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Exchange constants in spinel ferrites

C. M. Srivastava, G. Srinivasan, and N. G. Nanadikar
Department of Physics, Indian Institute of Technology, Powai, Bombay-400 076, India

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A three-sublattice analysis of $M^{2+}Fe_2{}^{3+}O_4$ ($M = Li_{0.5}{}^{+}Fe_{0.5}{}^{3+}$, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}) spinel ferrites based on the molecular-field approximation has been used to obtain exchange constants from the M_S vs T and χ^{-1} vs T experimental data. The magnitude and sign of the exchange constants have been examined using Anderson's theory of superexchange. The magnitudes of the transfer integrals for different exchange routes have been generally found to be in agreement with the chemical theory of covalency.

I. INTRODUCTION

The superexchange interaction in magnetically ordered insulators has been discussed by a number of authors.[1-10] However, only in very simple cases where the interaction could be adequately represented by one or two exchange constants have some successful attempts[4] been made to obtain these from experimental data in agreement with theory. In the case of spinel ferrites, due to the relatively large number of exchange constants, there has not been any serious attempt to analyze the experimentally obtained exchange constants. The purpose of this paper is to present the analysis of the experimental data on the variation with temperature of the magnetization and inverse susceptibility, on the basis of a three-sublattice molecular-field approximation which is shown to be more appropriate for the inverse spinel ferrites than the two-sublattice model proposed by Néel.[10] The inadequacy of the two-sublattice model became apparent when attempts were made to obtain the exchange constants on this basis. It was found[10] that not only the magnitude but in some cases also the sign of the exchange constant was in disagreement with theory. On the other hand, the present analysis based on the three-sublattice model shows reasonable agreement with theory.

In inverse spinel ferrites $M^{2+}Fe^{3+}O_4$, the B site is occupied by two types of ions, M^{2+} and Fe^{3+}, while the A site is occupied by Fe^{3+} ions. We denote by B' and B'' the sublattices occupied by the divalent and the trivalent metal ions, respectively. If n and n' denote the number of d electrons and i and j refer to the sublattices A, B', and B'', the results show regular variation of the $d^n(i)$-$d^{n'}(j)$ interaction with the variation in number of magnetic electrons. These exchange constants have been found generally to agree with the rules of Kanamori[2] which are based on the superexchange mechanisms of Anderson,[1] Slater,[9] Anderson and Hasegawa,[5] and Goodenough and Loeb.[6]

A detailed analysis of the experimental data on exchange constants has been carried out with a view to identifying the dominant contributions from among the variety of possible routes of the exchange process and to obtaining physically meaningful transfer integrals using Anderson's approach[11] for the exchange interactions $d^n(i)$-$d^{n'}(j)$. It is shown in Sec. III that both objectives are realized in this study and the results on transfer integrals are in agreement with the chemical theory of covalency.

The ferrites which have been analyzed are $MnFe_2O_4$, Fe_3O_4, $CoFe_2O_4$, $NiFe_2O_4$, $CuFe_2O_4$, and $Li_{0.5}Fe_{2.5}O_4$. These compositions have been chosen to study the variation of magnitude and sign of 180° and 90° superexchange interactions with the number of magnetic electrons for half or more than half filled d orbitals. It is shown in Sec. III that it is possible to interpret the experimental data on exchange constants in terms of transfer and exchange integrals for both the 90° and 180° interactions. The transfer integrals for 180° d^5-d^n and 90° d^n-d^n interactions are found to be the same for $6 \leq n \leq 9$. Considering that the bond lengths and bond angles are approximately equal for all the compositions of spinel ferrites discussed here the constancy of the transfer integrals is understandable.

II. THREE-SUBLATTICE MODEL

The Néel two-sublattice collinear model[10] was the first step in the understanding of the magnetic behavior of spinel ferrites. Néel analyzed the variation of the saturation magnetization and paramagnetic susceptibility with temperature for a number of ferrites on the basis of the two-sublattice collinear model and obtained the exchange constants J_{AA}, J_{AB}, and J_{BB}, where A and B refer to the ions on the tetrahedral and octahedral sites, respectively. Since in an inverse spinel there are two types of ions on the B sites, one divalent and the other trivalent, Néel for simplicity assumed that the interactions J_{AB} and J_{BB} could be represented by a single average constant even though there were two types of metal ions whose ground and excited states in the crystal field were expected to be very different. The results on exchange constants obtained by Néel on the basis of his two-sublattice model are given in Table I. These exchange constants are not in agreement with the predictions of the superexchange theory. For example, for the *AA* interactions, the metal ion-ligand distances are larger and the angle for the overlap of the orbitals unfavorable compared to the *BB* interaction; yet the magnitude of the *AA* interactions is large compared to *BB*. Further, on change of Zn concentration in $Zn_xNi_{1-x}Fe_2O_4$ from $x=0$ to 0.2, J_{AA} has increased by a factor of 2, while J_{AB} and J_{BB} remain almost constant. This cannot be explained on the basis of any mechanism of superexchange interaction.

Despite the early failure of the two-sublattice model to yield the exchange constants in conformity with the theory of superexchange, there have been attempts by several authors to use this model to deduce exchange constants in several ferrites. Notable among them are those of Rado and Folen,[12] Blasse,[13] and Volkova and Goryaga.[14] Their results show that in most cases of inverse spinels with two types of magnetic ions on the *B* sublattice, the exchange constants are not in agreement with the theories of superexchange.

A similar approach to obtain exchange constants for substituted yttrium iron garnets has been made by Pauthenet,[15] Aleonard,[16] and Dionne.[17] Dionne[17] has shown that to obtain a fit for the magnetization (M_S) as well as inverse susceptibility data in substituted garnets, using the two-sublattice model, not one but two entirely different sets of exchange constants are needed. He has also shown that on substitution of nonmagnetic ions in the magnetic sublattices the strength of all the exchange constants vary significantly. No attempt has been made by him to interpret the results on the basis of the theory of superexchange. Apparently, the results regarding significant variation of J_{ij} with nonmagnetic substitution and the two different sets of J_{ij}, one for the magnetization and the other for susceptibility, cannot be understood on the current theories of superexchange interaction.

