

Magnetostriction, Forced Magnetostriction, and Anomalous Thermal Expansion in Ferromagnets*

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In previous papers we have formulated the theory of magnetostriction arising from single-ion crystal-field effects, for cubic crystals, and we have shown that the theory accounts extremely well for the temperature dependence of the magnetostriction in yttrium iron garnet. We here summarize that theory, extend it to arbitrary crystal symmetry, augment it by the inclusion of two-ion interactions, analyze the dependence on magnetic field strength (the "forced magnetostriction"), and discuss the totally symmetric component (which exhibits itself as an anomalous thermal expansion). The first part of this paper is concerned with the above matters, and the analysis is based entirely on symmetry considerations. It culminates in expressions relating the macroscopic magnetostriction coefficients to the product of microscopic magnetoelastic coupling constants and certain spin correlation functions. Only three such correlation functions appear, and all temperature and field dependence enters through these correlation functions. In the second part of the paper, we evaluate these correlation functions by various approximate theories: molecular field theory, a cluster theory, and the random-phase approximation. Applications to Dy and to EuS are cited, and a detailed application to Gd is given. In Gd the sign inversion of a particular magnetostriction coefficient, and its full temperature dependence, are accurately accounted for theoretically. The field dependence of the forced magnetostriction of Gd is also discussed, with special reference to the observed persistence of a pseudo-linearity slightly above the Curie temperature.

1. INTRODUCTION

IN a previous paper¹ we discussed magnetostriction in cubic ferromagnets. It was there assumed that the magnetostriction arises from the modulation by the strain of single-ion energies, such as those involving crystal-field splittings. There are, in fact, materials in which this source of the magnetostriction is dominant, and the theory gave excellent agreement² with the temperature dependence of the magnetostriction in yttrium iron garnet (YIG). We here summarize and simplify that theory, generalize the analysis to arbitrary crystal symmetry, include more general mechanisms of the magnetoelastic coupling, study both the magnetic field and temperature dependence, and make several specific applications.

In addition to the single-ion contributions to the magnetoelastic coupling, we consider two-ion terms. These arise from the modulation by the strain of spin-interaction energies, such as dipolar, pseudodipolar, and exchange energies. Whereas the magnetocrystalline anisotropy energy and the dipolar and pseudodipolar coupling correspond to effective fields of the order of 10^3 – 10^5 Oe, the exchange interaction corresponds to 10^6 – 10^7 Oe for metals and spinels and to 10^9 Oe for rare

earth ions in garnets. One might then expect that the exchange term would usually dominate the magnetoelastic coupling. However, the exchange term is an isotropic invariant, and therefore it makes no contribution to that part of the magnetostriction which varies with the direction of the magnetization. It was for this reason that the one-ion theory reasonably could be isolated for separate investigation and that it could be applied successfully to YIG. However, in other materials (such as Gd), the dipolar terms may be particularly large and may compete effectively with the one-ion origins of the magnetostriction. Furthermore, in any material, the effect of strain on the isotropic exchange can contribute to the isotropic part of the magnetostriction, manifesting itself in the anomalous thermal expansion and the forced volume magnetostriction.

In the first three sections of this paper, the analysis is based on symmetry considerations imposed on the magnetoelastic Hamiltonian (in contrast to the classical approach³ in which the symmetry is imposed at the level of the phenomenological free energy). We show, in particular, that for purposes of classifying the magnetoelastic Hamiltonian, the 32 point groups divide into 11 symmetry types, two of which are subdivisions of the cubic system and two of the hexagonal system. In the 11 different types of Hamiltonians there appear various magnetoelastic coupling constants, which we take as

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¹ Earl R. Callen and Herbert B. Callen, *Phys. Rev.* **129**, 578 (1963).

² E. R. Callen, A. E. Clark, B. DeSavage, W. Coleman, and H. B. Callen, *Phys. Rev.* **130**, 1735 (1963).

³ W. Döring and G. Simon, *Ann. Physik* **7**, 373 (1960).

undetermined. The free energy then depends on the direction of the magnetization, and from it we find the equilibrium strains. The resulting expressions for the strains classify under the crystal symmetry analogously to the Hamiltonian. The coefficients in these expressions are the macroscopic magnetostriction coefficients; they are, in fact, the products of the magnetoelastic coupling constants and certain spin correlation functions. The temperature dependence and the magnetic field dependence of the magnetostriction coefficients derives entirely from these correlation functions. We show that only three distinct types of correlation functions enter the theory; the self-correlation functions $\langle(S_1^z)^2\rangle$, the isotropic correlation function $\langle\mathbf{S}_1\cdot\mathbf{S}_2\rangle$, and the longitudinal correlation function $\langle S_1^z S_2^z \rangle$.

