THE

PHYSICAL REVIEW

A journal of experimental and theoretical physics established by E. L. Nichols in 1893

SECOND SERIES, VOL. 122, NO. 5 JUNE 1, 1961

Theory of Magnetostriction in Cobalt-Manganese Ferrite

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(Received January 25, 1961)

The magnetostrictive effect of an orbitally degenerate magnetic ion in a cubic ferromagnet is calculated in detail using crystal-field theory. In contrast to our previous work, it is not assumed that inter-atomic exchange energy is large compared with spin-orbit energy. The results are applied to the effect of cobalt in cobalt-manganese ferrite. It is found that the theory is consistent with experimental results for the magnetostrictive parameters λ_{100} and λ_{111} in the compound $Co_{0.245}Mn_{0.747}Fe_{1.99}O_4$ from 225°–355°K. By fitting theory to experiment, a trigonal splitting of about 630 cm^{-1} for the ground state of the cobalt ion is inferred. The trigonal splitting has less than half its value in cobalt-iron ferrite.

I. INTRODUCTION

THE present work is an extension of an earlier calculation[1] of the magnetostrictive effect of cobalt substitutions in ferrites. In the earlier work it was assumed that the exchange energy coupling the cobalt spin to other spins in the crystal is large compared with spin-orbit energy. That case, which we may call strong exchange, was assumed because analysis of magnetocrystalline anisotropy[2] had indicated that it applied to cobalt-substituted magnetite. More recently it was concluded[3] that the anisotropy of cobalt-substituted manganese ferrite is consistent with the same orbital-doublet model found to work in the magnetite case. However, the magnitude of exchange energy required to bring about agreement in manganese ferrite was found to be *not* large compared to spin-orbit energy. We may call this the case of weak exchange.

Having this indication that manganese ferrite is an interesting host for the study of effects of cobalt-substitution, it seemed worthwhile to calculate magnetostriction for the case of weak exchange. In this paper, the calculation is given and the results are compared with experimental results for a cobalt-manganese ferrite.[4]

In general, magnetostrictive strain may be considered to arise from an internal stress which is a function of the orientation of the spontaneous magnetization. In the case of an ideal periodic crystal, the stress is homogeneous and is given by the differential of free energy with respect to strain. Then the central problem of the theory of magnetostriction is to calculate the first-order strain-dependence of the energy levels of the crystal.

If the magnetic crystal is not periodic, as in a solid solution, the problem is not changed in any essential respect as long as the one-ion model applies. It is true that in this case the internal stress field is not homogeneous. From the point of view of the elastic continuum model of a crystal, it may be regarded as residing at point singularities centered at the transition-metal ions or atoms. However, according to the theory of elasticity, the average strain of an elastically homogeneous body is equal to the average stress divided by the appropriate elastic constant. Therefore, the macroscopic magnetostrictive strain does not depend on the spacial distribution of the stress singularities but only on their strength and mean density. It follows that the results of a theory based on a one-ion model will apply for arbitrary concentration of the magnetostrictive ions if these ions do not interact with each other (except through exchange) and if the inhomogeneity of elasticity due to the solid solution is negligible.

The formal theory, which centers around the calculation of strain dependence of the energy of an orbitally degenerate ion, is given in Sec. II. In Sec. III the results are applied to cobalt-substituted manganese ferrite

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[1] J. C. Slonczewski, J. Phys. Chem. Solids **15**, 335 (1960).

[2] J. C. Slonczewski, Phys. Rev. **110**, 1341 (1958).

[3] J. C. Slonczewski, J. Phys. Chem. Solids **18**, 269 (1961).

[4] R. F. Pearson and P. J. Harbour (private communication).

and compared with Pearson's measurements of magnetostriction in $Co_{0.245}Mn_{0.747}Fe_{1.99}O_4$. Section III also summarizes the crystal-field information gathered to date from analyses of anisotropy and magnetostriction in $Co_xFe_{3-x}O_4$ and $Co_xFe_2Mn_{1-x}O_4$.