TABLE I. Superexchange constants in spinel ferrites obtained by Néel (Ref. 10) on the basis of the two-sublattice model.

Compound	J_{AA} (°K)	J_{AB} (°K)	J_{BB} (°K)
Fe_3O_4	−17.7	−23.4	+0.5
$NiFe_2O_4$	−9.1	−30.0	−8.4
$Zn_{0.2}Ni_{0.8}Fe_2O_4$	−20.9	−29.4	−9.5
$Zn_{0.4}Fe_2Ni_{0.6}O_4$	−61.8	−35.5	−10.6

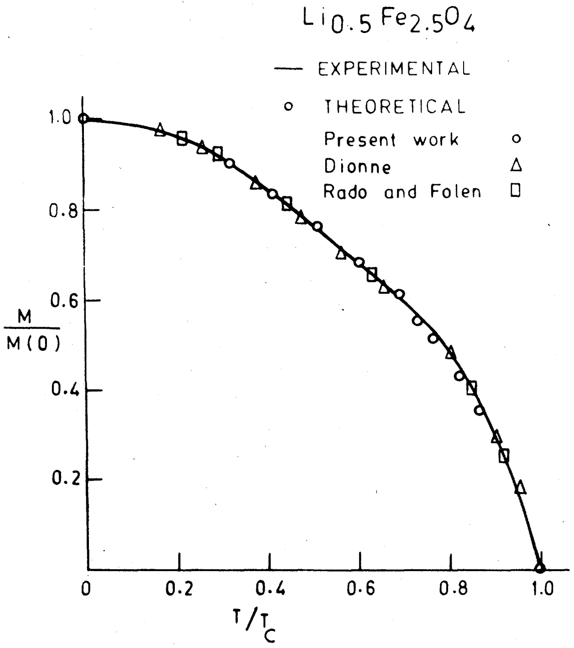

FIG. 1. Experimental and theoretical curves of reduced magnetization as a function of temperature for $Li_{0.5}Fe_{2.5}O_4$. The experimental curve is shown by the solid line. The points show the values of $M/M(0)$ obtained on the basis of the set of exchange constants J_{AA}, J_{AB}, and J_{BB} in the two-sublattice approximation assumed by Dionne (Ref. 17), Rado and Folen (Ref. 12), and values of the present authors. The values of the exchange constants are given in Table II. The agreement with experiment is good for all the three sets.

It has been observed by us that in many cases more than one set of exchange constants can fit the M_S vs T curves. This is true also when the two-sublattice model is valid. For example, lithium ferrite which is a Néel ferrimagnet and has only one type of magnetic ion, viz. Fe^{3+}, can be described by the two-sublattice model. Exchange constants have been obtained by us for this ferrite and compared with those obtained by Rado and Folen[12] and Dionne.[17] The theoretical curves for the magnetization are given in Fig. 1, and the values of the exchange constants are given in Table II. There is good fit for the magnetization data with each of the sets of exchange constants. However,

TABLE II. Comparison of exchange constants for $Li_{0.5}Fe_{2.5}O_4$ obtained by Rado and Folen (Ref. 12), Dionne (Ref. 17), and the present authors.

	J_{AA} (°K)	J_{AB} (°K)	J_{BB} (°K)
Rado and Folen	−19.5	−24.0	−10.6
Dionne	−28.0	−34	−15
Present data	−20	−29	−8

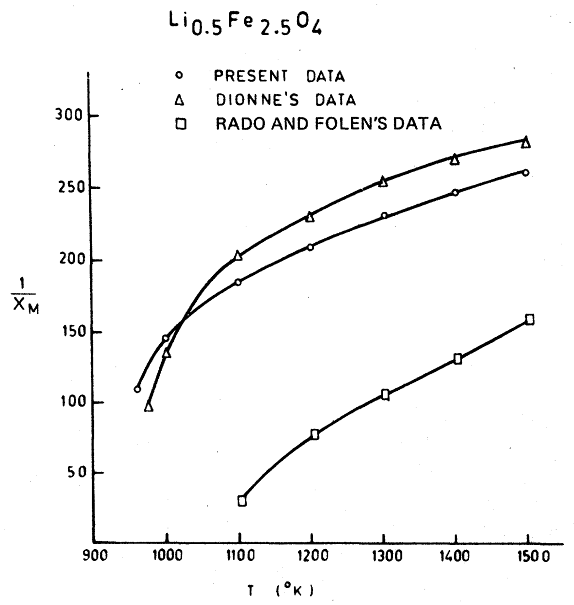

FIG. 2. Theoretical curves for inverse susceptibility of $Li_{0.5}Fe_{2.5}O_4$ as a function of temperature calculated on the basis of the exchange constants assumed by Dionne (Ref. 17), Rado and Folen (Ref. 12), and the present authors and given in Table II. Though the fit for magnetization obtained on the basis of the same set of J_{ij} agrees well with experiment (see Fig. 1) in all cases, the inverse susceptibility is different in each case.

from Table II it is noted that although there is reasonable agreement of our values with those of Rado and Folen, Dionne's values are higher for all the exchange constants. The paramagnetic susceptibility curves plotted from these data are given in Fig. 2. These are different in the three cases and it is possible to choose the proper set on the basis that the set of J_{ij} should satisfy both M_S and χ^{-1} experimental data simultaneously. Unfortunately the data on paramagnetic susceptibility of lithium ferrite is not available at present. We have chosen our set to be in conformity with the exchange constants obtained for other systems, like Fe_3O_4, having similar types of interactions and believe that this is the true set (see Table IV).

