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Theoretical Methods in the Magnetoelectric Effect. I. Formal Treatment*

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We consider a two-sublattice model of an antiferromagnet lacking inversion symmetry and possessing interaction between the magnetic atoms of the same and different sublattices, i.e., nearest- and next-nearest-neighbor coupling. Correlation functions are derived by the Green's-function method, which is linearized by the random-phase and Callen's decoupling approximation. Formal expressions for the parallel and perpendicular magnetic and magnetoelectric susceptibilities are then obtained. Comparison of these results with those gained in the molecular-field approximations elucidates the shortcomings of the latter method. The theory is applied to Cr_2O_3 with the simplification that this crystal is regarded as having two cations in the unit cell instead of (as in reality) four.

I. INTRODUCTION

In this work, we approach the problem of the magnetoelectric (ME) effect by the Green's-function method, derive general equations for the experimental quantities (susceptibilities), and compare the results obtained in various approximations of the Green's-function theory with each other. We also make comparison with the results of the molecular-field theory and some phenomenological Hamiltonians used previously by different authors.

The advantage of the Green's-function approach, first applied to magnetic problems by Tyablikov,[1] is the general manner in which it lends itself to approximative treatments. It also treats the whole temperature range from $T=0$ to $T\to\infty$, coinciding with spin-wave theory in the lower limit and with classical methods in the upper. For practical use, a decoupling or linearization procedure must be introduced in the equations at some stage; this may be the random-phase approximation (RPA) or the Callen decoupling approximation (CD).[2,3] For antiferromagnetics the same methods have been applied by Lee and Liu.[4]

The ME effect is one of the various manifestations of the couplings, in material media, between electrical and magnetic modes; as such, it enters our investigation. (Other manifestations of the same coupling, e.g., ferroelectric-ferromagnets, polaritons, and magnon sidebands in optical absorption, will be taken up at some later stage.) The possibility of the effect was envisaged by Landau and Lifshitz.[5] Its existence in Cr_2O_3 was demonstrated theoretically by Dzayloshinski[6] and shown experimentally by Astrov.[7] In antiferromagnetic Cr_2O_3, the product of time inversion and space inversion is a symmetry element, but each of them separately is not. This type of symmetry makes possible the ME effect.

The microscopic foundation of the ME rests on some rather high-order terms in perturbation theory, with the crystalline field, the spin-orbit coupling, anisotropic exchange, and Zeeman splittings regarded as perturbations. Consequently, a number of possible combinations of the perturbations have been suggested as explanation for the effect. Effects residing on one ion[8] or on a pair of ions[9] have been suggested. In the former category belongs also the suggestion of Alexander and Shtrikman[10] based on the change in the g factor due to the external applied field. The recent experimental work of Hornreich and Shtrikman[11] single out the g factor as responsible for the parallel ME susceptibility ($\chi_{\parallel}^{ME}$) near the absolute zero; at higher temperatures the two-ion (infra-sublattice) exchange coupling is important. The perpendicular ME susceptibility ($\chi_{\perp}^{ME}$) is dominated by the single-ion term advocated by Rado.[8] It should be emphasized, however, that the assignment in Ref. 11 of the causes of the ME effect is based on a semiempirical variant of the molecular-field theory. The object of the present work is, partly, to derive the relation of the molecular-field theory to the more rigorous Green's-function apparatus and to indicate what microscopic mechanisms are favored by the experimental results when interpreted through the Green's-function method.

The first part of this paper contains formal derivations of the formulas, culminating in a set of nonlinear self-consistent integral equations for the magnetization of the sublattices. It is therefore rather tedious to read, to our regret. The second part, containing the outcome of computations and comparison with experiment, should therefore be more interesting.

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[5] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Addison-Wesley Publishing Co., Reading, Mass., 1960), p. 119.

[6] I. E. Dzyaloshinskii, Zh. Eksperim. i Teor. Fiz. **37**, 881 (1959) [English transl.: Soviet Phys.—JETP **10**, 628 (1960)].

[7] D. N. Astrov, Zh. Eksperim. i Teor. Fiz. 38, 984 (1960) [English transl.: Soviet Phys.—JETP **11**, 708 (1960)].

[8] G. T. Rado, Phys. Rev. **128**, 2546 (1962).

[9] M. Date, J. Kanamori, and M. Tachiki, J. Phys. Soc. Japan **16**, 2589 (1961).

[10] S. Alexander and S. Shtrikman, Solid State Commun. **4**, 115 (1966).

[11] R. Hornreich and S. Shtrikman, Phys. Rev. **161**, 506 (1967).

While the scope of the paper is rather general, we are mainly interested, at this stage, in Cr_2O_3. There are four cations per unit cell. Our calculations for four inequivalent sublattices would have been extremely difficult. We have therefore retained the formalism for two sublattices. However, distances between a cation on one sublattice and different cations on another sublattice are not the same now. Therefore, we shall use the concept of "coordination polyhedron," meaning the polyhedron of cations of a sublattice around a cation. In the calculation, we employ mean values of the distances.

Another remark concerns terminology. We have so written our Hamiltonian that the strengths of all physical interactions are expressible in terms of dimensionless parameters a (e.g., a^g, a^{LS}, a^D, etc.). In Sec. IV, we make comparison with the Hornreich-Shtrikman work[11] and, therefore, we switch over to their terminology. We regret the need for this change in terminology.

One conclusion arising from the comparison should be stated here. It follows from our results that the susceptibilities are not the same functions of the moments of spin operators in different theories. The optimism concerning the molecular-field approximation is probably less justified than deemed by the authors of Ref. 11.

II. HAMILTONIAN

Below the transition temperature T_N, we write the Hamiltonian for the two-sublattice antiferromagnet of unit volume in the form

$$
\begin{aligned}
H={}&\underbrace{-\mu\sum_j \mathbf{H}\cdot\mathbf{S}_j}_{\text{(i)}}+\underbrace{\mu^2/J_d(a_{\parallel}{}^gH_zE_z+a_{\perp}{}^gH_xE_x+a_{\perp}{}^gH_yE_y)\sum_j \epsilon_{(j)}S_j{}^z}_{\text{(ii)}}\\
&\underbrace{+\mu a_{\parallel}{}^{LS}E_z\sum_j \epsilon_{(j)}(S_j{}^z)^2+\mu a_{\perp}{}^{LS}E_x\sum_j \epsilon_{(j)}\tfrac{1}{2}(S_j{}^xS_j{}^z+S_j{}^zS_j{}^x)}_{\text{(iii)}}\\
&\underbrace{+\tfrac{1}{2}\mu E_z\sum_{jl}\tfrac{1}{2}(\epsilon_{(j)}+\epsilon_{(l)})a_{\parallel}{}^J(j,l)\mathbf{S}_j\cdot\mathbf{S}_l+\tfrac{1}{2}\mu E_x\sum_{jl}\tfrac{1}{2}(\epsilon_{(j)}+\epsilon_{(l)})a_{\perp}{}^J(j,l)\mathbf{S}_j\cdot\mathbf{S}_l}_{\text{(iv)}}\\
&\underbrace{+\mu E_x\sum_{jl}\tfrac{1}{2}(\epsilon_{(j)}-\epsilon_{(l)})\mathbf{a}_{jl}{}^D(\mathbf{S}_j\times\mathbf{S}_l)}_{\text{(v)}}\underbrace{+\tfrac{1}{2}\sum_{jl}J_{jl}\mathbf{S}_j\cdot\mathbf{S}_l}_{\text{(vi)}}\underbrace{-\tfrac{1}{2}I_a\sum_j(S_j{}^z)^2}_{\text{(vii)}}\underbrace{-\tfrac{1}{2}\chi_{VV}H^2}_{\text{(viii)}}.
\end{aligned}
$$

The terms have the following meaning:

(i) Zeeman term, (ii) g-factor term.[10] $a_{\parallel}{}^g$, $a_{\perp}{}^g$ represent the change in the g factor due to the electric field E parallel and perpendicular to the magnetic axis z of the antiferromagnet. All a's are dimensionless. (iii) Single-ion term,[8] arising from spin-orbit coupling, (iv) two-ion term[9] due to the exchange integral J_{lj}

$$a_{\parallel}{}^J(j,l)=a_{\parallel}{}^J(l,j)=a_{\parallel}{}^J(|j-l|).$$

(v) Dzyaloshinskii term,[6] due to vectorial interaction between angular momenta on different ions.[12] This term appears only in the perpendicular case: $\mathbf{a}_{jl}{}^D=\mathbf{a}_{lj}{}^D=\mathbf{a}^D(|j-l|)$. (vi) Isotropic exchange interaction, (vii) anisotropic term, $I_a>0$, (viii) constant Van Vleck term.[13]

Further, we have used $\mu=\mu_Bg$, where μ_B is the Bohr magneton; $\epsilon_{(j)}=\pm1$ for the upper and lower sublattices, respectively; j is the index of atom; (j) is the index of the sublattice of the atom j; $\mathbf{S}_j$ is the spin operator on atom j; $J_d=\sum_l J_{jl}$, where the l summation is over cations in the nearest coordination polyhedron, all having different spins from j. For the purposes of future reference, we quote the relation between our microscopic coefficients and the coefficients of Hornreich and Shtrikman.[11] Relations between quantities not yet introduced are also shown for the sake of completeness:

$a_{\parallel}{}^g=J_dc_{\parallel}/\mu,\quad a_{\perp}{}^g=J_dc_{\perp}/\mu,$

$a_{\parallel}{}^{LS}=a_{\parallel},\quad a_{\perp}{}^{LS}=a_{\perp},$

$a_{\parallel}{}^J=\frac{1}{2}N\mu b_{\parallel}$ (N is the number of cations in a sublattice per unit volume, i.e., twice the reciprocal of the volume of a unit cell.)