II. CALCULATION

The approximations made in our strong-exchange calculation[1] introduced a relative error of the order $(\alpha\lambda/2\beta H)^2$ (α = effective orbital g factor, λ = spin-orbit constant, βH = exchange energy) into the final expression for magnetostrictive strain. This means that the spin of cobalt was assumed to be deflected by spin-orbit coupling only slightly from the direction of the molecular field in the state of lowest energy. Since this quantity is $(132/174)^2$ in $Co_xMn_{1-x}Fe_2O_4$ [3] [as compared to $(132/640)^2$ in $Co_xFe_{3-x}O_4$ [2]] the strong-exchange result cannot be applied to this compound.

Our general procedure now is the same as before. Magnetostriction is described by the functional dependence of the strain tensor $A_{ij}(\alpha_x,\alpha_y,\alpha_z)$ $(i,j=x,y,z)$ on the orientation of the spontaneous magnetization given by the direction cosines α_x, α_y, α_z. The particular magnetostrictive parameters λ_e and λ_s to be calculated were introduced earlier.[1] They are defined by the equations

$$\lambda_e=\tfrac{2}{3}[A_{zz}(001)-A_{zz}(010)], \tag{1}$$

$$\lambda_s=\tfrac{4}{3}A_{xy}(2^{-\frac{1}{2}}2^{-\frac{1}{2}}0), \tag{2}$$

where the coordinates refer to the cubic axes of the crystal. If the magnetostriction obeys the standard two-constant phenomenological expression, then λ_e and λ_s reduce to the standard coefficients λ_{100} and λ_{111}, respectively. It is more useful to calculate λ_e and λ_s than λ_{100} and λ_{111}, because the expansion of A_{ij} in powers of α_x, α_y, and α_z will not converge at sufficiently low temperatures. These parameters may be measured by applying the magnetic field and strain gauges in a (100) plane.

We introduce again the strength,

$$f_{ij}(\alpha_x\alpha_y\alpha_z)=\partial f(\alpha_x\alpha_y\alpha_z)/\partial A_{ij},$$

of the elastic stress singularity caused by the presence of an isolated cobalt impurity. Here f is the free energy. The stress is caused by the electrostatic forces of the cobalt ion acting on other ions. By minimizing the total energy of the crystal in the usual way, we obtain

$$\lambda_e=2N[f_{zz}(010)-f_{zz}(001)]/3(C_{11}-C_{12}), \tag{3}$$

$$\lambda_s=N[f_{xy}(\bar{1}10)-f_{xy}(110)]/6C_{44}. \tag{4}$$

Here N is the number of cobalt ions per unit volume and C_{11}, C_{12}, and C_{44} are elastic constants. It is assumed that the cobalt is distributed equally among the four octahedral sublattices of a spinel structure. In Eqs. (3) and (4), f_{zz} and f_{xy} are evaluated for a cobalt ion lying on a site for which [111] is the axis of threefold symmetry. The other cases $[\bar{1}11]$, $[1\bar{1}1]$, and $[11\bar{1}]$ were eliminated by considerations of symmetry.

We will need to consider the differential of f, which has the form

$$df=-kTdZ/Z, \tag{5}$$

where k is Boltzman's constant, T is temperature, and Z is the partition function. Chester[5] and others have discussed a general perturbation expansion for Z having the form

$$Z=Z_0+\sum_{n=1}^{\infty}Z_n, \tag{6}$$

$$Z_0=\textstyle\sum_q \exp(-\beta' E_q), \tag{7}$$

$$Z_n=-\beta'\sum_{q_1q_2\cdots q_n}V_{q_1q_2}V_{q_2q_3}\cdots V_{q_nq_1}$$
$$\times\exp(-\beta' E_{q_1})/\prod_{i=2}^{n}(E_{q_1}-E_{q_i})\quad(n>0), \tag{8}$$

where $\beta'=(kT)^{-1}$, E_q is an eigenvalue of the unperturbed Hamiltonian, and $V_{q_iq_j}$ is a matrix element of the perturbation. The summation in Eq. (8) carries over all sets $q_1q_2\cdots q_n$.

The convergence of this expansion does not necessarily place a restriction on the energy denominators appearing in Eq. (8). A limiting procedure involving a proper grouping of terms effectively replaces any $(E_{qi}-E_{qj})^{-1}$ which are greater than $(kT)^{-1}$ by a power series in $(kT)^{-1}$. Thus the expansion parameters are always $V_{q_iq_j}/kT$ or less. For detailed discussion of the properties of this expansion, Chester's article[5] should be consulted.