The inverse spinels have two types of ions on the B site; hence Néel's attempt to obtain the values of J_{ij}, in agreement with theory, using the two-sublattice model was not successful. One of the authors[18] proposed that in such cases a more realistic approach would be to use a three-sublattice model in which the B sublattice is split into two, B' and B'', to take proper account of the exchange constants relating to the divalent and trivalent metal ions present on the B site. An expression for the inverse susceptibility based on the three sublattices A, B', and B'' was also derived by him. However, on account of the complexity of solving simultaneously five equations, with two linear, two quadratic, and one cubic in exchange constants, not much progress was made in obtaining reliable values of exchange constants when only the inverse susceptibility data was used for analysis. Recently we have obtained the expression for the magnetization as a function of temperature on the basis of the three-sublattice model and have devised a method of obtaining the exchange constants from the observed variation of M_S with temperature. Only when a set of exchange constants simultaneously satisfies both the magnetization and the susceptibility data has it been accepted as the true set.

The three-sublattice model has already been used to explain the variation of magnetization with increase in Zn content in $Zn_xFe_{3-x}O_4$,[19] and $Zn_xNi_{1-x}Fe_2O_4$,[20] systems. It was shown that in both the systems the substitution of the divalent metal ions by Zn^{2+} did not significantly change the strength of the exchange constants. For $x=0$, in both the systems, the configuration was collinear Néel type. Hence in the present analysis of the magnetization curves for inverse spinels using the three-sublattice model, the spin configuration has been taken to be Néel type. This is true for all the ferrites considered here. The references for the experimental data on M_S, χ^{-1}, and spin ordering are given in Table III. The analysis of M_S data yields a set of six exchange constants J_{AA}, $J_{AB'}$, $J_{AB''}$, $J_{B'B'}$, $J_{B''B''}$, and $J_{B'B''}$. The same is used to obtain the inverse paramagnetic susceptibility and the values of the exchange constants are adjusted until the best fit with both the data is obtained. We discuss below the method which has been used for fitting the experimental data on magnetization and susceptibility.

A. Magnetization

The molecular fields for the inverse spinels $M^{2+}Fe_2^{3+}O_4$ on the three-sublattice model are given by

$$\vec{H}_i=\sum_j \lambda_{ij}\vec{M}_j, \quad i,j=A,B',B'' \tag{1}$$

TABLE III. References for the experimental data on M_S vs T, χ^{-1} vs T, and spin ordering used in the paper for spinel ferrites.

Compound	Reference for M_S vs T	Reference for χ^{-1} vs T	Reference for spin ordering
$MnFe_2O_4$	21	22	24
Fe_3O_4	21	10	19
$CoFe_2O_4$	21	10	23
$NiFe_2O_4$	21	10	24
$CuFe_2O_4$	26		26
$Li_{0.5}Fe_{2.5}O_4$	26		25

where $\vec{H}_i$ is the molecular field experienced by an ion on the ith sublattice, λ_{ij} are the molecular-field constants, and $\vec{M}_j$ is the magnetization of the jth sublattice. Hence

$$\lambda_{ij}=2Z_{ij}J_{ij}/N_j g_i g_j \mu_B{}^2 , \tag{2}$$

where Z_{ij} is the number of nearest-neighbor atoms on the jth sublattice to an atom on the ith sublattice, N_j is the number of atoms per unit volume on the jth sublattice, g_i and g_j are the Landé factors for the ions on the ith and jth sublattice, respectively, and μ_B is the Bohr magneton.

The molecular fields for the inverse spinel $M^{2+}Fe_2{}^{3+}O_4$ with Néel-type spin ordering are given by

$$H_A=\lambda_{AA}M_A-\lambda_{AB'}M_{B'}-\lambda_{AB''}M_{B''} , \tag{3a}$$

$$H_{B'}=-\lambda_{AB'}M_A+\lambda_{B'B'}M_{B'}+\lambda_{B'B''}M_{B''} , \tag{3b}$$

$$H_{B''}=-\lambda_{AB''}M_A+\lambda_{B'B''}M_{B'}+\lambda_{B''B''}M_{B''} . \tag{3c}$$

Here Fe^{3+} ions occupy A and B'' sublattices and M^{2+} ions occupy the B' sublattice. If the spin of the M^{2+} ions is denoted by s, the dependence of the sublattice magnetization on temperature is given by

$$M_A(T)/M_A(0)=B_{5/2}(5\mu_B H_A/kT) , \tag{4a}$$

$$M_{B'}(T)/M_{B'}(0)=B_s(2s\mu_B H_{B'}/kT) , \tag{4b}$$

$$M_{B''}(T)/M_{B''}(0)=B_{5/2}(5\mu_B H_{B''}/kT) , \tag{4c}$$

where B_{s_i} is the Brillouin function for spin s_i. Writing the set of equations in (4) in the form

$$y_i=B_{s_i}(x_i) , \quad i=A,B',B'' \tag{5}$$

we have,

$$\begin{aligned} x_A&=(1/T)(\xi_{AA}y_A-\xi_{AB'}y_{B'}-\xi_{AB''}y_{B''}) \\ x_{B'}&=(1/T)(-\xi_{B'A}y_A+\xi_{B'B'}y_{B''}+\xi_{B'B''}y_{B''}) \\ x_{B''}&=(1/T)(-\xi_{B''A}y_A+\xi_{B''B'}y_{B'}+\xi_{B''B''}y_{B''}) \end{aligned} \tag{6}$$

where

$$\xi_{ij}=(g_i s_i \mu_B/k)\lambda_{ij}M_j(0) , \quad i,j=A,B',B'' . \tag{7}$$

Note that $\xi_{ij}\neq\xi_{ji}$.

The procedure adopted to obtain the set of six exchange constants from the magnetization curves was as follows. Initially a probable set of six J_{ij} was assumed. Using these values of J_{ij}, the constants ξ_{ij} were obtained from Eq. (7). For a given temperature T_1, some values of $y_i(i=A,B',B'')$ were assumed. These were substituted in Eq. (6) and values of x_i were obtained. If these values of x_i agreed with those obtained from the plot of the Brillouin functions of Eq. (5), the assumed values of y_i gave the reduced sublattice magnetization for temperature T_1. If they did not agree suitable alterations in the values of y_i were made until the values of x_i obtained from Eq. (6) agreed with those obtained from Eq. (5). In this manner values of y_i for different values of T were obtained. If this led to the experimental M_S vs T curve the chosen set of exchange constants was considered appropriate for the system. In case this did not reproduce the experimental curve, a new set was tried. Although the technique seems tedius, after a few iterations it becomes easier to guess the changes which need to be made in the values of both y_i and J_{ij} to obtain agreement with experiment.