$a_{jl}{}^D=J_{jl}b_{\perp},$

$J_d=\frac{1}{2}N\mu^2A,\quad J_s=\frac{1}{2}N\mu^2\Gamma,$

$M_0=\frac{1}{2}N\mu\bar{S},\quad M_z=N\mu\bar{m}.$

III. THERMODYNAMICS OF OBSERVABLES

The thermodynamic quantities are the partition function:

$$Z=\mathrm{Tr}\colon e^{-\beta\mathcal{H}}\quad(\beta=1/kT,\ T\text{ is temperature}),$$

the free energy:

$$F=-\beta^{-1}\ln Z,$$

the magnetic moment per unit volume:

$$\mathbf{M}=-\frac{\partial F}{\partial\mathbf{H}}=\frac{1}{\beta}\frac{1}{Z}\frac{\partial Z}{\partial\mathbf{H}}$$
$$=0,$$

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[12] E. F. Bertaut, J. Phys. Radium 23, 460 (1962).

[13] S. D. Silberstein and I. S. Jacobs, Phys. Rev. Letters 12, 670 (1964).

in an antiferromagnet at $H=E=0$, the magnetic susceptibilities:

$$\chi_{\parallel}{}^{M}=-\frac{\partial^2F}{\partial H_z{}^2}=\frac{1}{\beta}\left[\frac{1}{Z}\frac{\partial^2Z}{\partial H_z{}^2}-\left(\frac{1}{Z}\frac{\partial Z}{\partial H_z}\right)^2\right]$$

$$\simeq\frac{1}{\beta}\left(\frac{1}{Z}\frac{\partial^2Z}{\partial H_z{}^2}\right)_{H=E=0},$$

$$\chi_{\perp}{}^{M}=-\frac{\partial^2F}{\partial H_x{}^2}=\frac{1}{\beta}\left[\frac{1}{Z}\frac{\partial^2Z}{\partial H_x{}^2}-\left(\frac{1}{Z}\frac{\partial Z}{\partial H_x}\right)^2\right]$$

$$\simeq\frac{1}{\beta}\left(\frac{1}{Z}\frac{\partial^2Z}{\partial H_x{}^2}\right)_{H=E=0}.$$

For small magnetic and electric fields the susceptibilities are insensitive to the fields. Therefore, we consider all derivatives of Z in the limit of $H=E=0$.

The magnetoelectric susceptibilities are

$$\chi_{\parallel}{}^{\mathrm{ME}}=-\frac{\partial^2F}{\partial H_z\partial E_z}=\frac{1}{\beta}\left[\frac{1}{Z}\frac{\partial^2Z}{\partial H_z\partial E_z}-\left(\frac{1}{Z}\frac{\partial Z}{\partial H_z}\right)\left(\frac{1}{Z}\frac{\partial E}{\partial E_z}\right)\right]$$

$$\simeq\frac{1}{\beta}\left(\frac{1}{Z}\frac{\partial^2Z}{\partial H_z\partial E_z}\right)_{H=E=0},$$

$$\chi_{\perp}{}^{\mathrm{ME}}=-\frac{\partial^2F}{\partial H_x\partial E_x}=\frac{1}{\beta}\left[\frac{1}{Z}\frac{\partial^2Z}{\partial H_x\partial E_x}-\left(\frac{1}{Z}\frac{\partial Z}{\partial H_x}\right)\left(\frac{1}{Z}\frac{\partial Z}{\partial E_x}\right)\right]$$

$$\simeq\frac{1}{\beta}\left(\frac{1}{Z}\frac{\partial^2Z}{\partial H_x\partial E_x}\right)_{H=E=0}.$$

There are no other susceptibilities, by symmetry. The magnetic moments may now be written as

$$M_z=\chi_{\parallel}{}^{M}H_z+\chi_{\parallel}{}^{\mathrm{ME}}E_z,$$
$$M_x=\chi_{\perp}{}^{M}H_x+\chi_{\perp}{}^{\mathrm{ME}}E_x.$$

Further, it may be shown that

$$\frac{\partial Z}{\partial H_\alpha}=-\beta\ \mathrm{Tr}\colon\frac{\partial\mathcal{H}}{\partial H_\alpha}e^{-\beta\mathcal{H}},$$

$$\frac{\partial^2Z}{\partial H_\alpha\partial E_\alpha}=-\beta\ \mathrm{Tr}\colon\left\{\frac{\partial^2\mathcal{H}}{\partial H_\alpha\partial E_\alpha}\right.$$

$$+\beta\frac{\partial\mathcal{H}}{\partial E_\alpha}\frac{\partial\mathcal{H}}{\partial H_\alpha}-\frac{1}{2!}\beta^2\frac{\partial\mathcal{H}}{\partial E_\alpha}\left[\mathcal{H},\frac{\partial\mathcal{H}}{\partial H_\alpha}\right]$$

$$\left.+\frac{\beta^3}{3!}\frac{\partial\mathcal{H}}{\partial E_\alpha}\left[\mathcal{H},\left[\mathcal{H},\frac{\partial\mathcal{H}}{\partial H_\alpha}\right]\right]+\cdots\right\}e^{-\beta\mathcal{H}}.$$

Note now that from our Hamiltonian

$$(\partial\mathcal{H}/\partial H_z)_{H=E=0}=-\mu\sum_j S_j{}^z=-\mu S^z,$$

$$(\partial\mathcal{H}/\partial H_x)_{H=E=0}=-\mu S^x,$$

$$(\mathcal{H})_{H=E=0}=\tfrac{1}{2}\sum_{jl}J_{jl}\mathbf{S}_j\cdot\mathbf{S}_l-\tfrac{1}{2}I_a\sum_j(S_j{}^z)^2.$$

Therefore, $\partial\mathcal{H}/\partial H_z$ commutes with the zero-field Hamiltonian, yielding ultimately for the parallel susceptibilities

$$\chi_{\parallel}{}^{M}=\beta\left\langle\left(\frac{\partial\mathcal{H}}{\partial H_z}\right)^2\right\rangle_0,$$

$$\chi_{\parallel}{}^{\mathrm{ME}}=-\left\langle\frac{\partial^2\mathcal{H}}{\partial E_z\partial H_z}\right\rangle_0+\beta\left\langle\frac{\partial\mathcal{H}}{\partial E_z}\frac{\partial\mathcal{H}}{\partial H_z}\right\rangle_0,$$

where

$$\langle R\rangle_0\equiv(\mathrm{Tr}\colon Re^{-\beta\mathcal{H}})_{H=E=0}/(\mathrm{Tr}\colon e^{-\beta\mathcal{H}})_{H=E=0}.$$

In the formulas for the perpendicular susceptibilities, we encounter commutators like $[\mathcal{H},\partial\mathcal{H}/\partial H_x]$, which do not vanish owing to the presence of the anisotropy term (vii) in the Hamiltonian. However, in general, $I_a/J_d\ll1$ and the noncommutativity may be expected to have little effect on the susceptibilities.[14]

With the neglect of the commutators, we find then that

$$\chi_{\perp}{}^{M}=\beta\left\langle\left(\frac{\partial\mathcal{H}}{\partial H_x}\right)^2\right\rangle_0,$$

$$\chi_{\perp}{}^{\mathrm{ME}}=-\left\langle\frac{\partial^2\mathcal{H}}{\partial E_x\partial H_x}\right\rangle_0+\beta\left\langle\frac{\partial\mathcal{H}}{\partial E_x}\frac{\partial\mathcal{H}}{\partial H_x}\right\rangle_0.$$

Returning to the Hamiltonian, we get

$$\chi_{\parallel}{}^{M}\ =\beta\mu^2\sum_{jl}\langle S_j{}^zS_l{}^z\rangle_0,$$

$$\chi_{\perp}{}^{M}\ =\beta\mu^2\sum_{jl}\langle S_j{}^xS_l{}^x\rangle_0,$$

$$\chi_{\parallel}{}^{\mathrm{ME}}=-(\mu^2a_{\parallel}{}^{g}/J_d)\sum_j\epsilon_{(j)}\langle S_j{}^z\rangle_0$$

$$-\beta\mu^2a_{\parallel}{}^{LS}\sum_{jk}\epsilon_{(j)}\langle S_k{}^z(S_j{}^z)^2\rangle_0$$

$$+\tfrac{1}{2}\sum_k\sum_{jl:s}{}'\,\epsilon_{(j)}a_{\parallel}{}^{J}(jl)\langle S_k{}^z(\mathbf{S}_j\cdot\mathbf{S}_l)\rangle_0,$$

where $jl\colon s$ denotes the restriction that jl are taken to be on the same sublattice, and we have

$$\chi_{\perp}{}^{\mathrm{ME}}=-(\mu^2a_{\perp}{}^{g}/J_d)\sum_j\epsilon_{(j)}\langle S_j{}^z\rangle_0$$

$$-\tfrac{1}{2}\beta\mu^2a_{\perp}{}^{LS}\sum_{jk}\epsilon_{(j)}\langle S_k{}^x(S_j{}^xS_j{}^z+S_j{}^zS_j{}^x)\rangle_0$$

$$+\sum_{jkl}\tfrac{1}{2}(\epsilon_{(j)}-\epsilon_{(l)})a_{jl}{}^{D(y)}\langle S_k{}^x(S_j{}^zS_l{}^x-S_j{}^xS_l{}^z)\rangle_0.$$

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[14] S. Foner, Phys. Rev. **130**, 183 (1963).