The quantities f_{zz} and f_{xy} will be calculated using a one-ion Hamiltonian of the form

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_e+\mathcal{H}_s+\mathcal{V}. \tag{9}$$

Here $\mathcal{H}_0$ represents the internal energy of the Co^{2+} electrons including their kinetic energy, Coulomb interaction with the nucleus, mutual Coulomb interaction, and electrostatic energy in the crystalline potential for vanishing strain. The exchange energy $\mathcal{H}_e$ has the form $2\beta\mathbf{H}\cdot\mathbf{S}$, where β is the Bohr magneton, $\mathbf{S}$ is the cobalt spin, and $\mathbf{H}$ is the molecular field due to other spins in the crystal. $\mathcal{H}_s$ is the spin-orbit energy and $\mathcal{V}$ is the increment of crystal-field energy depending on A_{ij}.

The unperturbed basis functions diagonalize $\mathcal{H}_0+\mathcal{H}_e+\mathcal{H}_s^0$, where $\mathcal{H}_s^0$ is the submatrix of $\mathcal{H}_s$ in the ground multiplet. For the unperturbed states $|Mm)$ of the ground orbital doublet, the $2(2S+1)$ unperturbed energy levels are

$$E_{Mm}=|2\beta\mathbf{H}+mU_0\mathbf{k}|M$$
$$(M=-S,\,-S+1,\,\cdots S;\,m=\pm1), \tag{10}$$

where $U_0=-\alpha\lambda$ is the effective spin-orbit parameter

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[5] G. V. Chester, Phys. Rev. **93**, 606 (1954).

and M is the spin quantum number with spin quantized along the axis $2\beta\mathbf{H}+mU_0\mathbf{k}$. The perturbation consists of $\mathcal{H}_s'+\mathcal{V}$, where $\mathcal{H}_s'$ is $\mathcal{H}_s$ less its submatrix in the doublet manifold. One excited multiplet, an orbital singlet $|M0)$, will be considered. Its unperturbed energy is

$$E_{M0}=2\beta HM+E_t \quad (M=-S,\ -S+1,\ \cdots S), \tag{11}$$

where E_t is the trigonal field splitting. The doublet and singlet taken together comprise an effective P state.

When calculating Z in the denominator of Eq. (5), we apply the expansion (6)–(8) only to the term $\mathcal{H}_s'$ of the perturbation. We will further approximate Z by Z_0, thereby incurring a relative error of order not greater than λ^2/E_tkT. When calculating dZ in Eq. (5), we apply the expansion to the perturbation $\mathcal{H}_s'+d\mathcal{V}$, where $d\mathcal{V}$ is the first-order differential of $\mathcal{V}$ with respect to strain, keeping only terms to first order in $d\mathcal{V}$ in the final expression.

As shown previously,[1] the diagonal matrix elements of $d\mathcal{V}$ in the ground multiplet give rise to a fixed, nonmagnetostrictive strain. These matrix elements are neglected in what follows. We have then that $dZ_1=0$. Substituting in Eq. (8) we find

$$\begin{aligned} df_2 &= -kTdZ_2/Z_0 \\ &= -Z_0^{-1} \sum_{MM'm=\pm1} \exp(-\beta' E_{Mm})(Mm|\mathcal{H}_s'|M'0) \\ &\qquad \times (M'0|d\mathcal{V}|Mm)/E_t+\text{c.c.}, \end{aligned} \tag{12}$$

and

$$\begin{aligned} df_3 &= -kTdZ_3/Z_0 \\ &= Z_0^{-1} \sum_{MM'M''m=\pm1} \exp(-\beta' E_{Mm})(Mm|d\mathcal{V}|M'-m) \\ &\qquad \times (M'-m|\mathcal{H}_s'|M''0)(M''0|\mathcal{H}_s'|Mm) \\ &\qquad \times (E_{M'-m}-E_{Mm})^{-1}E_t^{-1}+\text{c.c.} \end{aligned} \tag{13}$$

In these equations c.c. means complex conjugate. We have neglected Boltzmann factors containing E_t in the exponent. We have also neglected βH and U_0 in comparison with E_t in the energy denominators. In Eq. (13) we made use of the fact that $d\mathcal{V}$ commutes with $\mathbf{S}$.