B. Paramagnetic susceptibility

To have a further check on the exchange constants so obtained we used them to calculate the variation of paramagnetic susceptibility with temperature and compared this with experiment. In case both the magnetization and susceptibility gave satisfactory results the set was accepted. If not, it was modified until the best possible agreement with both the experimental data was achieved.

The expression for the paramagnetic susceptibility for the three-sublattice model was obtained as follows. In the paramagnetic phase the sublattice magnetization is given by

$$M_i=(c_i/T)(H_i+H_0) , \quad i=A,B',B'' \tag{8a}$$

$$c_i=N_i\mu_B^2 g_i^2 s_i(s_i+1)/3k \tag{8b}$$

where c_i is the Curie constant of the ith sublattice, N_i is the number of atoms per unit volume, g_i is the Landé g factor, s_i is the spin, H_i is the molecular field given by Eq. (3), and H_0 is the external field. Using Eq. (8) a bit tedius but straightforward calculation yields the expression for the inverse susceptibility χ^{-1}.

$$\frac{1}{\chi}=\frac{H_0}{\sum_i M_i}=\frac{1}{\chi_0}+\frac{T}{c}-\frac{k_1}{T-\theta_1}+\frac{k_2}{T-\theta_2} , \tag{9}$$

where

$$c=\sum_i c_i ,$$

$$\frac{1}{\chi_0}=\frac{1}{2c^2}\left(\sum_{\substack{i,j\\ i\neq j}} c_i c_j(\lambda_{ii}+\lambda_{jj})-2c_i c_i\lambda_{ij}\right)-\frac{1}{c}\sum_i c_i\lambda_{ii},$$

$$k_1=\frac{1}{c}\frac{S+R\theta_1}{(p^2-4q)^{1/2}} , \quad k_2=\frac{1}{c}\frac{S+R\theta_2}{(p^2-4q)^{1/2}} ,$$

$$\theta_1=\tfrac{1}{2}[p+(p^2-4q)^{1/2}] , \quad \theta_2=\tfrac{1}{2}[p-(p^2-4q)^{1/2}]$$

$$p=\frac{c}{\chi_0}+\sum_i c_i\lambda_{ii} ,$$

$$q=\frac{c_A c_{B'} c_{B''}}{2c}\sum_{\substack{i,j,k\\ i\neq j\neq k}}\left[\tfrac{4}{3}\lambda_{ij}(\lambda_{jk}-\lambda_{kk})-\lambda_{ij}^2+\lambda_{ii}\lambda_{jj}\right] ,$$

$$R = \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} c_i c_j (\lambda_{ij}^2 - \lambda_{ii}\lambda_{jj}) - \frac{cp}{\chi_0} + q \, ,$$

$$S = c_A c_{B'} c_{B''} \Big(\lambda_{AA} \lambda_{B'B'} \lambda_{B''B''} + 2\lambda_{AB'} \lambda_{B'B''} \lambda_{AB''} - \frac{1}{3} \sum_{\substack{i,j,k \\ i \neq j \neq k}} \lambda_{ij}^2 \lambda_{kk} \Big) + \frac{cq}{\chi_0} \, , \quad i,j,k = A, B', B'' \, .$$

For a given set of six molecular field constants λ_{ij}, the values of $1/\chi_0, k_1, k_2, \theta_1, \theta_2$ are calculated using the Curie constants c_i which are obtained from the chemical composition of the ferrite. The theoretical curves obtained from Eq. (9) are compared with experiment and the set of exchange constants which simultaneously satisfies both the M_S and χ^{-1} data is taken to be the valid set.

III. RESULTS AND DISCUSSION

In Table IV are listed the values of the exchange constants obtained using the method of analysis discussed above for ferrites with composition $M^{2+}Fe_2^{3+}O_4$ where M stands for $Li_{0.5}Fe_{0.5}$, Mn, Fe, Co, Ni, and Cu. Here all except the Mn ferrite are inverse spinels. For the Li and Cu ferrites the data on χ^{-1} are not available, hence only the M_S vs T curve has been used for analysis. In the Mn ferrite 96% of the Mn^{2+} ions are on A site. We have therefore treated it as a normal spinel in our analysis.

The experimental and theoretical curves for magnetization and susceptibility for Mn, Fe, Co, Ni, and Cu ferrites are given in Fig. 3. From Table IV we note that the cell constant does not vary much, among the chosen set, except for the Mn ferrite which has slightly greater cell constant, due to the larger radius of the Mn^{2+} ions (0.80 Å). Since bond angles and bond distances remain constant the variations in the magnitude and sign of the exchange constants can be attributed to the change in the electronic state of the magnetic ions as the number of d electrons is varied. From neutron diffraction and magnetization measurements the spin ordering in each of these ferrites has been found to be Néel type (see Table III). The condition for the change from Néel to Yafet-Kittel (YK) configuration has been discussed earlier.[20] For YK spin ordering in $M Fe_2O_4$ we obtain the following expression for the Yafet-Kittel angle α_{YK},

$$\cos\alpha_{YK} = \frac{S_A S_{B'} \lambda_{AB'} + S_A S_{B''} \lambda_{AB''}}{S_{B'}^2 \lambda_{B'B'} + S_{B''}^2 \lambda_{B''B''} + 2 S_{B'} S_{B''} \lambda_{B'B''}} \, . \qquad (10)$$

When values of the λ_{ij} obtained from the J_{ij} given in Table IV are substituted in Eq. (10) we obtain inadmissible values of α_{YK} in each case. This shows that our set of exchange constants predicts Néel-type spin ordering in these ferrites in agreement with experiment.