In the second part of the paper, we turn to various approximation schemes to evaluate the spin-correlation functions and to permit the application of the theory to specific materials.

In Sec. 5, we review existing theories for the one-ion spin averages. H. Callen and S. Shtrikman have shown that for all "renormalized collective excitation" theories (and molecular field theory, the random-phase approximation, and other Green's function theories are all in this class) the one-ion averages are the *same* functions of the magnetization. Hence the one-ion magnetostriction coefficients can be expressed as functions of the magnetization in a way which is not quite model independent, but which at least has validity over a wide range of models. We have previously explicitly evaluated this functional dependence for large spin. Citing the measurements of Clark, Bozorth, and DeSavage⁴ on the temperature and field dependence of magnetostriction in dysprosium metal, we show that the theory fits the data accurately over a range of about four decades.

In Sec. 6, we demonstrate the relationship of the anomalous thermal expansion and the volume magnetostriction to the isotropic correlation function. In Sec. 7, we calculate the scalar correlation function $\langle\mathbf{S}_1\cdot\mathbf{S}_2\rangle$ by a cluster approximation and by the random-phase approximation. We show that the temperature and magnetic-field dependence of the volume magnetostriction and of the *c*-axis strain of gadolinium are consistent with the theory. The behavior of the scalar correlation function in the paramagnetic region is then discussed in Sec. 8.

In Sec. 9, we calculate the nearest- and next-nearest-neighbor longitudinal correlation functions, $\langle S_1^z S_2^z \rangle$, in the cluster approximation. Although this quantity varies as the cube of the magnetization (M^3) at sufficiently low temperatures, over almost the entire temperature range it is closely approximated by M^2 , for all separations of spins \mathbf{S}_1 and \mathbf{S}_2 , and almost independently of the ratios of successive exchange constants. Approximating all longitudinal correlation functions by M^2 ,

we show that an appropriate anisotropic magnetostriction of gadolinium, which changes sign before vanishing at T_c , is accurately represented as the sum of one-ion and two-ion magnetostriction terms.

2. SYMMETRY OPERATORS AND THE HAMILTONIAN

We take the Hamiltonian of the system as

$$H = H_m + H_e + H_{me} + H_a. \quad (2.1)$$

H_m is the Hamiltonian of the spin system, consisting of isotropic exchange terms and the Zeeman interaction with an external field. We exclude anisotropic exchange and Dzyaloshinski interactions.

H_e is the elastic energy associated with the homogeneous strain components ϵ_{xx} , ϵ_{yy} , ϵ_{zz} , ϵ_{xy} , ϵ_{yz} and ϵ_{zx} . The nonhomogeneous strains, or phonon modes, are not included in the Hamiltonian. We define the shear strains by $\epsilon_{xy} = \frac{1}{2}[(\partial u_y/\partial x) + (\partial u_x/\partial y)]$, whereas the coefficient $\frac{1}{2}$ is often omitted. We assume the crystal to be constrained so that all "antisymmetric strains" such as $\frac{1}{2}[(\partial u_y/\partial x) - (\partial u_x/\partial y)]$, which correspond to homogeneous rotations of the crystal, vanish.

H_{me} is the magnetoelastic interaction, coupling the spin system to the strains.

H_a is the magnetocrystalline anisotropy energy, representing the effect of the unstrained lattice on the spin system.

The terms H_{me} and H_a will be treated as a perturbation, H_m will play the role of the "unperturbed" Hamiltonian, and H_e will appear as an essentially classical additive term. The classical nature of H_e results from the fact that we restrict our attention to the homogeneous strain modes, for which the natural vibrational frequencies vanish. Consequently, in the harmonic oscillator Hamiltonian of the form $[\frac{1}{2}c\epsilon^2 + (\omega_0/2c)p_\epsilon^2]$, the natural frequency ω_0 vanishes, and the term involving the momentum p_ϵ , conjugate to the strain ϵ , does not appear in the Hamiltonian. Thus H_e is simply quadratic in the strains, which can be treated as classical variables.