Terms involving expectation values of odd powers of S^x have been equated to zero. We see that the parallel magnetoelectric susceptibility contains the g-factor term,[10] the single-ion term, and the double-ion term, whereas in the perpendicular susceptibility instead of the last term we have the Dzyaloshinskii term.

We shall now continue the "processing" of the perpendicular susceptibilities, first by the algebra of spin operators and then by applying an approximating, linearization procedure. The parallel susceptibilities will be simplified later, using a different method. From

$$S_j^x S_l^x = \tfrac{1}{4}(S_j^+ + S_j^-)(S_l^+ + S_l^-),$$
$$S_j^+ S_l^- - S_l^- S_j^+ = 2\delta_{jl} S_j^z,$$

we derive that

$$\langle S_j^x S_l^x\rangle_0 = \tfrac{1}{4}\langle S_j^+ S_l^- + S_j^- S_l^+\rangle_0$$
$$= \tfrac{1}{2}\langle S_j^- S_l^+\rangle_0 + \tfrac{1}{2}\langle S_j^z\rangle_0 \delta_{jl}.$$

The last term when summed over jl is zero in an antiferromagnet. Therefore, we have

$$\chi_\perp^M = \tfrac{1}{2}\beta\mu^2 \sum_{jl} \langle S_l^- S_j^+\rangle_0 .$$

By similar manipulations and the introduction of $\bar{S}$, the positive sublattice magnetization, we can rewrite $\chi_\perp^{\mathrm{ME}}$ as

$$\chi_\perp^{\mathrm{ME}} = -N\mu^2 a_\perp^g \bar{S}/J_d$$
$$-\tfrac{1}{4}\beta\mu^2\Big[a_\perp^{LS} \sum_{jm} \epsilon_{(j)}\, \mathrm{Re}\langle S_m^-(S_j^+ S_j^z + S_j^z S_j^+)\rangle_0$$
$$+\sum_{jlm} \tfrac{1}{2}(\epsilon_{(j)} - \epsilon_{(l)}) a_{jl}^{D(y)}\, \mathrm{Re}\langle S_m^-(S_j^z S_l^+ - S_l^z S_j^+)\rangle_0\Big],$$

where Re denotes the "real part of."

We next reduce the expectation values of a product of three operators to those involving at most two operators. This is accomplished by applying the Callen approximation,[2,3] originally designed for the linearization of the Green's function, to the thermal expectation values. We shall justify this in a later section.

The procedure is to put

$$\langle S_m^-(S_j^+ S_j^z + S_j^z S_j^+)\rangle_0$$
$$= 2\langle S_j^z\rangle(1 - \alpha\tfrac{1}{2}\langle S_j^- S_j^+ + S_j^+ S_j^-\rangle_0)\langle S_m^- S_j^+\rangle_0$$
$$= 2\epsilon_{(j)}\bar{S} B_0 \langle S_m^- S_j^+\rangle_0 ,$$

defining B_0 as $1 - \alpha\frac{1}{2}\langle S_j^- S_j^+ + S_j^+ S_j^-\rangle_0$, which is independent of j. α is 0 in the RPA, and $(2S^2)^{-1}$ in Callen's approximation. Further, we have

$$\langle S_m^-(S_j^z S_l^+ - S_l^z S_j^+)\rangle_0$$
$$= \epsilon_{(j)}\bar{S}(1 + \alpha\epsilon_{(j)}\epsilon_{(l)}\langle S_l^- S_j^+\rangle_0)\langle S_m^- S_l^+\rangle_0$$
$$- \epsilon_{(l)}\bar{S}(1 + \alpha\epsilon_{(j)}\epsilon_{(l)}\langle S_j^- S_l^+\rangle_0)\langle S_m^- S_j^+\rangle_0 .$$

Then, we have

$$\chi_\perp^{\mathrm{ME}} = -(N\mu^2/J_d) a_\perp^g \bar{S} - \tfrac{1}{2}\beta\mu^2\Big[a_\perp^{LS} B_0 \bar{S} \sum_{jm} \langle S_m^- S_j^+\rangle_0$$
$$+\tfrac{1}{4}\bar{S} \sum_{jlm} a_{jl}^{D(y)}(\epsilon_{(j)} - \epsilon_{(l)})(1 + \alpha\epsilon_{(j)}\epsilon_{(l)}\langle S_l^- S_j^+\rangle)$$
$$\times(\epsilon_{(j)}\langle S_m^- S_l^+\rangle - \epsilon_{(l)}\langle S_m^- S_j^+\rangle)\Big].$$

Because of the factor $(\epsilon_{(j)} - \epsilon_{(l)})$ in the last sum we can rewrite the brackets following as

$$1 - \alpha\langle S_l^- S_j^+\rangle \equiv B_d ,$$

since the l and j must belong to different sublattices.

We obtain, therefore, in terms of the magnetic susceptibility and $a_\perp^D = \sum a_{jl}^{D(y)}$ (lj on different sublattices),

$$\chi_\perp^{\mathrm{ME}} = -N\mu^2 J_d^{-1} a_\perp^g \bar{S} - \chi_\perp^M \bar{S}(a_\perp^{LS} B_0 + a_\perp^D B_d).$$

We shall return to the perpendicular susceptibilities after we have calculated, by the Green's-function method, the averages $\bar{S}$, B_0, and B_d evaluated at zero fields. Here we wish merely to note that above the Néel temperature the magnetoelectric susceptibility is zero since $\bar{S} = 0$. The same result would also follow from general thermodynamical arguments.

The formulas for the parallel susceptibilities require the calculation of thermal averages of the sort $\langle S_j^z S_l^z\rangle$ and $\langle S_m^z (S_j^z)^2\rangle$. The first of these, so-called longitudinal correlation functions, was calculated in the Callen approximation, but only with nearest-neighbor interaction, by Lee and Liu.[4] The method turned out to be rather difficult, much more so than for the perpendicular case, and may be prohibitively involved for the third-order longitudinal correlation with next-nearest-neighbor forces. [The reason for the contrast with the perpendicular case is that there we have to calculate averages of S^x, $(S^x)^2$, etc., which are small quantities, whereas now we are concerned with deviations from the finite quantities S^z, $(S^z)^2$, etc.]

We shall therefore start with the alternative definitions, based on M_z:

$$\chi_{\parallel}^M = \partial M_z/\partial H_z, \quad \chi_{\parallel}^{\mathrm{ME}} = \partial M_z/\partial E_z ,$$

where

$$M_z = \mu \sum_j \langle S_j^z\rangle - \mu^2 J_d^{-1} a_{\parallel}^g E_z \sum_j \epsilon_{(j)} \langle S_j^z\rangle_0$$
$$= \mu \sum_j \langle S_j^z\rangle - N\mu^2 J_d^{-1} a_{\parallel}^g E_z \bar{S} ,$$

since in the second term, which is already proportional to the electric field, we can evaluate the average at zero fields; not so in the first term. Consequently, we have

$$\chi_{\parallel}^M = \mu \sum_j \frac{\partial}{\partial H_z}\langle S_j^z\rangle ,$$

$$\chi_{\parallel}^{\mathrm{ME}} = \mu \sum_j \frac{\partial}{\partial E_z}\langle S_j^z\rangle - N\mu^2 J_d^{-1} a_{\parallel}^g \bar{S} .$$

The coefficient a^g appears only in the form explicitly shown, so we can start with a Hamiltonian without the g-factor term, calculate with it the first term in $\chi_{\parallel}{}^{\mathrm{ME}}$ and add on the second term. Another additive term χ_{VV}, indicative of Van Vleck paramagnetism in Cr_2O_3 and not derivable from the spin Hamiltonian, appends a constant to $\chi_{\parallel}{}^{M}$.[15]

Using the calculations carried out in Sec. IV, we obtain the results given below.

We define $J_s \equiv$ the sum $\sum_j J_{ij}$ over next-nearest neighbors having same spin as i. Previously, we defined $J_d \equiv$ the sum $\sum_j J_{ij}$ over nearest neighbors having opposite spin to i. We further recall that

$$\begin{aligned}\alpha &= 0 \text{ in RPA}\\ &= (2S^2)^{-1} \text{ in Callen's approximation.}\end{aligned}$$

Also, we write that I_a is the anisotropy-term coupling constant in the Hamiltonian; $B_0 = 1 - \alpha\langle S_j^- S_j^+\rangle_0$; $B_d = 1 - \alpha\langle S_i^- S_j^+\rangle_0$, where j is on a different sublattice from i; $B_s = 1 - \alpha\langle S_i^- S_j^+\rangle_0$, where j is on the same sublattice as i; $N(x) = (e^{\beta x} - 1)^{-1}$. Let Z_1 be the number of cations on the first coordination polyhedron round a cation, and Z_2 the number on the next coordination polyhedron. Let the mean distances in the polyhedra be a_1 and a_2.