In the discussion that follows we use the Anderson's approach to obtain a rough estimate of the transfer integrals and to see if these lead to results consistent with the symmetries of the orbitals. Along with Anderson we assume that the energy difference between the antiparallel and parallel spin arrangements of the two interacting magnetic ions can be expressed in the form

$$\Delta E(\uparrow\downarrow - \uparrow\uparrow) = -\sum_k \frac{2b_k^2}{U_k} + \sum_l J_l \, , \qquad (11)$$

where the summation k is over the different routes of the superexchange interaction via the ligand, and l is over the various direct ferromagnetic exchange interactions. The experimental data is analyzed using the Heisenberg-Dirac Hamiltonian

$$E_{ex} = -\sum_{i,j} 2J_{ij} \vec{S}_i \cdot \vec{S}_j \qquad (12)$$

From (11) and (12)

$$J_{ij} = -\frac{1}{4S_i S_j} \left(\sum_k \frac{2b_k^2}{U_k} - \sum_l J_l \right) . \qquad (13)$$

Anderson's approximate estimates[11] for U_k are 6 eV for the Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}, and 10 eV for Mn^{2+} and Fe^{3+}. We have used these values in our calculations which are given below.

TABLE IV. Superexchange constants in spinel ferrites expressed in °K obtained on the basis of the three-sublattice model. n indicates the number of d electrons in the divalent atom on the B site. The last column gives the lattice constant.

Compound	n	J_{AA} d^5-d^5	$J_{AB'}$ d^5-d^n	$J_{AB''}$ d^5-d^5	$J_{B'B'}$ d^n-d^n	$J_{B'B''}$ d^5-d^n	$J_{B''B''}$ d^5-d^5	a (Å)
$Li_{0.5}Fe_{2.5}O_4$		−20		−29			−8	8.332
$MnFe_2O_4$	5	−14.6	−19.1				−10	8.512
Fe_3O_4	6	−21	−23.8	−28	48.4	−13.2	−10	8.392
$CoFe_2O_4$	7	−15	−22.7	−26	46.9	−18.5	−7.5	8.380
$NiFe_2O_4$	8	−15	−27.4	−30.7	30.0	−2.7	−5.4	8.332
$CuFe_2O_4$	9	−15	−28	−24	20	−6	−8	8.372

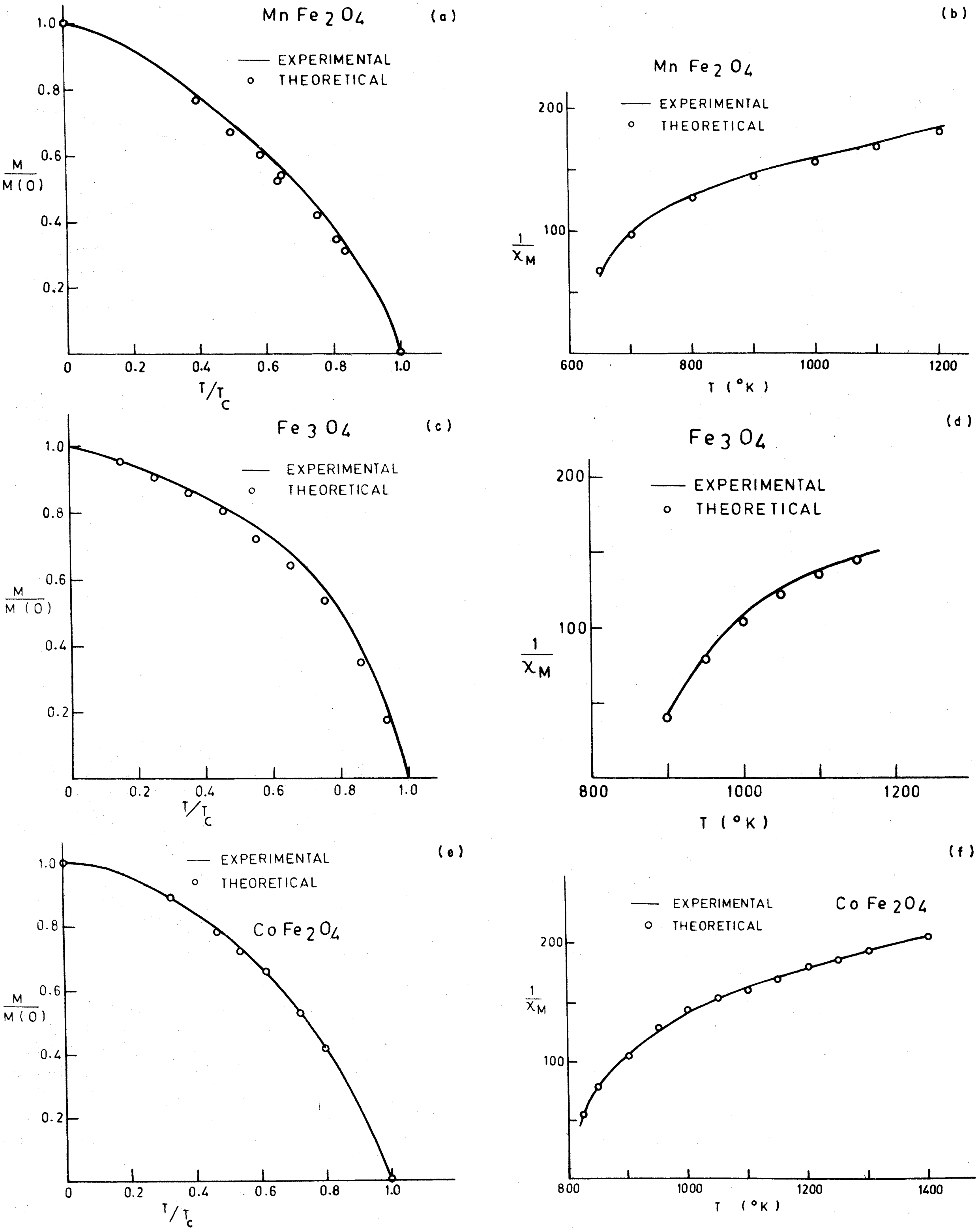

FIG. 3. Experimental and theoretical curves for magnetization and inverse susceptibility as a function of temperature for $MnFe_2O_4$ [(a) and (b)], Fe_3O_4 [(c) and (d)], $CoFe_2O_4$ [(e) and (f)], $NiFe_2O_4$ [(g) and (h)], and $CuFe_2O_4$ [(i)]. The theoretical curves have been obtained on the basis of the three-sublattice approximation using the set of exchange constants given in Table IV. The agreement between theory and experiment is satisfactory in each case.