Now df_2 is of the order U_0dV/E_t and df_3 may be as great as order U_0^2dV/E_tkT. Both terms are significant in the temperature range of usual interest. The term $\partial f_2/\partial A_{ij}$ represents the stress singularity caused by the change in electron density associated with the "classical" tilting of the electron orbits of the degenerate orbital states out of the plane normal to the trigonal axis. The term $\partial f_3/\partial A_{ij}$ represents the stress singularity caused by the electron density introduced by wave mechanical interference between the degenerate orbital states by virtue of indirect transitions via the excited singlet. It may be seen that higher order dZ_n contribute smaller corrections to f.

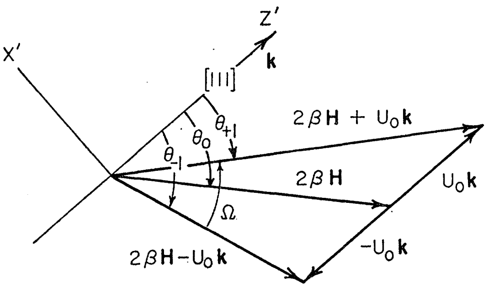

FIG. 1. Geometrical relationships used in the calculation.

For a single spin-multiplet, spin-orbit energy may be written in the form

$$\mathcal{H}_s=\mathbf{U}\cdot\mathbf{S}=\textstyle\sum_{i=+,-,z'}U_i^\dagger S_i, \tag{14}$$

where

$$U_\pm=\tfrac{1}{2}(U_{x'}\pm iU_{y'}), \tag{15}$$

and

$$S_\pm=S_{x'}\pm iS_{y'}. \tag{16}$$

Here the z' axis of quantization is the trigonal axis $\mathbf{k}$ (see Fig. 1). The axis x' lies in the $(\mathbf{H},\mathbf{k})$ plane. $\mathbf{U}$ operates on the space part of the wave function only and is equal to $-\alpha\lambda\mathbf{l}$ in the effective -P approximation. Here $\mathbf{l}$ is the effective orbital angular momentum operator. For purposes of this calculation, the state $|Mm)$ may be written in the form $|M)_m|m)$ where the subscript m specifies the axis of spin quantization $2\beta\mathbf{H}+mU_0\mathbf{k}$.

From our previous work[1] we have, in the effective -P approximation,

$$(+1|\partial\mathcal{V}/\partial A_{zz}|-1)=(-1|\partial\mathcal{V}/\partial A_{zz}|+1)=V_e, \tag{17}$$

$$(+1|\partial\mathcal{V}/\partial A_{zz}|0)=-(-1|\partial\mathcal{V}/\partial A_{zz}|0)=-V_e, \tag{18}$$

$$(+1|\partial\mathcal{V}/\partial A_{xy}|-1)=(-1|\partial\mathcal{V}/\partial A_{xy}|+1)=V_s, \tag{19}$$

$$(+1|\partial\mathcal{V}/\partial A_{xy}|0)=-(-1|\partial\mathcal{V}/\partial A_{xy}|0)=\tfrac{1}{2}V_s, \tag{20}$$

where V_e and V_s are real constants. Making the above substitutions, we have

$$f_{zz}=V_eZ_0^{-1}E_t^{-1}(\Sigma_2+\Sigma_3), \tag{21}$$

$$f_{xy}=V_sZ_0^{-1}E_t^{-1}(-\tfrac{1}{2}\Sigma_2+\Sigma_3), \tag{22}$$

where

$$\begin{aligned} \Sigma_2 = \sum_{MM'm=\pm1i} & m\exp(-\beta' E_{Mm})(m|U_i^\dagger|0) \\ & \times (M|{}_m S_i|M')_0\,(M'|{}_0\,|M)_m+\text{c.c.}, \end{aligned} \tag{23}$$

$$\begin{aligned} \Sigma_3 = \sum_{MM'M''m=\pm1ij} & \exp(-\beta' E_{Mm})(M|{}_m|M')_{-m} \\ & \times(-m|U_i^\dagger|0)(M'|{}_{-m}S_i|M'')_0\,(0|U_j^\dagger|m) \\ & \times (M''|{}_0S_j|M)_m(E_{M'-m}-E_{Mm})^{-1}+\text{c.c.}, \end{aligned} \tag{24}$$

and

$$Z_0=\textstyle\sum_{Mm}\exp(-\beta' E_{Mm}). \tag{25}$$

Since several axes of spin quantization are involved in these equations, it is necessary to introduce the unitary transformations connecting them. The transformation matrix is[6]

$$d_{MM'}(\phi)=(M|\exp(i\phi S_{y'})|M')=(M|_{\phi}|M'),$$

which is equivalent to

$$(M|_{\phi}=\sum_{M'}d_{MM'}(\phi)(M'|.$$

In this context only, the subscript ϕ means that $(M|_{\phi}$ is the initial state $(M|$ rotated through the angle ϕ in the right-hand screw sense about the y' axis.