Define the sums over the first and second polyhedra:

$$\gamma_{d\mathbf{k}} = (1/Z_1)\sum_{\mathbf{j}} e^{i\mathbf{k}\cdot(\mathbf{i}-\mathbf{j})a_1},$$

$$\gamma_{s\mathbf{k}} = (1/Z_2)\sum_{\mathbf{i}} e^{i\mathbf{k}\cdot(\mathbf{i}-\mathbf{j})a_2}.$$

We introduce the energies (in terms of the as yet undefined $\bar{S}$)

$$w_{\mathbf{k}} = \bar{S}[(J_dB_d + I_aB_0 - J_sB_s(1-\gamma_{s\mathbf{k}}))^2 - (J_dB_d\gamma_{d\mathbf{k}})^2]^{1/2},$$

and define the k averages of an operator $R_{\mathbf{k}}$:

$$\langle R_{\mathbf{k}}\rangle_{\mathbf{k}} = (2/N)\sum_{\mathbf{k}} w_{\mathbf{k}}^{-1} R_{\mathbf{k}} \coth\tfrac{1}{2}\beta w_{\mathbf{k}},$$

where the sum runs over all values of $\mathbf{k}$ (N in number) in the Brillouin zone.

We now define

$$\begin{aligned}D = 1 &+ \alpha\bar{S}^2[I_a\langle 1\rangle_{\mathbf{k}} + J_s\langle\gamma_{s\mathbf{k}}(1-\gamma_{s\mathbf{k}})\rangle_{\mathbf{k}}]\\ &+ \alpha^2\bar{S}^4 J_s I_a(\langle\gamma_{s\mathbf{k}}\rangle_{\mathbf{k}}{}^2 - \langle 1\rangle_{\mathbf{k}}\langle\gamma_{s\mathbf{k}}{}^2\rangle_{\mathbf{k}}),\end{aligned}$$

$$\begin{aligned}X_0 = \bar{S}\{&(J_dB_d + I_a)[\langle 1\rangle_{\mathbf{k}} + \alpha\bar{S}^2 J_s(\langle\gamma_{s\mathbf{k}}\rangle_{\mathbf{k}}{}^2 - \langle 1\rangle_{\mathbf{k}}\langle\gamma_{s\mathbf{k}}{}^2\rangle_{\mathbf{k}})]\\ &- J_s\langle 1-\gamma_{s\mathbf{k}}\rangle_{\mathbf{k}}\}/D,\end{aligned}$$

$$\bar{S} = \tfrac{1}{2}\left((2S+1)\frac{(X_0+1)^{2S+1} + (X_0-1)^{2S+1}}{(X_0+1)^{2S+1} - (X_0-1)^{2S+1}} - X_0\right).$$

It is clear that all quantities and functionals between $w_{\mathbf{k}}$ and $\bar{S}$ are only implicitly given. An approximate or numerical evaluation is a major programmatic aim of the present work.

We define, finally,

$$A(\bar{S},\beta) = 4(2S+1)^2\frac{(X_0{}^2-1)^{2S}}{[(X_0+1)^{2S+1} - (X_0-1)^{2S+1}]^2} - 1$$

and

$$\begin{aligned}C = 1 &+ 2\alpha\bar{S}^2\left[I_a\left\langle\frac{dN}{dw_{\mathbf{k}}}\right\rangle_{\mathbf{k}} + J_s\left\langle\gamma_{s\mathbf{k}}(1-\gamma_{s\mathbf{k}})\frac{dN}{dw_{\mathbf{k}}}\right\rangle_{\mathbf{k}}\right]\\ &+ 4\alpha^2\bar{S}^4 I_a J_s\left[\left(\gamma_{s\mathbf{k}}\frac{dN}{dw_{\mathbf{k}}}\right)_{\mathbf{k}} - \left\langle\frac{dN}{dw_{\mathbf{k}}}\right\rangle_{\mathbf{k}}\left\langle\gamma_{s\mathbf{k}}{}^2\frac{dN}{dw_{\mathbf{k}}}\right\rangle_{\mathbf{k}}\right]\\ &+ [J_dB_d - I_a(2B_0-1)]\\ &\times\left[\left\langle\frac{dN}{dw_{\mathbf{k}}}\right\rangle_{\mathbf{k}} + 2\alpha\bar{S}^2 J_s\left(\left\langle\gamma_{s\mathbf{k}}\frac{dN}{dw_{\mathbf{k}}}\right\rangle_{\mathbf{k}}^2\right.\right.\\ &\left.\left.-\left\langle\frac{dN}{dw_{\mathbf{k}}}\right\rangle_{\mathbf{k}}\left\langle\gamma_{sk}{}^2\frac{dN}{dw_{\mathbf{k}}}\right\rangle_{\mathbf{k}}\right)\right]A(\bar{S},\beta)\\ &+ J_s(2B_s-1)\left\langle(1-\gamma_{s\mathbf{k}})\frac{dN}{dw_{\mathbf{k}}}\right\rangle_{\mathbf{k}} A(\bar{S},\beta).\end{aligned}$$

The parallel susceptibilities are now given in terms of the quantities defined above, and the coefficients in the Hamiltonian:

$$\chi_{\parallel}{}^M = \chi_{VV} + N\mu^2 A(\bar{S},\beta)\left\{\left\langle\frac{dN}{dw_{\mathbf{k}}}\right\rangle_{\mathbf{k}} + 2\alpha\bar{S}^2 J_s\left(\left\langle\gamma_{s\mathbf{k}}\frac{dN}{dw_{\mathbf{k}}}\right\rangle_{\mathbf{k}}^2 - \left\langle\frac{dN}{dw_{\mathbf{k}}}\right\rangle_{\mathbf{k}}\left\langle\gamma_{s\mathbf{k}}{}^2\frac{dN}{dw_{\mathbf{k}}}\right\rangle_{\mathbf{k}}\right)\right\}\Big/C,$$

$$\begin{aligned}\chi_{\parallel}{}^{\mathrm{ME}} = &-N\mu^2 J_d{}^{-1}a_{\parallel}{}^g\bar{S}\\ &-(\chi_{\parallel}{}^M - \chi_{VV})\bar{S}\left\{2a_{\parallel}{}^{LS}B_0 + a_{\parallel}{}^J B_s\frac{\langle(1-\gamma_{s\mathbf{k}})dN/dw_{\mathbf{k}}\rangle_{\mathbf{k}}}{\langle dN/dw_{\mathbf{k}}\rangle_{\mathbf{k}} + 2\alpha\bar{S}^2 J_s(\langle\gamma_{s\mathbf{k}}dN/dw_{\mathbf{k}}\rangle_{\mathbf{k}}{}^2 - \langle dN/dw_{\mathbf{k}}\rangle_{\mathbf{k}}\langle\gamma_{s\mathbf{k}}{}^2 dN/dw_{\mathbf{k}}\rangle_{\mathbf{k}})}\right\}.\end{aligned}$$

We note that the second term in each curly bracket is due to the next-nearest neighbors. Date *et al.*[9] and Hornreich and Shtrikman[11] stressed the importance of this term.

IV. GREEN'S-FUNCTION METHOD

We shall apply this method, with the inclusion of the Callen approximation, to the calculation of the perpendicular magnetoelectric susceptibilities for a zero-field Hamiltonian which contains next-nearest-neighbor (n.n.n.) interactions and the anisotropy term. Previ-

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[15] S. D. Silberstein and I. S. Jacobs, Phys. Rev. Letters **12**, 670 (1964).

ously χ^{ME} was calculated by Rado[8] and Hornreich and Shtrikman[11] in the molecular-field approximation. As an additional step, for the parallel susceptibilities we shall derive the magnetization as a linear function of the electric field, and *a fortiori* for zero fields. This latter result was obtained in the Callen approximation for antiferromagnets in Refs. 3 and 4, but only for nearest-neighbor (n.n.) interactions. The earlier work of Lines[16] did include next-nearest neighbors, but they were treated only in the RPA.

A. Zero Field

We have

$$\mathcal{H}_0=\tfrac{1}{2}\sum_j J_{jl}\mathbf{S}_j\cdot\mathbf{S}_l-\tfrac{1}{2}I_a\sum_j (S_j^z)^2$$

as the Hamiltonian. In the thermal averages in this section we shall dispense with the 0 subscript indicating zero fields, this being understood.

Define the retarded Green's function (G.f.)

$$\begin{aligned}G^{(a)}(S_g^+(t),e^{aS^z(0)}S_h^-(0))&\\ &\equiv[\theta(t)/i]\langle[S_g^+(t),e^{aS_h^z(t=0)}S_h^-(t=0)]\rangle\\ &\equiv\langle\langle S_g^+(t),B_h^a(t=0)\rangle\rangle.\end{aligned}$$

We introduce the spectral G.f.[17] through the equation

$$\langle\langle S_g^+(t),B_h(0)\rangle\rangle=\int e^{-iwt}\langle\langle S_g^+;\,B_h\rangle\rangle_w dw.$$

Its equation of motion is

$$\begin{aligned}\langle\langle S_g^+;\,B_h\rangle\rangle_w&\\ &=\frac{1}{2\pi}\langle[S_g^+,B_h]\rangle_{\text{equal time}}+\langle\langle[S_g^+,\mathcal{H}_0];\,B_h\rangle\rangle_w,\end{aligned}$$

which takes the explicit form

$$\begin{aligned}w\langle\langle S_g^+;\,B_h\rangle\rangle&=(2\pi)^{-1}F_h^{(a)}\delta_{g,h}\\ &\quad+\tfrac{1}{2}I_a\langle\langle(S_g^zS_g^++S_g^+S_g^z);\,B_h\rangle\rangle_w+\\ &\quad-\sum_j J_{jg}\langle\langle(S_g^+S_j^z-S_g^zS_j^+);\,B_h\rangle\rangle_w.\end{aligned}$$

The quantity $F_h^{(a)}$, defined by the above two equations, depends (apart from the parameter a entering through B_h) only on the sublattice of h, not on the atoms.