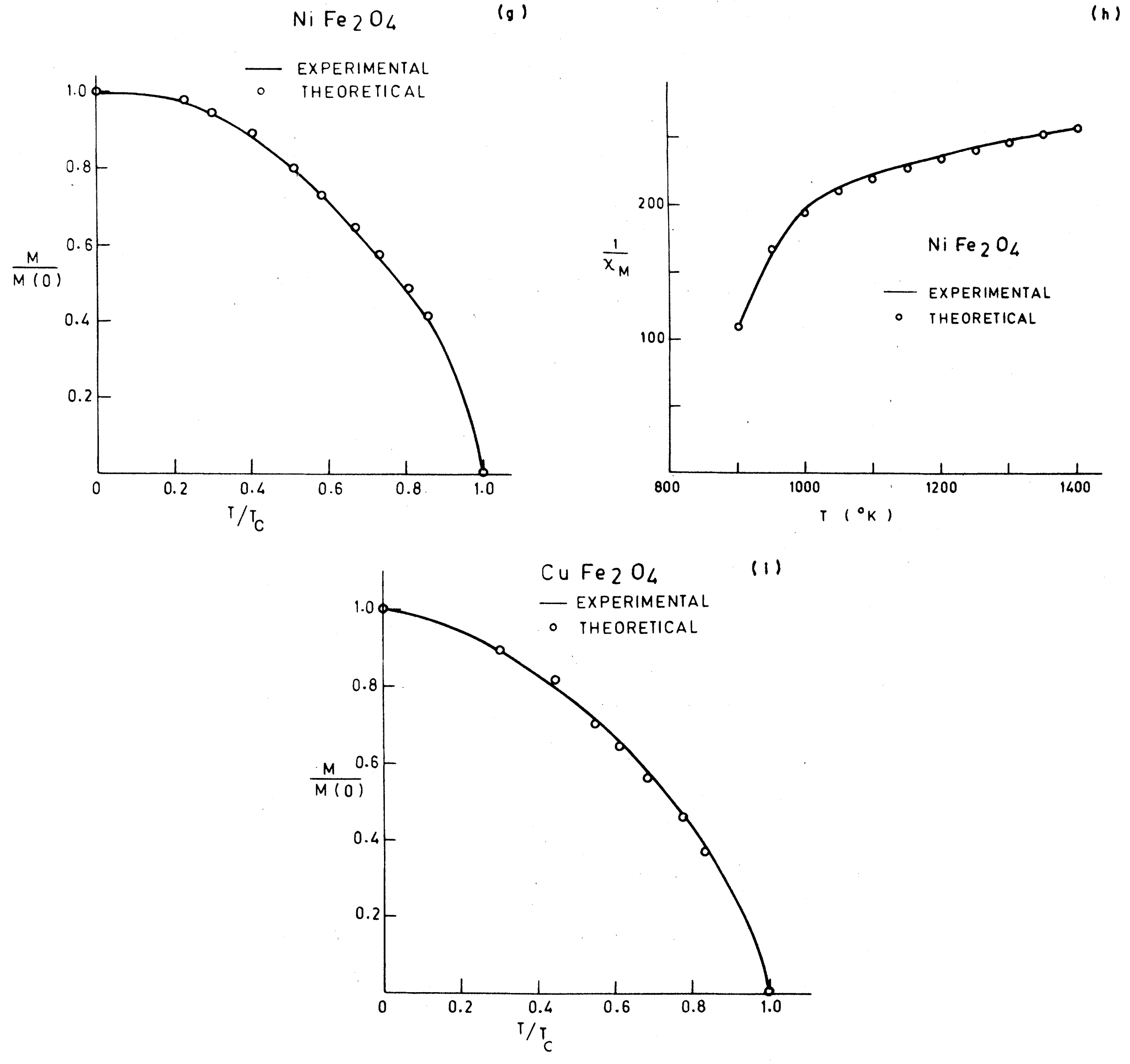

FIG. 3. (*Continued*)

A. 180° interaction ($J_{AB'}$ and $J_{AB''}$)

From Table IV it is observed that there are two kinds of 180° interactions, $J_{AB'}$ and $J_{AB''}$. The former relates to the d^5-d^n interaction for $6 \leq n \leq 9$, while the latter represents the d^5-d^5 interaction. For the d^5-d^5 interaction, using the Anderson approach[11] we obtain

$$d^5\text{-}d^5:\ J_{AB''} = -\frac{1}{25}\left(\frac{2b_{\sigma\sigma}^2}{U} + \frac{4b_{\pi\pi}^2}{U} - 4J_{\pi\sigma} - 2J_\pi - 2J_\sigma\right),$$

where $b_{\sigma\sigma}$ ($b_{\pi\pi}$) is the transfer integral for the electron in the e_g (t_{2g}) state of atom 1 to the e_g (t_{2g}) state on atom 2. $J_{\pi\sigma}$ is the direct exchange between t_{2g} on 1 and e_g on 2, J_π is between t_{2g} on 1 and t_{2g} on 2, and J_σ is e_g on 1 and e_g on 2. The direct exchange in the spinel ferrites for 180° interaction should be negligible due to the large separation between the ions ($R_{AB} = \frac{1}{8}a\sqrt{\pi}$), the inversion of the electronic crystal-field states in going from A to the B site, and the presence of the intervening oxygen ions. We therefore assume that

$$d^5\text{-}d^5:\ J_{AB''} = -\frac{1}{25}\left(\frac{2b_{\sigma\sigma}^2}{U} + \frac{4b_{\pi\pi}^2}{U}\right), \tag{14}$$

where U is equal to 10 eV.