In our basis we have

$$\sum_{M}|M)_0(M|_0=1=\sum_{M}|M)(M|, \tag{26}$$

where the spin state $|M)$ with no subscript satisfies

$$S_{z'}|M)=M|M). \tag{27}$$

Making these substitutions and noting that $d_{MM'}(\phi)$ is real, we find

$$\begin{aligned}\Sigma_2=&\sum_{MM'm=\pm1iM''}m\exp(-\beta'E_{Mm})\\&\times(m|U_i^{\dagger}|0)d_{MM''}(-\theta_m)\\&\qquad\times(M''|S_i|M')d_{MM'}(-\theta_m)+\text{c.c.},\end{aligned} \tag{28}$$

and

$$\begin{aligned}\Sigma_3=&\sum_{MM'M''m=\pm1ijM'''M^{iv}}\exp(-\beta'E_{Mm})d_{MM'}(m\Omega)\\&\times(-m|U_i^{\dagger}|0)d_{M'M'''}(-\theta_{-m})(M'''|S_i|M'')\\&\times(m|U_j^{\dagger}|0)^*d_{MM^{iv}}(-\theta_m)\\&\qquad\times(M^{iv}|S_j|M'')^*/(E_{M'-m}-E_{Mm})+\text{c.c.}\end{aligned} \tag{29}$$

Here the angles $\theta_{\pm1}$ are defined by Fig. 1.

We may use the standard representation for $S_{\pm}$:

$$\begin{aligned}(M'|S_+|M)&=(M|S_-|M')\\&=(S-M)^{\frac{1}{2}}(S+M+1)^{\frac{1}{2}}\delta_{M',M+1}.\end{aligned} \tag{30}$$

The matrix elements of $\mathcal{U}$ were calculated assuming that the phase of $|m)$ was fixed in the xyz frame. For the matrix elements of $\mathbf{U}$ we transform from xyz to $x'y'z'$ and obtain, with the help of Table III of reference 1,

$$\begin{aligned}(1|U_+|0)&=(-1|U_-|0)^*\\&=U_0(\omega^*\alpha_x+\omega\alpha_y+\alpha_z)(3^{\frac{1}{2}}\sin\theta_0)^{-1},\end{aligned} \tag{31}$$

$$(m|U_{z'}|m)=mU_0,\quad m=-1,\,0,\,+1,$$

all other matrix elements vanishing. Here $\omega=\exp(2\pi i/3)$. We have used here the relationship[1]

$$\begin{aligned}\omega(+1|U_x|0)&=\omega^*(+1|U_y|0)=(+1|U_z|0)\\&=\omega^*(-1|U_x|0)=\omega(-1|U_y|0)\\&=(-1|U_z|0)=-3^{-\frac{1}{2}}U_0,\end{aligned} \tag{32}$$

which holds in the effective -P approximation.

Making these substitutions we find

$$\begin{aligned}\Sigma_2=U_0&(2\alpha_z-\alpha_x-\alpha_y)(3^{\frac{1}{2}}\sin\theta_0)^{-1}\textstyle\sum_{Mm=\pm1}m\\&\times\exp(-\beta'E_{Mm})\textstyle\sum_{M'}(S+mM')^{\frac{1}{2}}(S-mM'+1)^{\frac{1}{2}}\\&\qquad\times d_{M'-mM}(\theta_m)d_{M'M}(\theta_m),\end{aligned} \tag{33}$$

$$\begin{aligned}\Sigma_3=U_0^2&p(\alpha)(3\sin^2\theta_0)^{-1}\textstyle\sum_{Mm=\pm1}\exp(-\beta'E_{Mm})\\&\times\textstyle\sum_{M'M''}[(S+mM''+2)(S+mM''+1)\\&\times(S-mM'')(S-mM''-1)]^{\frac{1}{2}}d_{MM'}(m\Omega)\\&\times d_{M''M}(\theta_m)d_{M''+2MM'}(\theta_{-m})\\&\qquad\times(E_{M'-m}-E_{Mm})^{-1},\end{aligned} \tag{34}$$