The free energy of the system, to first order in the perturbation, is of the form

$$F = F_m + H_e + \langle H_{me} \rangle + \langle H_a \rangle, \quad (2.2)$$

where F_m is the unperturbed free energy of the spin system (in the absence of magnetoelastic interactions and anisotropy), H_e is the elastic energy, and the averages of H_{me} and H_a are to be carried out in the unperturbed density operator of the spin system. The equilibrium strains will be evaluated by minimizing the free energy.

The chemical point group of the crystal is denoted by \mathcal{G} ; it is the group obtained by replacing all translation operations by the identity operation in the chemical space group of the crystal. The macroscopic magnetostriction has the full symmetry of this group. As we shall

⁴ A. E. Clark, B. DeSavage, and R. M. Bozorth, Phys. Rev. **138**, A216 (1965).

TABLE I. Isomorphisms of spherical harmonics, elastic strain components, one-ion spin operators, and two-ion spin operators.^a

Classical polynomials or spherical harmonics	Strain functions	One-ion operators of spherical tensor operators	Two-ion spin operators	Bilinear direction cosines
$1 = (4\pi)^{1/2} Y_0^0$ $(\sqrt{3}/2)(x^2 - y^2) = c Y_2^0$ $\frac{1}{2}(x^2 - y^2) = (c/\sqrt{2})[Y_2^2 + Y_2^{-2}]$ $xy = (-ic/\sqrt{2})[Y_2^2 - Y_2^{-2}]$ $yz = (ic/\sqrt{2})[Y_2^1 + Y_2^{-1}]$ $xz = -(c/\sqrt{2})[Y_2^1 - Y_2^{-1}]$	$\epsilon^{\alpha 1} \equiv \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}$ $(\sqrt{3}/2)[\epsilon_{zz} - \frac{1}{3}\epsilon^{\alpha 1}]$ $\frac{1}{2}[\epsilon_{xx} - \epsilon_{yy}]$ ϵ_{xy} ϵ_{yz} ϵ_{zx}	$1 = (2S+1)^{1/2} \mathcal{Y}_0^0$ $(\sqrt{3}/2)[(S_z)^2 - \frac{1}{2}S(S+1)] = (1/\sqrt{2}n_s) \mathcal{Y}_2^0$ $\frac{1}{2}[(S_x)^2 - (S_y)^2] = (1/2n_s)[\mathcal{Y}_2^2 + \mathcal{Y}_2^{-2}]$ $\frac{1}{2}[S_x S_y + S_y S_x] = (-i/2n_s)[\mathcal{Y}_2^2 - \mathcal{Y}_2^{-2}]$ $\frac{1}{2}[S_y S_z + S_z S_y] = (i/2n_s)[\mathcal{Y}_2^1 + \mathcal{Y}_2^{-1}]$ $\frac{1}{2}[S_x S_z + S_z S_x] = (-1/2n_s)[\mathcal{Y}_2^1 - \mathcal{Y}_2^{-1}]$	$\mathbf{S}_f \cdot \mathbf{S}_g$ $(\sqrt{3}/2)[S_f^z S_g^z - \frac{1}{2}\mathbf{S}_f \cdot \mathbf{S}_g]$ $\frac{1}{2}[S_f^x S_g^x - S_f^y S_g^y]$ $\frac{1}{2}[S_f^x S_g^y + S_f^y S_g^x]$ $\frac{1}{2}[S_f^y S_g^z + S_f^z S_g^y]$ $\frac{1}{2}[S_f^z S_g^z + S_f^x S_g^x]$	1 $(\sqrt{3}/2)[\alpha_x^2 - \frac{1}{3}]$ $\frac{1}{2}[\alpha_x^2 - \alpha_y^2]$ $\alpha_x \alpha_y$ $\alpha_y \alpha_z$ $\alpha_x \alpha_z$

^a Here $c = (4\pi/15)^{1/2}$. The phase convention of the spherical harmonics is that of M. E. Rose [*Elementary Theory of Angular Momentum* (John Wiley & Sons, New York, 1957)], and the \mathcal{Y}_l^m are orthonormalized with respect to integration over the unit sphere. The spherical tensor operators are orthonormalized with respect to the trace operation; trace $[(\mathcal{Y}_l^m)^\dagger \mathcal{Y}_l^m] = \delta_{ll'} \delta_{mm'}$. Following A. Meckler [Nuovo Cimento Suppl. 12, 1 (1959)], the operators are defined by

$$\mathcal{Y}_l^l = n_l (S^+)^l; (n_l)^2 = \frac{2^l (2l+1)! (2S-l)!}{(l!)^2 (2S+l+1)!}; \mathcal{Y}_l^{m-1} = \sqrt{2} [l(l+1) - m(m+1)]^{-1/2} [S^-, \mathcal{Y}_l^m]; \mathcal{Y}_l^{-m} = (-1)^m (\mathcal{Y}_l^m)^\dagger; S^\pm = (\mp S_x \pm iS_y)/\sqrt{2}.$$

see, the only terms in H_{me} and H_a which contribute in first order to the observed magnetostriction and anisotropy are the terms which are fully symmetric under \mathcal{G} .