For the d^5-d^n interactions we observe that the $b_{\sigma\sigma}$ contribution is the same for $n = 6, 7, 8$, viz.,

TABLE V. (a). Comparison of the experimental values of 180° $J_{AB'}$ and $J_{AB''}$ interactions with those calculated using the Anderson theory (Ref. 11). The values of the transfer integrals used for the calculation of the $J_{AB'}$ interactions are $b_{\sigma\sigma}=0.31$ eV and $b_{\pi\pi}=0.18$ eV, while for $J_{AB''}$ interactions are $b_{\sigma\sigma}=0.48$ eV and $b_{\pi\pi}=0.18$ eV. (b) Comparison of the experimental values of 90° J_{AA}, $J_{B'B'}$, $J_{B'B''}$, and $J_{B''B''}$ interactions with those calculated using the Anderson theory (Ref. 11). The values of the transfer integrals used for the calculations of J_{AA} are $b_{\sigma\sigma'}=0.12$ eV, $b_{\pi\sigma}=0.30$ eV while for all the BB interactions, $b_{\sigma\sigma'}=0.12$ eV, $b_{\pi\sigma}=0.25$ eV, and $J_{\pi}=0.025$ eV.

(a)

		$J_{AB'}$ (d^5-d^n)		$J_{AB''}$ (d^5-d^5)	
Compound	n	$J_{AB'}$ (°K) observed	$J_{AB'}$ (°K) calculated	$J_{AB''}$ (°K) observed	$J_{AB''}$ (°K) calculated
$Li_{0.5}Fe_{2.5}O_4$	5			−29	−28
$MnFe_2O_4$	5	−19.1	−15.0		
Fe_3O_4	6	−23.8	−20.2	−28	−28
$CoFe_2O_4$	7	−22.7	−22.7	−26	−28
$NiFe_2O_4$	8	−27.4	−27.4	−30.7	−28
$CuFe_2O_4$	9	−28.0	−27.4	−24	−28

(b)

		$J_{B'B'}$ (°K)(d^n-d^n)		$J_{B'B''}$ (°K)(d^5-d^n)		$J_{B''B''}$ (°K) (d^5-d^5)		J_{AA} (°K)	
Compound	n	observed	calculated	observed	calculated	observed	calculated	observed	calculated
$Li_{0.5}Fe_{2.5}O_4$	5					−8	−9	−20.0	−14
$MnFe_2O_4$	5					−10	−9	−14.6	−14
Fe_3O_4	6	48.4	44	−13.2	−11	−10	−9	−21.0	−14
$CoFe_2P_4$	7	46.9	46	−18.5	−10	−7.5	−9	−15	−14
$NiFe_2O_4$	8	30.0	29	−2.7	−10	−5.4	−9	−15	−14
$CuFe_2O_4$	9	20.0	29	−6.0	−10	−8	−9	−15	−14

$2b_{\sigma\sigma}^2/U$, but for $n=9$ it is reduced by half since the lone e_g electron has equal probability of being in (x^2-y^2) and z^2 states, and in the case of the former, this contribution vanishes. Regarding the $b_{\pi\pi}$ interaction, as the t_{2g} orbitals get filled up the contribution from this term reduces. Thus we obtain

$$d^5\text{-}d^6:\quad J_{AB'}=-\frac{1}{20}\left(\frac{2b_{\sigma\sigma}^2}{\overline{U}}+\frac{4}{3}\,\frac{2b_{\pi\pi}^2}{\overline{U}}\right), \tag{15}$$

$$d^5\text{-}d^7:\quad J_{AB'}=-\frac{1}{15}\left(\frac{2b_{\sigma\sigma}^2}{\overline{U}}+\frac{2}{3}\,\frac{2b_{\pi\pi}^2}{\overline{U}}\right), \tag{16}$$

$$d^5\text{-}d^8:\quad J_{AB'}=-\frac{1}{10}\left(\frac{2b_{\sigma\sigma}^2}{\overline{U}}\right), \tag{17}$$

$$d^5\text{-}d^9:\quad J_{AB'}=-\frac{1}{5}\,\frac{b_{\sigma\sigma}^2}{\overline{U}}, \tag{18}$$

where $\overline{U}$ has been taken as the mean of the d^5-d^5 and d^n-d^n values of U. Assuming the U value of all the divalent ions except Mn^{2+} to be 6 eV, the value of $\overline{U}$ is 8 eV, which is the average for the Fe^{3+} and M^{2+} ions.

Using Eqs. (16) and (17) an estimate of $b_{\sigma\sigma}$ and $b_{\pi\pi}$ can be obtained from the observed values of $J_{AB'}$ given in Table IV. This yields the value of 0.31 and 0.18 eV for $b_{\sigma\sigma}$ and $b_{\pi\pi}$, respectively. The above values of $b_{\pi\pi}$ and $b_{\sigma\sigma}$ are used to calculate the d^5-d^5, d^5-d^6, and d^5-d^9 exchange interaction constants and are given in Table V(a). There is reasonably good agreement between the calculated and observed values.

The value of the d^5-d^5 A-B interaction from Table IV is observed to be different for the two cases Mn^{2+}-Fe^{3+} and Fe^{3+}-Fe^{3+}. The exchange constant for the former is −19 °K while for the latter it is −28 °K. In this case the exchange constant is given by Eq. (14) where the value of U is 10 eV. If we assume $b_{\sigma\sigma}=0.31$ eV and $b_{\pi\pi}=0.18$ eV we obtain a value of −15 °K for $J_{AB''}$ which is close to the observed value for Mn^{2+}-Fe^{3+}. For Fe^{3+}-Fe^{3+} interaction, we keep $b_{\pi\pi}$ the same, and change the value of $b_{\sigma\sigma}$ to get agreement with experiment. For $b_{\sigma\sigma}=0.48$ eV and $b_{\pi\pi}=0.18$ eV, $J_{AB''}=-28$ °K.

These results are in general agreement with the chemical theory of valency. The transfer integral relating to σ bonding is about 2–3 times larger than the π bonding. Also the transfer integral is larger in case of like ions (Fe^{3+}-Fe^{3+}) compared to the unlike ions (Mn^{2+}-Fe^{3+}).