$$p(\alpha)=2\alpha_z^2-\alpha_x^2-\alpha_y^2+4\alpha_x\alpha_y-2\alpha_z\alpha_x-2\alpha_y\alpha_z, \tag{35}$$

$$\sin^2\theta_0=1-\tfrac{1}{3}(\alpha_x+\alpha_y+\alpha_z)^2, \tag{36}$$

and from Eq. (10)

$$\begin{aligned}E_{Mm}=M[&(2\beta H)^2+U_0^2+4\times3^{-\frac{1}{2}}m\beta HU_0\\&\times(\alpha_x+\alpha_y+\alpha_z)]^{\frac{1}{2}}.\end{aligned} \tag{37}$$

Equations (3), (4), (21), (22), (25), and (33)–(37), and the formulas for $d_{MM'}$ given by Edmonds[6] are sufficient to calculate the magnetostrictive parameters.

The magnetostriction calculated here in the "weak exchange" approximation is correct to all orders in $\alpha\lambda/2\beta H$. The perturbation approximations introduced relative errors of orders $2\beta H/E_t$, $\alpha\lambda/E_t$, and $(\alpha\lambda)^2/E_tkT$. The thermal populations of all $2(2S+1)$ states of the ground multiplet were taken into account. This is to be compared with the earlier "strong exchange" approximation[1] which caused errors of order $(\alpha\lambda/2\beta H)^2$, $(2\beta H/E_t)^2$, $\alpha\lambda/E_t$, and $(\alpha\lambda)^2/E_tkT$, and neglected all thermal populations except those of the two lowest states with $M_s=-S$. Either result applies only if $|\alpha\lambda|\ll E_t$ and the choice between the two approximations hinges on whether $2\beta H$ is smaller or greater than $(\alpha\lambda E_t)^{\frac{1}{2}}$.

III. COMPARISON WITH EXPERIMENT

We may apply the formulas of the previous section to the case of $Co_{0.245}Mn_{0.747}Fe_{1.99}O_4$ (chemically analyzed) for which λ_{100} and λ_{111} have been measured by the strain-gauge method.[4] The temperature range of 270°–360°K is high enough so that we may reasonably approximate λ_{100} with λ_e and λ_{111} with λ_s. The experimental error is 5% at room temperature and rises to 10% at the highest and lowest temperature used.

The measurements were made in a (111) plane instead of the (100) plane more appropriate to this calculation. However, our previous experience[1] indicates that the distinction is not very important at the temperatures under consideration. In view of the many other approximations which were made, the large amount of additional computation which would be required to correct this deficiency is not justified.

For numerical values we take the following: $U_0=132$ cm^{-1} and $\beta H=87$ cm^{-1} from the analysis of magnetocrystalline anisotropy,[3] and $N=0.245\times1.35\times10^{22}$ cm^{-3}.

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[6] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957), Chap. 4.

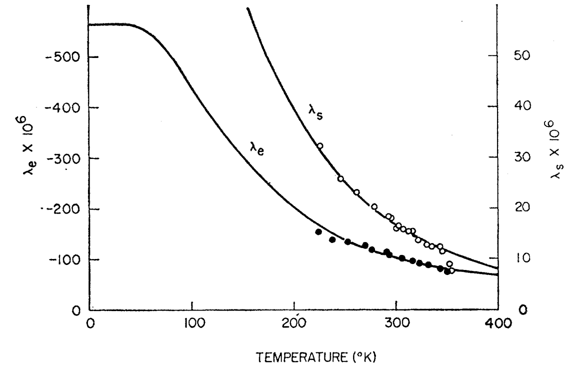

FIG. 2. Magnetostriction vs temperature for $Co_{0.247}Mn_{0.747}Fe_{1.99}O_4$. Each theoretical curve was fitted to experimental data[4] by adjusting one parameter. The quantities λ_e and λ_s are equal, approximately, to the conventional magnetostriction parameters λ_{100} and λ_{111}, respectively.