Although the form of H_e is well known, we briefly review the considerations which dictate its form. We thereby introduce notation and establish a prototype for the derivation of H_{me} . Under the operations of \mathcal{G} , the six strain components transform into each other and thereby generate a six-dimensional representation of \mathcal{G} . This representation is reducible. In particular, the quantity $\epsilon^\alpha \equiv (\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz})$ always transforms under the fully symmetric representation Γ_α of \mathcal{G} . The remaining five-dimensional representation is further reduced by the linear combinations $[\epsilon_{zz} - \frac{1}{3}(\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz})]$, $[\epsilon_{xx} - \epsilon_{yy}]$, ϵ_{xy} , ϵ_{yz} , and ϵ_{zx} . These are the combinations which transform isomorphically with the real combinations of spherical harmonics, as shown in Table I. The basis strains (or rather their isomorphic classical polynomials) which correspond to each of the irreducible representations are given in Table II for all 32 point groups. It is seen from Table II that the 32 point groups classify into 11 distinct symmetry types.

In several cases, the real representations generated by the linear combinations of strains listed in Table I can be further reduced by taking complex combinations. Thus, in the tetragonal groups 4, $4/m$, and $\bar{4}$, the two-dimensional representation with basis functions ϵ_{yz} and ϵ_{zx} can be reduced to two one-dimensional representations by the complex functions $\epsilon_{yz} \pm i\epsilon_{zx}$. Such cases are indicated explicitly in Table II.

Now let ϵ_1^Γ , ϵ_2^Γ be a pair of strain functions which support the two-dimensional representation Γ . Then the scalar invariant $\epsilon_1^{\Gamma*} \epsilon_1^\Gamma + \epsilon_2^{\Gamma*} \epsilon_2^\Gamma$ is fully symmetric, and the elastic Hamiltonian can contain the term $\frac{1}{2} c^\Gamma [\epsilon_1^{\Gamma*} \epsilon_1^\Gamma + \epsilon_2^{\Gamma*} \epsilon_2^\Gamma]$, where c^Γ is a phenomenological elastic constant. Similarly, with one-dimensional and three-dimensional representations.

Two special cases require comment. For all point groups other than those in the cubic system there are two different strain functions, each of which supports the fully symmetric representation Γ_α . These are $\epsilon^{\alpha 1} \equiv \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}$ and $\epsilon^{\alpha 2} \equiv \epsilon_{zz} - \frac{1}{3}\epsilon^{\alpha 1}$. Then the elastic

Hamiltonian can contain the three terms $\frac{1}{2} c_{11}^\alpha (\epsilon^{\alpha 1})^2 + \frac{1}{2} c_{22}^\alpha (\epsilon^{\alpha 2})^2 + c_{12}^\alpha \epsilon^{\alpha 1} \epsilon^{\alpha 2}$. A similar situation arises in the trigonal point groups 32, $3m$, $\bar{3}m$, where $[\epsilon_{yz}, \epsilon_{zx}]$ and $[\frac{1}{2}(\epsilon_{xx} - \epsilon_{yy}), \epsilon_{xy}]$ each support the same two-dimensional representation; again there are three elastic constants, one of which corresponds to the cross term.

Finally, a closely analogous situation arises for the complex representations. Thus, if $\epsilon_{yz} \pm i\epsilon_{zx}$, each supports a one-dimensional representation, we might expect two independent fully symmetric products $|\epsilon_{yz} + i\epsilon_{zx}|^2$ and $|\epsilon_{yz} - i\epsilon_{zx}|^2$, but these are equal. Hence, there is only one phenomenological elastic constant. Equivalently, we can ignore the possibility of reduction of the real two-dimensional representation. This discussion applies to the complex representations which appear in the first set of tetragonal point groups, in the first set of hexagonal point groups, and in the first set of cubic point groups. However, a slight additional complication appears in the first set of trigonal point groups. Here *two* distinct real representations are each reducible in complex form, forming the same two one-dimensional representations. In particular, $[\frac{1}{2}(x^2 - y^2) + ixy] = \frac{1}{2} e^{2i\phi}$ and $[\frac{1}{2}(x^2 - y^2) - ixy] = \frac{1}{2} e^{-2i\phi}$ form the same one-dimensional representations as do $[xz - iyx] = e^{-i\phi}$ and $[xz + iyz] = e^{i\phi}$. From the first two functions we get one elastic constant and from the second two we get one elastic constant, and the two cross terms are distinct, giving two additional elastic constants.