After introducing the Callen decoupling approximation,[2-4] CD, namely,

$$\begin{aligned}\langle\langle(S_g^zS_g^++S_g^+S_g^z);\,B_h\rangle\rangle_w&\\ &=2\langle S_g^z\rangle[1-\alpha\langle\tfrac{1}{2}(S_g^+S_g^-+S_g^-S_g^+)\rangle]\langle\langle S_g^+;\,B_h\rangle\rangle_w,\\ \langle\langle S_j^zS_g^+;\,B_h\rangle\rangle_w=\langle S_j^z\rangle\langle\langle S_g^+B_h\rangle\rangle_w&\\ &-\alpha\epsilon_{(j)}\epsilon_{(g)}\langle S_g^z\rangle\langle S_j^-S_g^+\rangle\langle\langle S_j^+;\,B_h\rangle\rangle_w,\end{aligned}$$

where

$$\begin{aligned}\alpha&=0\text{ in RPA}\\ &=(2S^2)^{-1}\text{ in CD},\end{aligned}$$

and as before $\epsilon_{(j)}=\pm1$ depending on the sublattice of j, we find that the equation of motion has become

$$\begin{aligned}&[w+\sum J_{jg}\langle S_j^z\rangle(1+\alpha\epsilon_{(j)}\epsilon_{(g)}\langle S_g^-S_j^+\rangle)\\ &\qquad-I_a\langle S_g^z\rangle(1-\alpha\langle\tfrac{1}{2}(S_g^+S_g^-+S_g^-S_g^+)\rangle)]\langle\langle S_g^+;\,B_h\rangle\rangle_w\\ &\quad=(2\pi)^{-1}F_h^a\delta_{g,h}+\langle S_g^z\rangle\sum_j J_{jg}(1+\alpha\epsilon_{(j)}\epsilon_{(g)}\langle S_j^-S_g^+\rangle)\\ &\qquad\qquad\times\langle\langle S_j^+;\,B_h\rangle\rangle_w.\end{aligned}$$

We shall now utilize the translational invariance of the lattice and the Hermitian properties of the spin operators to rewrite the last equation in the wave-vector **k** representation. For each **k** we get a set of two coupled equations for the quantity $G_{(g),(h)}{}^a(\mathbf{k},w)$ depending only on the sublattices of atoms g and h, and defined by

$$\begin{aligned}&\langle\langle S_g^+,B_h\rangle\rangle_w=(2/N)\sum e^{i\mathbf{k}\cdot(\mathbf{g}-\mathbf{h})}G_{(g)(h)}{}^a(\mathbf{k},w),\\ &[w+\bar{S}_{(\bar{h})}J_dB_d+\bar{S}_{(h)}J_sB_s(1-\gamma_{s\mathbf{k}})-\bar{S}_{(h)}I_aB_0]G_{(h)(h)}{}^a\\ &\qquad=(2\pi)^{-1}F_{(h)}{}^a+\bar{S}_{(h)}J_dB_d\gamma_{d\mathbf{k}}G_{(\bar{h})(h)}{}^a,\\ &[w+\bar{S}_{(h)}J_dB_d+\bar{S}_{(\bar{h})}J_sB_s(1-\gamma_{s\mathbf{k}})-\bar{S}_{(\bar{h})}I_aB_0]G_{(\bar{h})(h)}{}^a\\ &\qquad=\bar{S}_{(\bar{h})}J_dB_d\gamma_{d\mathbf{k}}G_{(h)(h)}{}^a.\end{aligned}$$

The bar on h in $(\bar{h})$ denotes the sublattice complementary to (h), and

$$\gamma_{d\mathbf{k}}=Z_1^{-1}\sum_{\mathbf{j}} e^{i\mathbf{k}\cdot(\mathbf{i}-\mathbf{j})a_1},$$

$$\gamma_{s\mathbf{k}}=Z_2^{-1}\sum_{\mathbf{j}} e^{i\mathbf{k}\cdot(\mathbf{i}-\mathbf{j})a_2},$$

where Z_1 and Z_2 are the number of cations on the first and second cation coordination polyhderon round the cation j, and a_1 and a_2 are the mean distances in the polyhedron. The summations above also go over the first and second type of cations. In a crystal with two cations per unit cell (instead of four as in Cr_2O_3) the two polyhedra consist simply of the nearest and next-nearest neighbors. In Cr_2O_3, the distance in the same polyhedra are necessarily different. We have circumvented this complication, which would have resulted in having a set of four equations instead of two, by summing over atomic indices rather than distances.[18]

J_s and J_d have been defined previously as sums of J_{ij} and j running over the nearest coordination polyhedron of the same and different magnetization as i, and

$$B_0\equiv1-\alpha\langle\tfrac{1}{2}(S_g^-S_g^++S_g^+S_g^-)\rangle,$$

$$B_d\equiv1-\alpha\langle S_g^-S_j^+\rangle,\quad g\text{ and }j\text{ on different sublattices}$$

$$B_s\equiv1+\alpha\langle S_g^-S_j^+\rangle,\quad g\text{ and }j\text{ on same sublattices.}$$

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[16] M. E. Lines, Phys. Rev. **135**, A1336 (1964).

[17] D. N. Zubarev, Usp. Fiz. Nauk **71**, 17 (1960) [English transl.: Soviet Phys.—Usp. **3**, 320 (1960)].

[18] A small adjustment in some Cr-Cr distances and in the angle between the primitive vectors yields a unit cell with one formula unit.

We shall assume that, as a consequence of the antiferromagnetic nature of the lattice, in the absence of electric and magnetic fields,

$$\bar{S}_{(h)}=-\bar{S}_{(\bar{h})}=\epsilon_{(h)}\bar{S}\quad(\bar{S}>0).$$

In what follows we shall mainly be concerned with solving for $\bar{S}$ as a function of temperature and of the coefficients of the Hamiltonian and the structure of the lattice (which enters through $\gamma_{s\mathbf{k}}$ and $\gamma_{d\mathbf{k}}$).

The solution of the previous coupled equations is now written in terms of

$$\lambda_{\mathbf{k}}=J_dB_d-J_sB_s(1-\gamma_{s\mathbf{k}})+I_aB_0,$$

and the spin-wave energies

$$w_{\mathbf{k}}=\bar{S}[\lambda_{\mathbf{k}}^2-(J_dB_d\gamma_{d\mathbf{k}})^2]^{1/2}.$$

Let the suffixes h or $\bar{h}$ take the values u (for the upper spin sublattice, with $\bar{S}_u>0$) and l (lower, with $\bar{S}_l<0$). Then explicitly, we have

$$G_{uu}{}^a=\frac{F_u{}^a}{4\pi}\left(\frac{1+w_{\mathbf{k}}{}^{-1}\bar{S}\lambda_{\mathbf{k}}}{w-w_{\mathbf{k}}}+\frac{1-w_{\mathbf{k}}{}^{-1}\bar{S}\lambda_{\mathbf{k}}}{w+w_{\mathbf{k}}}\right),$$

$$G_{ll}{}^a=\frac{F_l{}^a}{4\pi}\left(\frac{1-w_{\mathbf{k}}{}^{-1}\bar{S}\lambda_{\mathbf{k}}}{w-w_{\mathbf{k}}}+\frac{1+w_{\mathbf{k}}{}^{-1}\bar{S}\lambda_{\mathbf{k}}}{w+w_{\mathbf{k}}}\right),$$

$$G_{lu}{}^a=-\frac{F_u{}^a}{4\pi}\frac{\bar{S}J_dB_d\gamma_{d\mathbf{k}}}{w_{\mathbf{k}}}\left(\frac{1}{w-w_{\mathbf{k}}}-\frac{1}{w+w_{\mathbf{k}}}\right),$$

$$G_{ul}{}^a=\frac{F_l{}^a}{4\pi}\frac{\bar{S}J_dB_d\gamma_{d\mathbf{k}}}{w_{\mathbf{k}}}\left(\frac{1}{w-w_{\mathbf{k}}}-\frac{1}{w+w_{\mathbf{k}}}\right).$$

Formally equivalent solutions to these equations were obtained by Anderson and Callen,[3] but without the appearance of J_s in λ_k. In the results of Lines,[16] based on RPA, $B_0=B_d=B_s=1$.