Of course an error is incurred in treating H as a constant. One may expect the temperature variation of H to resemble that of the spontaneous magnetization M of $MnFe_2O_4$. Since $M(300°K)/M(0°K)=0.67$,[7] we expect H to vary considerably over the temperature range of the experiment. Although this circumstance may have an appreciable effect on the temperature dependence of magnetostriction, the complexity of the magnetostriction formulas and the existence of other errors do not make a more precise analysis worthwhile. For the elastic constants we assume the room-temperature values of magnetite[8] ($C_{11}-C_{12}=1.67\times10^{12}$ erg cm^{-3}, $C_{44}=0.97\times10^{12}$ erg cm^{-3}) for lack of more appropriate values.

Using the numerical values given above, the parameters λ_e and λ_s are completely determined except for the constants of proportionality V_e/E_t and V_s/E_t, respectively. Adjusting these constants to obtain the best fit to Pearson's data, we obtain the results shown in Fig. 2. The numerical values are $V_e/E_t=6.32$ and $V_s/E_t=-4.36$. In this comparison, no correction was made for the magnetostrictive effects of Fe and Mn ions. An empirical correction would be ambiguous because of the inconsistency of published[9] values of λ_{100}, λ_{111}, and polycrystalline magnetostriction for $MnFe_2O_4$. At the present time we cannot say how important this correction is.

It should be remarked that the agreement for temperature dependence of magnetostriction is fairly specific. Phenomenological theories[10] of magnetostriction always predict the *same* temperature dependence for λ_{100} as for λ_{111}. However, experiment shows them to be different and a similar difference appears in our calculated results as well (at room temperature the logarithmic slope of λ_{111} is 50% steeper than that of λ_{100}). The reason for this is that the phenomenological theories consider only spin degrees of freedom, while orbital as well as spin degrees are important in the compound considered here.

Concerning the numerical values of V_e, V_s, and E_t, we may say that the most important difference between the hosts Fe_3O_4 and $MnFe_2O_4$ in so far as crystal-field effects are concerned is that Fe_3O_4 has the inverse spinel structure and $MnFe_2O_4$ has an 80% normal structure.[11] Since the lattice parameters[11] are quite similar (Fe_3O_4: $a=8.39$ A, $u=0.379$; $MnFe_2O_4$: $a=8.50$ A, $u=0.3846$) the oxygen positions scarcely differ. Therefore the parameters V_e and V_s which are governed predominantly by the nearest oxygen neighbors are expected to be nearly the same in both hosts. On the other hand, the value of E_t is expected to be sensitive to the cation distribution because it is much smaller than the cubic splitting. In fact, point-charge calculations of Tsuya[12] indicate that the trigonal potential of the nearest B-site cations is quite appreciable. Therefore, it is reasonable to assume that V_e and V_s are the same for all ferrite hosts but that E_t depends on the cation distribution. Using the value $V_e=4000$ cm^{-1} estimated from Kanamori's analysis[13] of tetragonal distortion in CoO, we get from the above ratio $E_t=633$ cm^{-1} for $Co_xMn_{1-x}Fe_2O_4$. Substituting this value into the above ratio for V_s/E_t, we have $V_s=-2800$ cm^{-1}. This value of V_s is consistent with the value of -2500 cm^{-1} deduced[1] from the room temperature magnetostriction of $Co_{0.8}Fe_{2.2}O_4$ (it was assumed that this wholly inverse spinel had the magnetite value of E_t).

We have recapitulated in Table I the numerical values of crystal-field parameters for the Co^{2+} ion in magnetite and manganese ferrite. This table requires some comments. All of the quantities except V_e were determined by analyzing anisotropy and magnetostriction of cobalt-iron ferrite and cobalt-manganese ferrite. The value of V_e was estimated from the tetragonal distortion of CoO, using Kanamori's[13] theoretical analysis. The values of $\alpha\lambda$ and V_e were assumed to be equal in the two hosts. The value of V_s for the Fe_3O_4

TABLE I. Crystal-field parameters (in cm^{-1}) of Co^{2+} substitutions in Fe_3O_4 and $MnFe_2O_4$.

Host crystal	Fe_3O_4	$Co_{0.25}Mn_{0.75}Fe_2O_4$ and $MnFe_2O_4$
$\alpha\lambda$	-132	-132
βH	320	87
E_t	1600	630
V_e	4000	4000
V_s	-2500	-2800

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[7] J. Smit and H. P. J. Wijn, *Ferrites* (John Wiley & Sons, Inc., New York, 1959), Chap. VIII, p. 156.

