fig. 3, follows smoothly from above T_C. Therefore, this line must be from favorably-oriented domains. The downward shift of its H_r and the anomalies at various spin-reorientation transitions then reflects the appearance of the anisotropy field H_a in the above-quoted resonance condition. The same condition then suggests that the broader line is due to unfavorably-oriented domains since for these domains H_a is larger and increases rapidly below T_C, resulting in the observed rapid shifts of this line towards zero field. We note that the appearance of such a line is quite common in ferrimagnetic oxides with high anisotropy such as barium-magnesium ferrites.[15] In the above discussion we have ignored any shifts in H_r due to demagnetizing fields since for a powdered sample (nearly spherical particles),

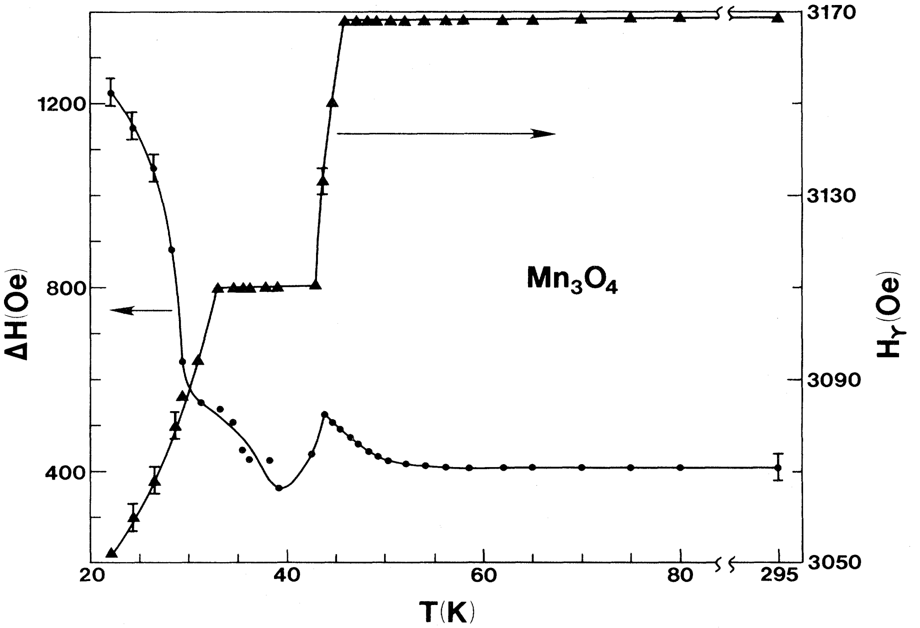

FIG. 3. Temperature variation of the resonance field H_r and the peak-to-peak linewidth ΔH at an ESR frequency of ~9 GHz. The solid lines are drawn connecting the data points for visual aid.

demagnetizing fields do not shift H_r.[16] This is confirmed by the lack of any change in H_r above 46 K (Fig. 3), where the effect due to H_a would be negligible.

The increase of ΔH on approach to T_C from the paramagnetic region is typical of what is expected for an anisotropic magnetic system.[17] The fact that the anomaly in ΔH is quite weak near T_C is indicative of the ferrimagnetic ordering in Mn_3O_4 (rather than antiferromagnetic ordering where the anomaly in ΔH is usually much stronger). The anomalous change in ΔH near T_C in magnetic systems has been discussed in considerable detail in the literature.[16,17] For Mn_3O_4, any significant additional information (such as on anisotropy) can come only from studies on single crystals.

C. Evaluation of exchange constants

With the use of the fitted parameters $n=54.3$, $\alpha=0.479$, and $\beta=1.454$, the exchange constants for Mn_3O_4 are now estimated. First we rewrite n,α,β in terms of the more familar molecular field contants λ_{AB}, λ_{AA}, and λ_{BB} between the A and B sites. From the definitions of n,α,β we obtain $\lambda_{AB}=n=54.3$, $\lambda_{AA}=26.0$, and $\lambda_{BB}=78.9$. These are related to the exchange constants J_{ij} via[13]

$$\lambda_{ij}=\frac{2Z_{ij}J_{ij}}{N_j g_i g_j \mu_B^2}\ , \qquad (12)$$

where Z_{ij} is the number of nearest neighbors on the jth sublattice for an ion on the ith sublattice, and N_j is the number of magnetic ions per g mol of the jth sublattice. For Mn_3O_4, $Z_{ij}=4$, $N_j=N_A$ (Avogadro's number) for λ_{AA}, $Z_{ij}=12$, $N_j=2N_A$ for λ_{AB}, and $Z_{ij}=6$, $N_j=2N_A$ for λ_{BB}. These substitutions yield $J_{AA}=4.9$ K, $J_{BB}=19.9$ K, and $J_{AB}=6.8$ K. Thus the strongest exchange coupling in Mn_3O_4 is amongst the Mn^{3+} ions at the B sites.

D. Paramagnetic g value

The measured g value of Mn_3O_4, equal to 2.01 in the paramagnetic region, is now related to the individual g values of Mn^{2+} and Mn^{3+} ions in Mn_3O_4. Assuming Mn^{2+} ion on the A site to have $g=2$, the g values of Mn^{3+} can be calculated from Huber's expression for g_{eff} in exchange-coupled systems with unlike spins.[18] This is given by

$$g_{\text{eff}}=\frac{g_A S_A(S_A+1)N_A+g_B S_B(S_B+1)N_B}{S_A(S_A+1)N_A+S_B(S_B+1)N_B}\ , \qquad (13)$$

where N_A and N_B is the relative concentration of A and B spins with g values of g_A and g_B. Using the experimental value of $g_{\text{eff}}=2.01$, $S_A=\frac{5}{2}$, $S_B=2$, $N_A=1$, and $N_B=2$, we get $g_B=2.017$, the g value for Mn^{3+} on the B sites.

This observation of $g \simeq 2$ for Mn^{3+} in Mn_3O_4 is consistent with similar observations for Mn^{3+} in Al_2O_3 (Ref. 19) and in mixed-valence compounds $CaMnO_6$ and $CaMnO_8$.[20] Our observation of temperature-independent ΔH in the paramagnetic region (Fig. 3) is consistent with $g \simeq 2$ for Mn^{3+}, since in a state with unquenched orbital moment, temperature-dependent line broadening due to strong spin-phonon coupling is expected.[21] The paramagnetic g value of Mn_3O_4 clusters in the MnO matrix[11] is essentially similar to the observations reported here.

V. SUMMARY

The exchange constants derived from the measured χ vs T data explain well the magnetic properties of Mn_3O_4 both above and below T_C. In particular, the calculated values of the canting angle of the B sublattice, the Curie temperature T_C, and the asymptotic Curie temperature T_a, using these exchange constants, agree well with the experimental values. The condition for canting of the B sublattices is satisfied by the exchange constants. The ESR parameters indicate a spin-only g value for the Mn^{3+} ions on the B sites of Mn_3O_4

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