We have still to solve for $\bar{S}$. This is done by means of the result of the Green's-function theory,[17] namely,

$$\langle B_hS_g{}^+\rangle=\lim_{\eta\to0}i\int N(\beta w)$$

$$\times(\langle\langle S_g{}^+;B_h\rangle\rangle_{w+i\eta}-\langle\langle S_g{}^+;B_h\rangle\rangle_{w-i\eta})dw,$$

$$N(z)=(e^z-1)^{-1}.$$

Remembering that $B_h\equiv e^{\alpha S_h{}^z}S_h{}^-$, we can manipulate the equation to yield[19]

$$\bar{S}=\frac{1}{2}\left((2S+1)\frac{(X_0+1)^{2S+1}+(X_0-1)^{2S+1}}{(X_0+1)^{2S+1}-(X_0-1)^{2S+1}}-X_0\right),$$

in terms of the spin multiplicity $2S+1$ of the cations.

$$X_0\equiv\langle\bar{S}\lambda_{\mathbf{k}}\rangle_{\mathbf{k}}$$

$$=(2/N)\sum_{\mathbf{k}}(\bar{S}\lambda_{\mathbf{k}})w_{\mathbf{k}}{}^{-1}\coth(\tfrac{1}{2}\beta w_{\mathbf{k}})$$

$$=\{\bar{S}(J_dB_d+I_a)[\langle1\rangle_{\mathbf{k}}+\alpha S^2J_s(\langle\gamma_{s\mathbf{k}}\rangle_{\mathbf{k}}{}^2-\langle1\rangle_{\mathbf{k}}\langle\gamma_{s\mathbf{k}}{}^2\rangle_{\mathbf{k}})]$$

$$-J_s\langle1-\gamma_{s\mathbf{k}}\rangle_{\mathbf{k}}\}/D,$$

$$D=1+\alpha\bar{S}^2[I_a\langle1\rangle_{\mathbf{k}}+J_s\langle\gamma_{s\mathbf{k}}(1-\gamma_{s\mathbf{k}})\rangle_{\mathbf{k}}]$$

$$+\alpha^2\bar{S}^4J_sI_a[\langle\gamma_{s\mathbf{k}}\rangle_{\mathbf{k}}{}^2-\langle1\rangle_{\mathbf{k}}\langle\gamma_{s\mathbf{k}}{}^2\rangle_{\mathbf{k}}].$$

Near the Néel temperature, we have $T_N=(k_B\beta_N)^{-1}$, $\bar{S}\to0$. Then, because $w_k\propto\bar{S}$, from its definition, $X_0\to(\bar{S})^{-1}$. Expanding the curly brackets in the above equation for $\bar{S}$ in the limit of large X_0, we find

$$\bar{S}X_0\to\tfrac{2}{3}S(S+1),\quad\text{as}\quad T\to T_N$$

from which T_N may be found as a function of the parameters of the Hamiltonian, crystal structure, etc.

Returning to temperatures below T_N, and supposing $\bar{S}$ to be available from its self-consistent equation, we can retrace our steps to find first $w_{\mathbf{k}}$, $\lambda_{\mathbf{k}}$, then the Fourier components G, from these the correlation functions of the atomic spins, and from these latter, the perpendicular susceptibilities.

B. Presence of Fields

We retain now the terms up to linear in the electric or magnetic fields, i.e., (i), (iii), (iv), (vi), and (vii), in the original Hamiltonian. The Dzyaloshinskii term (v) is irrelevant for the parallel susceptibilities and is excluded.

The theory in this part will be formally quite analogous to that in Sec. IV A with two differences, however: (1) The quantum-mechanical averages are to be evaluated in the presence of fields. We shall emphasize this by adding the superscript f. Thus, we have $\langle S_g{}^-S_j{}^+\rangle^f$; (2) as a consequence of the above, the averages will be different on the upper and lower sublattices. Therefore, we shall have to write for an average going over the same sublattice $\langle S_g{}^-S_j{}^+\rangle_{u\text{ or }l}{}^f$. No extra subscript will be needed for averages over different sublattices, by symmetry.

We are led to the following equations:

$$[w+\bar{S}_{(\bar{h})}J_dB_d{}^f+\bar{S}_{(h)}J_sB_s{}^f{}_{(h)}(1-\gamma_{s\mathbf{k}})$$

$$-\bar{S}_{(h)}I_aB_{0(h)}{}^f-\mu H+2\mu a_{11}{}^{LS}E\epsilon_{(h)}\bar{S}_{(h)}B_{0(h)}{}^f$$

$$+\mu a_{11}{}^JE\epsilon_{(h)}\bar{S}_{(h)}B_{s(h)}{}^f(1-\gamma_{s\mathbf{k}})]G_{(h)(h)}{}^a(\mathbf{k},w)$$

$$=F_{(h)}{}^a/2\pi+\bar{S}_{(h)}J_dB_d{}^f\gamma_{d\mathbf{k}}G_{(\bar{h})(h)}{}^a(\mathbf{k},w),$$

$$[w+\bar{S}_{(h)}J_dB_d{}^f+\bar{S}_{(\bar{h})}J_sB_{s(h)}{}^f(1-\gamma_{s\mathbf{k}})$$

$$-\bar{S}_{(\bar{h})}I_aB_{0(h)}{}^f-\mu H-2\mu a_{11}{}^{LS}E\epsilon_{(\bar{h})}\bar{S}_{(\bar{h})}B_{0(\bar{h})}{}^f$$

$$-\mu a_{11}{}^JE\epsilon_{(\bar{h})}\bar{S}_{(\bar{h})}B_{s(\bar{h})}{}^f(1-\gamma_{s\mathbf{k}})]G_{(\bar{h})(h)}{}^a(\mathbf{k},w)$$

$$=\bar{S}_{(\bar{h})}J_dB_d{}^f\gamma_{d\mathbf{k}}G_{(h)(h)}{}^a(\mathbf{k},w).$$

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[19] R. A. Tahir-Khelli and D. Ter Haar, Phys. Rev. **127**, 88 (1962).

The solutions are now

$$G_{uu}{}^a=\frac{F_u{}^a}{4\pi}\left(\frac{1+(w_{\mathbf{k}}{}^+-w_{\mathbf{k}}{}^-)^{-1}(\bar{S}_u-\bar{S}_l)\lambda_{\mathbf{k}}{}^f}{w-w_{\mathbf{k}}{}^+}+\frac{1-(w_{\mathbf{k}}{}^+-w_{\mathbf{k}}{}^-)^{-1}(\bar{S}_u-\bar{S}_l)\lambda_{\mathbf{k}}{}^f}{w-w_{\mathbf{k}}{}^-}\right),$$

$$G_{ll}{}^a=\frac{F_l{}^a}{4\pi}\left(\frac{1-(w_{\mathbf{k}}{}^+-w_{\mathbf{k}}{}^-)^{-1}(\bar{S}_u-\bar{S}_l)\lambda_{\mathbf{k}}{}^f}{w-w_{\mathbf{k}}{}^+}+\frac{1+(w_{\mathbf{k}}{}^+-w_{\mathbf{k}}{}^-)^{-1}(\bar{S}_u-\bar{S}_l)\lambda_{\mathbf{k}}{}^f}{w-w_{\mathbf{k}}{}^-}\right),$$

$$G_{lu}{}^a=-\frac{F_u{}^a}{4\pi}\,\frac{2\bar{S}_lJ_dB_d{}^f\gamma_{d\mathbf{k}}}{w_{\mathbf{k}}{}^+-w_{\mathbf{k}}{}^-}\left(\frac{1}{w-w_{\mathbf{k}}{}^+}-\frac{1}{w-w_{\mathbf{k}}{}^-}\right),$$

$$G_{ul}{}^a=\frac{F_l{}^a}{4\pi}\,\frac{2\bar{S}_uJ_dB_d{}^f\gamma_{dk}}{w_{\mathbf{k}}{}^+-w_{\mathbf{k}}{}^-}\left(\frac{1}{w-w_{\mathbf{k}}{}^+}-\frac{1}{w-w_{\mathbf{k}}{}^-}\right).$$

The following amended definitions have been introduced:

$$w_{\mathbf{k}}{}^{\pm}=\pm\tfrac{1}{2}(\bar{S}_u-\bar{S}_l)\{(\lambda_{\mathbf{k}}{}^f)^2+[4\bar{S}_u\bar{S}_l/(\bar{S}_u-\bar{S}_l)^2]\times(J_dB_d{}^f\gamma_{d\mathbf{k}})^2\}^{1/2}+\mu_{\mathbf{k}}$$

with

$$\begin{aligned}\mu_{\mathbf{k}}=\mu H&-\mu a_{11}{}^{LS}E(\bar{S}_uB_{0u}{}^f-\bar{S}_lB_{0l}{}^f)\\&-\tfrac{1}{2}\mu Ea_{11}{}^J(\bar{S}_uB_{su}{}^f-\bar{S}_lB_{sl}{}^f)(1-\gamma_{s\mathbf{k}})\\&-\tfrac{1}{2}J_dB_d{}^f(\bar{S}_u+\bar{S}_l)-\tfrac{1}{2}J_s(\bar{S}_uB_{su}{}^f+\bar{S}_lB_{sl}{}^f)\\&+\tfrac{1}{2}I_a(\bar{S}_uB_{0u}{}^f+\bar{S}_lB_{0l}{}^f)\end{aligned}$$

and

$$\begin{aligned}\lambda_{\mathbf{k}}{}^f=J_dB_d{}^f&-J_s\frac{\bar{S}_uB_{su}{}^f-\bar{S}_lB_{sl}{}^f}{\bar{S}_u-\bar{S}_l}(1-\gamma_{s\mathbf{k}})\\&+I_a\frac{\bar{S}_uB_{0u}{}^f-\bar{S}_lB_{0l}{}^f}{\bar{S}_u-\bar{S}_l}-2\mu a_{11}{}^{LS}E\frac{\bar{S}_uB_{0u}{}^f+\bar{S}_lB_{0l}{}^f}{\bar{S}_u-\bar{S}_l}\\&-\mu a_{11}{}^JE\frac{\bar{S}_u\mathrm{B}_{su}{}^f-\bar{S}_l\mathrm{B}_{sl}{}^f}{\bar{S}_u-\bar{S}_l}(1-\gamma_{s\mathbf{k}}).\end{aligned}$$

It may be noted that although we wrote $\bar{S}_u-\bar{S}_l$, to the linear approximation in the field the difference is really $2\bar{S}$, twice the zero-field sublattice magnetization. The correction is $O(H^2)$.