B. 90° interactions ($J_{B'B'}$, $J_{B'B''}$, $J_{B''B''}$)

We have again two types of interactions, d^5-d^n and d^n-d^n ($n=5$–9). Here d^5 is the trivalent Fe^{3+} ion while d^n ($n\neq5$) are all divalent ions. The ionic radius of the Fe^{3+} ion is 0.64 Å which is about 20%

smaller than the radius of divalent ions. The d^5 ions therefore may not participate in direct exchange. Following the Anderson and Kanamori approaches, the $J_{B'B''}$ exchange constant has two terms, one ferromagnetic and the other antiferromagnetic. The ferromagnetic interaction involves two p orbitals (σ, σ') of the ligand and z^2 orbitals of the magnetic ions in σ-bonding states. We denote the transfer integral for this process by $b_{\sigma\sigma'}$. The antiferromagnetic contribution is between a t_{2g} state on one and z^2 state on the other magnetic ion via a single p orbital of the ligand with π for t_{2g} and σ for e_g bonding states. The transfer integral for this process is denoted here by $b_{\pi\sigma}$. We thus obtain

$$d^5\text{-}d^5:\quad J_{B''B''} = -\frac{1}{25}\left(\frac{4b_{\pi\sigma}^2}{U} - \frac{4b_{\sigma\sigma'}^2}{U}\right), \tag{19}$$

where $U = 10$ eV,

$$\begin{aligned} d^5\text{-}d^6:&\quad J_{B'B''} = -\frac{1}{20}\left(\frac{5}{3}\,\frac{2b_{\pi\sigma}^2}{\overline{U}} - \frac{4b_{\sigma\sigma'}^2}{\overline{U}}\right), \\ d^5\text{-}d^7:&\quad J_{B'B''} = -\frac{1}{15}\left(\frac{4}{3}\,\frac{2b_{\pi\sigma}^2}{\overline{U}} - \frac{4b_{\sigma\sigma'}^2}{\overline{U}}\right), \\ d^5\text{-}d^8:&\quad J_{B'B''} = -\frac{1}{10}\left(\frac{2b_{\pi\sigma}^2}{\overline{U}} - \frac{4b_{\sigma\sigma'}^2}{\overline{U}}\right), \\ d^5\text{-}d^9:&\quad J_{B'B''} = -\frac{1}{5}\left(\frac{1}{2}\,\frac{2b_{\pi\sigma}^2}{\overline{U}} - \frac{1}{2}\,\frac{4b_{\sigma\sigma'}^2}{\overline{U}}\right), \end{aligned} \tag{20}$$

where $\overline{U} = 8$ eV.

For the d^n-d^n $(n = 6-9)$ interaction we assume that there is a direct ferromagnetic exchange J_π, since the radii of the divalent ions is large compared to the Fe^{3+} ions. When the direct exchange between the t_{2g} orbitals becomes significant, the $b_{\pi\sigma}$ interaction will be reduced since the t_{2g} magnetic orbitals will be involved in the ferromagnetic direct exchange. If we assume that $b_{\pi\sigma}$ is negligible when direct exchange dominates, we obtain

$$\begin{aligned} d^6\text{-}d^6:&\quad J_{B'B'} = \tfrac{1}{16}(4b_{\sigma\sigma'}^2/U + 2J_\pi), \\ d^7\text{-}d^7:&\quad J_{B'B'} = \tfrac{1}{9}(4b_{\sigma\sigma'}^2/U + J_\pi), \\ d^8\text{-}d^8:&\quad J_{B'B'} = \tfrac{1}{4}(4b_{\sigma\sigma'}^2/U), \\ d^9\text{-}d^9:&\quad J_{B'B'} = \tfrac{1}{4}(4b_{\sigma\sigma'}^2/U), \end{aligned} \tag{21}$$

where $U = 6$ eV.

The approximate values of the transfer integrals which yield the observed exchange constants are $b_{\pi\sigma} = 0.25$ eV, $b_{\sigma\sigma'} = 0.122$ eV, and $J_\pi = 0.025$ eV. The calculated values of $J_{B'B'}$, $J_{B'B''}$, and $J_{B''B''}$ are given in Table V(b). The agreement with experiment is satisfactory.

C. 90° interaction (J_{AA})

The M-O-M angle for the J_{AA} interaction is 79°, hence we approximate it to 90° interaction. For this case, as in 90° $J_{B''B''}$, we obtain

$$d^5\text{-}d^5:\quad J_{AA} = \tfrac{1}{25}(4b_{\pi\sigma}^2/U - 4b_{\sigma\sigma'}^2/U),$$

where $U = 10$ eV. For the tetrahedral A sites the crystal field states are inverted compared to the octahedral sites and also the distances of the metal ion to ligand are different from the BB interaction. We therefore expect $b_{\pi\sigma}$ and $b_{\sigma\sigma'}$ to be different for J_{AA} and $J_{B''B''}$ interactions. Since $b_{\sigma\sigma'}$ involves two p orbitals, it may not be as sensitive to the variation in distances and angles as $b_{\pi\sigma}$ which involves only one p orbital. Assuming that $b_{\sigma\sigma'}$ is the same for J_{AA} as for the $J_{B''B''}$ interaction, viz., $b_{\sigma\sigma'} = 0.12$ eV, we obtain $b_{\pi\sigma} = 0.3$ eV which is 20% more than for the BB interaction.

IV. CONCLUSION

An attempt has been made to use a more realistic three-sublattice molecular-field approximation to obtain the exchange constants for spinel ferrites. The reliability of the data on exchange constants has been improved by simultaneously satisfying the magnetization and paramagnetic susceptibility variation with temperature. The magnitude and sign of the various exchange constants have been explained on the basis of possible superexchange and direct-exchange interactions. An important result which has emerged from the analysis is that the magnitudes of transfer integrals and direct exchange integrals do not change as the magnetic orbitals go on filling with increasing the number of d electrons. The next step could be to examine if similar conclusions can be drawn for other systems, particularly those involving the less than half filled d subshell.

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