[8] M. S. Doraiswami, Proc. Indian Acad. Sci. **A26**, 413 (1947).

[9] *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957), pp. 5–223.

[10] A recent reference is C. Kittel and J. H. Van Vleck. Phys. Rev. **118**, 1231 (1960).

[11] Reference 7, Chap. VIII, p. 144.

[12] N. Tsuya, Sci. Repts. Research Insts. Tohoku Univ. **Ser. B8**, 161 (1957).

[13] J. Kanamori, Progr. Theoret. Phys. (Kyoto) **17**, 177, 197 (1957).

host was based on only the room temperature value of λ_{111} in $Co_{0.8}Fe_{2.2}O_4$ because the crystal-field calculation was not consistent with the experimental data available for small cobalt concentrations.[1] Finally, it should be remarked that the values of E_t, V_e, and V_s of both hosts may be raised or lowered by a common factor (say 40%) without impairing seriously agreement with experiment. The main reason for this is that the value of V_e is not fixed well by the tetragonal distortion of CoO because of some uncertainty in the wave function (Kanamori's factor $a^2+c^2-2b^2$) and because of the lack of assurance that V_e should be the same in CoO as in cobalt-substituted ferrites.

Further work is suggested by the observation that anisotropy and magnetostriction of cobalt-substituted magnetite and cobalt-substituted manganese ferrite are consistent with the orbital doublet model of the Co^{2+} ion. It would be worthwhile to carry out further experiments at low temperatures where the highly specific effects of the cobalt ion would be more striking. At absolute zero one should expect nearly discontinuous curves of torque versus angle[14] and radically nonsinusoidal strain-vs-angle curves which are calculable from our work. The manganese ferrite host is perhaps the better choice for such experiments because the agreement at higher temperatures is better and because it has no structural complications such as the orthorhombic transition[15] occurring at 120°K in magnetite.[16]

The manganese-ferrite host has the disadvantage of a partially inverse (20%) structure, which means that there is a largely disordered distribution of divalent and trivalent cations on both octahedral and tetrahedral sites. This means that some unsymmetric random crystal field may act on the cobalt ion and complicate its magnetic properties. In magnetite there is also a mixture of divalent and trivalent iron on octahedral sites. This distribution, however, becomes ordered[15] in the orthorhombic phase. If the crystal field due to the ordering has an appreciable effect on the state of the cobalt ion, then low temperature studies of cobalt-substituted magnetite would provide valuable information about magnetite itself as well as about the specific effects of the cobalt ion.

ACKNOWLEDGMENTS

The author is very grateful to R. F. Pearson and P. J. Harbour for access to their results before publication.

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PHYSICAL REVIEW VOLUME 122, NUMBER 5 JUNE 1, 1961

Behavior of Hot Electrons in Microwave Fields

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(Received December 23, 1960)

A strong external electric field in a semiconductor produces hot electrons. In the present paper, we investigate theoretically the currents produced by such electrons in a microwave field. We discuss two special cases: Case A deals with a strong steady electric field on which a weak microwave field of frequency ω is superimposed. It is found that in addition to a steady current there is an alternating current of frequency ω which leads the microwave field by a phase given by Eq. (30). The phase difference is negligible at low frequency, but becomes appreciable at frequencies $\omega\approx(1/\tau_0)(1/100)$, at liquid-nitrogen temperature. Here τ_0 is the electron-phonon relaxation time of thermal electrons. (Interaction with acoustic modes only is considered.) In case B, we consider the effect of a strong microwave field by itself. Here the current has a strong component of frequency ω and a weaker component of frequency 3ω. We find phases similar to those in case A. Results for case B are valid if $1/\tau_0>\omega>(1/\tau_0)(1/100)$ at liquid-nitrogen temperature.

1. INTRODUCTION

THE purpose of the present paper is to investigate theoretically the currents introduced by an alternating field in a nonpolar semiconductor when the current carriers have average energy per particle appreciably larger than that of the lattice.

The idea of hot carriers was first introduced by Fröhlich[1] in connection with the theory of dielectric breakdown. In the presence of an external electric field F, the free electrons (or holes) in a semiconductor continuously gain energy from the field. In a steady state, they must lose it to the lattice at the same average rate as they gain it. Since the rate of loss of

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