To complete the solution, we have to write out the equations for the individual sublattice magnetizations. There are now two equations of the form

$$\bar{S}_h=\frac{1}{2}\left((2S+1)\frac{(X_h+1)^{2S+1}+(X_h-1)^{2S+1}}{(X_h+1)^{2S+1}-(X_h-1)^{2S+1}}-X_h\right),\qquad (h=u,\, l)$$

$$X_h=\frac{2}{N}\sum_{\mathbf{k}}[N(\beta w_{\mathbf{k}}{}^+)+N(\beta w_{\mathbf{k}}{}^-)+1]+\frac{2}{N}\sum_{\mathbf{k}}\frac{\bar{S}_h-\bar{S}_{\bar{h}}}{w_{\mathbf{k}}{}^+-w_{\mathbf{k}}{}^-}\lambda_{\mathbf{k}}{}^f[N(\beta w_{\mathbf{k}}{}^+)-N(\beta w_{\mathbf{k}}{}^-)].$$

The susceptibilities are now derived by solving for $\bar{S}_u$, $\bar{S}_l$ from this set of four equations, remembering that $\langle S_j{}^z\rangle=\bar{S}_u$ or $\bar{S}_l$, depending on whether j is in the upper or lower sublattice and then substituting $\langle S_j\rangle$ into

$$\chi_{11}{}^M=\mu\sum_j\frac{\partial}{\partial H_z}\langle S_j{}^z\rangle:$$

$$\chi_{11}{}^{\mathrm{ME}}=\mu\sum\frac{\partial}{\partial E_z}\langle S_j{}^z\rangle-N\mu^2J_d{}^{-1}a_{11}{}^g\bar{S},$$

where one puts $H=E=0$ after differentiation.

V. MOLECULAR-FIELD APPROXIMATION

We derive the observables (susceptibilities) by this method, with a view to comparing the results with those of the previous section.

Our starting point in this method is to write

$$\mathbf{S}_j=\langle\mathbf{S}_j\rangle+(\mathbf{S}_j-\langle\mathbf{S}_j\rangle),$$

and to regard the second term as small, so that the square can be neglected. $\mathbf{S}_j\cdot\mathbf{S}_l$ then becomes

$$\langle\mathbf{S}_j\rangle\cdot\langle\mathbf{S}_l\rangle+(\mathbf{S}_j-\langle\mathbf{S}_j\rangle)\cdot\langle\mathbf{S}_l\rangle+\langle\mathbf{S}_j\rangle\cdot(\mathbf{S}_l-\langle\mathbf{S}_l\rangle)+(\mathbf{S}_j-\langle\mathbf{S}_j\rangle)\cdot(\mathbf{S}_l-\langle\mathbf{S}_l\rangle).$$

Neglecting the last term and rewriting, we obtain the linearized expression

$$\mathbf{S}_j\cdot\mathbf{S}_l\simeq\mathbf{S}_j\cdot\langle\mathbf{S}_l\rangle+\mathbf{S}_l\cdot\langle\mathbf{S}_j\rangle-\langle\mathbf{S}_j\rangle\cdot\langle\mathbf{S}_l\rangle.$$

We further write the averages $\langle S_j{}^z\rangle$ as $\epsilon_j\bar{S}+\bar{m}$, while $\langle S_j{}^x\rangle=\langle S_j{}^y\rangle=0$ by the same token.

The Hamiltonian for the parallel case now takes the form

$$\begin{aligned}(\mathcal{H})_{11}=&-\mu\sum S_j{}^z[H_z-\bar{m}\mu^{-1}(J_d+J_s)+\bar{S}\epsilon_{(j)}\mu^{-1}(J_d-J_s)]\\&+\mu^2J_d{}^{-1}a_{11}{}^gH_zE_z\sum_j\epsilon_{(j)}S_j{}^z+\mu a_{11}{}^{LS}E_z\sum_j\epsilon_{(j)}(S_j{}^z)^2\\&+\mu a_{11}{}^JE_z\sum_j[S_j{}^z\bar{S}+\epsilon_{(j)}S_j{}^z\bar{m}]-N\mu E_za_{11}{}^J\bar{S}\bar{m}\\&+\tfrac{1}{2}N\bar{S}^2(J_d-J_s)-\tfrac{1}{2}N\bar{m}^2(J_d+J_s),\end{aligned}$$

with $a_{11}{}^J=\sum_l a_{11}{}^J(jl)$, where the summation runs over next-nearest neighbors of the same sublattice.

It is noted that the above Hamiltonian resembles (apart from the term with the coefficient $a_{11}{}^{LS}$) the familiar molecular-field Hamiltonian. This resemblance can be made more apparent by introducing a number of notational changes.

Define A, Γ, M_0, M_2, G_{11}, c_{11}, a_{11}, V_0, $\mathcal{H}^+$, and $\mathcal{H}^-$ by

$$J_d=\tfrac{1}{2}N\mu^2A,\quad J_s=\tfrac{1}{2}N\mu^2\Gamma,\quad M_0=\tfrac{1}{2}N\mu\bar{S},$$

$$M_2=N\mu\bar{m},\quad a_{11}{}^J=\tfrac{1}{2}N\mu b_{11},\quad a_{11}{}^g=J_dc_{11}/\mu,\quad a_{11}{}^{LS}=a_{11},$$

$$V_0=M_0{}^2(A-\Gamma)-b_{11}EM_0M-\tfrac{1}{4}M^2(A+\Gamma)=\text{a } c \text{ number.}$$

$\mathcal{H}^{\pm}$ are the Hamiltonians acting on the spin S_z of an atom of either the + or − sublattice. (Previously we denoted these by u,l.)

$$\mathcal{H}^{\pm}=-\mu S_z\{(A-\Gamma)M_0\pm[H-\tfrac{1}{2}(A+\Gamma)M]\}$$
$$\pm\mu a_{\parallel}E_z(S_z^2)+\mu b_{\parallel}M_0S_z+\mu(c_{\parallel}HE+\tfrac{1}{2}b_{\parallel}EM)S_z.$$

The Hamiltonian on the previous page then becomes

$$(\mathcal{H})_{\parallel}=V_0+\tfrac{1}{2}N\mathcal{H}^{+}+\tfrac{1}{2}N\mathcal{H}^{-}.$$

The aim of the redefinitions was to bring the notation of the present work in line with that of Hornreich and Shtrikman.[11]

In order to obtain the susceptibilities, we must first find the energies of the Hamiltonian and then obtain the free energy F from the position function. The trace will involve energies over the eigenvalues $\pm m$ of S_z. The free energy correct to terms bilinear in E, H will then be

$$F=F_0-\tfrac{1}{4}M^2(A+\Gamma)+N\mu\langle m\rangle c_{\parallel}HE$$
$$-\tfrac{1}{2}N\beta\mu^2\{[H-\tfrac{1}{2}(A+\Gamma)M-Eb_{\parallel}M_0]^2(\langle m^2\rangle-\langle m\rangle^2)$$
$$-2a_{\parallel}E[H-\tfrac{1}{2}(A+\Gamma)M-Eb_{\parallel}M_0](\langle m^3\rangle-\langle m^2\rangle\langle m\rangle)\}.$$

This contains the hitherto unknown M, which is to be determined by the self-consistency requirement that $M=-\partial F/\partial H$ or, which is more convenient for our purposes, by writing

$$M=\chi_{\parallel}{}^{M}H+\chi_{\parallel}{}^{\mathrm{ME}}E$$

and

$$\chi_{\parallel}{}^{M}=-\partial^2F/\partial H^2,$$
$$\chi_{\parallel}{}^{\mathrm{ME}}=-\partial^2F/\partial H\partial E.$$

The first of this pair yields a quadratic self-consistency equation for $\chi_{\parallel}{}^{M}$, which has two solutions:

$$\chi_{\parallel}{}^{M}=2(A+\Gamma)^{-1}+\chi_{VV}$$

and

$$\chi_{\parallel}{}^{M}=\frac{N\beta\mu^2(\langle m^2\rangle-\langle m\rangle^2)}{1+\tfrac{1}{2}N\beta\mu^2(\langle m^2\rangle-\langle m\rangle^2)(A+\Gamma)}+\chi_{VV}.$$

The latter solution is physical. We then get

$$\chi_{\parallel}{}^{\mathrm{ME}}=-N\mu\langle m\rangle c_{\parallel}$$
$$-(\chi_{\parallel}{}^{M}-\chi_{VV})\left(a_{\parallel}\frac{\langle m^3\rangle-\langle m^2\rangle\langle m\rangle}{\langle m\rangle(\langle m^2\rangle-\langle m\rangle^2)}+\tfrac{1}{2}N\mu b_{\parallel}\right)\langle m\rangle,$$

which agrees with Ref. 11.

In an analogous treatment of the *perpendicular case*, the Hamiltonian reduces in the molecular-field approximation to

$$(\mathcal{H})_{\perp}=-\mu\sum_j S_j{}^x[H-\tfrac{1}{2}(A+\Gamma)M]$$
$$-\mu\sum_j\epsilon_{(j)}S_j{}^z(A-\Gamma)M_0+\mu^2a_{\perp}{}^gJ_d{}^{-1}HE\sum_j\epsilon_{(j)}S_j{}^z$$
$$+\tfrac{1}{2}\mu a_{\perp}{}^{LS}E\sum_j\epsilon_{(j)}(S_j{}^xS_j{}^z+S_j{}^zS_j{}^x)$$
$$+\mu Ea^D(AM_0\sum_j S_j{}^x+\tfrac{1}{2}AM\sum_j\epsilon_{(j)}S_j{}^z)$$
$$-Ea^DAMM_0+M_0{}^2(A-\Gamma)-\tfrac{1}{4}M^2(A+\Gamma).$$

The second term in the parentheses led by a^D differs from the corresponding term $[A/(A-\Gamma)][H-\tfrac{1}{2}(A+\Gamma)M]\times\sum_j\epsilon_{(j)}S_j{}^z$, which is required to prove the equivalence with the Hamiltonian of Ref. 11.

With notational changes introducing $a_{\perp}$, $b_{\perp}$, $c_{\perp}$, V_0, $\mathcal{H}_0$, and $V^{\pm}$:

$$a_{\perp}{}^{LS}=a_{\perp},\quad a^D=b_{\perp}(A-\Gamma)A^{-1},\quad a_{\perp}{}^g=J_dc_{\perp}\mu^{-1},$$
$$V_0=-b_{\perp}E(A-\Gamma)MM_0-\tfrac{1}{4}M^2(A+\Gamma)+M_0{}^2(A-\Gamma),$$
$$\mathcal{H}_0{}^{\pm}=\pm\mu S^z(A-\Gamma)M_0,$$
$$V^{\pm}=\pm\mu\{[H-\tfrac{1}{2}(A+\Gamma)M-E(A-\Gamma)b_{\perp}M_0]S^x$$
$$-\tfrac{1}{2}Ea_{\perp}(S^xS^z+S^zS^x)\}+\mu[c_{\perp}HE+\tfrac{1}{2}(A-\Gamma)b_{\perp}ME]S^z,$$

we can write the Hamiltonian in the form

$$(\mathcal{H})_{\perp}=V_0+\tfrac{1}{2}N\mathcal{H}_0{}^{+}+\tfrac{1}{2}N\mathcal{H}_0{}^{-}+\tfrac{1}{2}NV^{+}+\tfrac{1}{2}NV^{-}.$$

The perturbational solution of the Hamiltonian and the expansion of the free energy to the desired order leads to

$$F=F_0(\text{a constant})+M_0{}^2(A-\Gamma)$$
$$-\tfrac{1}{4}M^2(A+\Gamma)+N\mu HEc_{\perp}\langle m\rangle$$
$$-\frac{N\mu}{2(A-\Gamma)M_0}\{\langle m\rangle[H-\tfrac{1}{2}(A+\Gamma)M-Eb_{\perp}(A-\Gamma)M_0]^2$$
$$-3Ea_{\perp}[H-\tfrac{1}{2}(A+\Gamma)M-Eb_{\perp}(A-\Gamma)M_0]$$
$$\times[\langle m^2\rangle-S(S+1)/3]\}.$$

Putting $M=\chi_{\perp}{}^{M}H+\chi_{\perp}{}^{\mathrm{ME}}E$ we again determine $\chi_{\perp}{}^{M}$ self-consistently from

$$-\frac{\partial^2F}{\partial H^2}=\chi_{\perp}{}^{M}=\frac{A+\Gamma}{2}(\chi_{\perp}{}^{M})^2$$
$$+\frac{N\mu}{(A-\Gamma)M_0}\langle m\rangle\left(1-\frac{A+\Gamma}{2}\chi_{\perp}{}^{M}\right)^2,$$

leading to

$$\chi_{\perp}{}^{M}=2/(A+\Gamma),$$

or

$$=1/A,$$

of which the second is physical.

The magnetoelectric susceptibility is, accordingly,

$$\chi_{\perp}{}^{\mathrm{ME}}=-N\mu\langle m\rangle c_{\perp}-\chi_{\perp}{}^{M}\langle m\rangle$$
$$\times\left(a_{\perp}\times\frac{3}{2}\,\frac{\langle m^2\rangle-S(S+1)/3}{\langle m\rangle^2}+\tfrac{1}{2}N\mu(A-\Gamma)b_{\perp}\right),$$

which agrees with the Hornreich-Shtrikman result, as corrected.[20]

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[20] R. Hornreich and S. Shtrikman, Phys. Rev. **166**, 598 (1968).

VI. COMPARISON OF DIFFERENT METHODS AND SUMMARY

In Sec. III of this work, we derived expressions for the susceptibilities by the Green's-function method, starting with a microscopic Hamiltonian. From the same Hamiltonian we derived the susceptibilities of Hornreich and Shtrikman, based on a phenomenological Hamiltonian, and using the molecular-field approximation. We have thereby established the connection between the two starting points.

A further point is important in the choice of the theoretical method, and for other reasons, too.

Callen and Shtrikman[21] showed that the functional relationships between the statistical means of the powers of the spin operator are the same in the molecular-field approximation as in the Green's-function theory, and may be generally valid. In Ref. 11, the formulas of the MFA were therefore used, albeit with empirical values substituted for the first moment.

We have shown, however, that the susceptibilities are not the same functionals of the moment in the different theoretical procedures.[22]

In conclusion, we give the list of susceptibilities in the MFA and the RPA and CD of the Green's-function theory. The notation of Ref. 11 is used:

$$\text{MFA:}\quad \chi_\perp{}^M = A^{-1},$$
$$\text{RPA:}\quad \chi_\perp{}^M = A^{-1},$$
$$\text{CD:}\quad \chi_\perp{}^M = A^{-1}B_d{}^{-1}.$$

For the parallel susceptibility $\chi_{\parallel}{}^M$, the expressions in terms of the moments are altogether different and do not bear comparison. For the results the reader is referred to Secs. III and V.

$$\text{MFA:}\quad \chi_\perp{}^{\mathrm{ME}} = -N\mu\langle m\rangle c_\perp - A^{-1}\langle m\rangle\{a_\perp\tfrac{3}{2}[\langle m^2\rangle - \tfrac{1}{3}S(S+1)]/\langle m\rangle^2 + \tfrac{1}{2}N\mu(A-\Gamma)b_\perp\},$$

$$\text{RPA:}\quad \chi_\perp{}^{\mathrm{ME}} = -N\mu\langle m\rangle c_\perp - A^{-1}\langle m\rangle[a_\perp + \tfrac{1}{2}N\mu(A-\Gamma)b_\perp],$$

$$\text{CD:}\quad \chi_\perp{}^{\mathrm{ME}} = -N\mu\langle m\rangle c_\perp - A^{-1}\langle m\rangle\left[\frac{a_\perp}{B_d}\left(\frac{2S-1}{2S} + \frac{\langle m^2\rangle}{2S^2}\right) + \tfrac{1}{2}N\mu(A-\Gamma)b_\perp\right],$$

$$\text{MFA:}\quad \chi_\parallel{}^{\mathrm{ME}} = -N\mu\langle m\rangle c_\parallel - (\chi_\parallel{}^M - \chi_{VV})\left(a_\parallel\frac{\langle m^3\rangle - \langle m^2\rangle\langle m\rangle}{\langle m\rangle(\langle m^2\rangle - \langle m\rangle^2)} + \tfrac{1}{2}N\mu b_\parallel\right),$$

$$\text{RPA:}\quad \chi_\parallel{}^{\mathrm{ME}} = -N\mu\langle m\rangle c_\parallel - (\chi_\parallel{}^M - \chi_{VV})\left(2a_\parallel + \tfrac{1}{2}N\mu b_\parallel\frac{\langle(1-\gamma_{s\mathbf{k}})dN_{\mathbf{k}}/dw_{\mathbf{k}}\rangle}{\langle dN_{\mathbf{k}}/dw_{\mathbf{k}}\rangle}\right),$$

$$\text{CD:}\quad \chi_\parallel{}^{\mathrm{ME}} = -N\mu\langle m\rangle c_\parallel - (\chi_\parallel{}^M - \chi_{VV})\Bigg[a_\parallel\left(\frac{2S-1}{S} + \frac{\langle m^2\rangle}{S^2}\right)$$
$$+ N\mu b_\parallel B_S\frac{\langle(1-\gamma_{s\mathbf{k}})dN_{\mathbf{k}}/dw_{\mathbf{k}}\rangle}{2\langle dN_{\mathbf{k}}/dw_{\mathbf{k}}\rangle + (N\mu^2\Gamma\langle m\rangle^2/S^2)[\langle\gamma_{s\mathbf{k}}(dN_{\mathbf{k}}/dw_{\mathbf{k}})\rangle^2 - \langle(dN_{\mathbf{k}}/dw_{\mathbf{k}})\rangle\langle\gamma_{s\mathbf{k}}{}^2(dN_{\mathbf{k}}/dw_{\mathbf{k}})\rangle]}\Bigg].$$

Within the last set, the similarity (even as far as it exists) is deceptive since the factors $(\chi_\parallel{}^M - \chi_{VV})$ have to be evaluated in their own approximations; these do not bear comparison, as we have just remarked.

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[21] H. B. Callen and S. Shtrikman, Solid State Commun. 3, 5 (1965).

[22] We have been informed by Professor H. B. Callen that Dr. A. B. Harris has reached similar conclusions for sublattice magnetization.