The number of phenomenological elastic constants for each point group is listed in the fifth and sixth columns of Table II.

Summarizing, then, let $\epsilon_i^{\Gamma, j}$ ($i=1, 2, \dots, n$) be the strain functions which form the basis for the n -dimensional representation Γ . There may be two such sets, in which case we distinguish them by the superscripts $j=1, 2$. Then the elastic energy density is

$$H_e = \sum_{\Gamma} \sum_{j, j'} \frac{1}{2} c_{jj'}^\Gamma \sum_i \epsilon_i^{\Gamma, j} \epsilon_i^{\Gamma, j'}. \quad (2.3)$$

The elastic energy H_e can be read directly from the group properties given in Column 3 of Table II. As a specific example, and for subsequent application to Dy

TABLE II. Group table for crystal point groups.

System	Point groups	Basis functions*	Dimensionality of irreducible representation	Number of elastic constants		Number of one-ion magneto-elastic coupling constants		Number of two-ion magneto-elastic coupling constants (= number of macroscopic magnetostriction coefficients) for $l=0,2$	
Triclinic	$1, \bar{1}$	$x^2, y^2, z^2, xy, yz, xz$	1	21	21	30	30	36	36
Monoclinic	$2, m, 2/m$	x^2, y^2, z^2, xy xz, yz	1 1	10 3	13	12 4	16	16 4	20
Orthorhombic	$222,$	x^2, y^2, z^2	1	6		6		9	
	$mm2,$	xy	1	1	9	1	9	1	12
	mmm	yz	1	1		1		1	
		xz	1	1		1		1	
Tetragonal	$4, \bar{4},$	$x^2+y^2+z^2, (\sqrt{3}/2)(z^2-\frac{1}{3}r^2)$	1	3		3		4	
	$4/m$	$\frac{1}{2}(x^2-y^2), xy$	1	3	7	4	9	4	10
		$\{yz, xz\}$	{1 complex 1 complex	1		2		2	
	$422,$	$x^2+y^2+z^2, (\sqrt{3}/2)(z^2-\frac{1}{3}r^2)$	1	3		3		4	
	$4/mmm,$	$\frac{1}{2}(x^2-y^2)$	1	1	6	1	6	1	7
$4mm,$	xy	1	1		1		1		
$42m$	$[yz, xz]$	2	1		1		1		
Trigonal	$3, \bar{3}$	$x^2+y^2+z^2, (\sqrt{3}/2)(z^2-\frac{1}{3}r^2)$ $\{(x^2-y^2)/2, xy\}, \{yz, xz\}$	1 {1 complex 1 complex	3 4	7	3 8	11	4 8	12
	$32, 3m,$	$x^2+y^2+z^2, (\sqrt{3}/2)(z^2-\frac{1}{3}r^2)$ $[(x^2-y^2)/2, xy], [yz, xz]$	1 2	3 3	6	3 4	7	4 4	8
	$3m$	$x^2+y^2+z^2, (\sqrt{3}/2)(z^2-\frac{1}{3}r^2)$	1	3		3		4	
Hexagonal	$6, \bar{6},$	$\{xy, xz\}$	{1 complex 1 complex	1	5	2	7	2	8
	$6/m$	$\{(x^2-y^2)/2, xy\}$	{1 complex 1 complex	1		2		2	
	$622,$	$x^2+y^2+z^2, (\sqrt{3}/2)(z^2-\frac{1}{3}r^2)$	1	3		3		4	
	$6mm,$	$[yz, xz]$	2	1	5	1	5	1	6
$6m2,$	$[(x^2-y^2)/2, xy]$	2	1		1		1		
$6/mmm$									
Cubic	$23,$	$x^2+y^2+z^2$	1	1		0		1	
	$m\bar{3}$	$\{(x^2-y^2)/2, (\sqrt{3}/2)(z^2-\frac{1}{3}r^2)\}$	{1 complex 1 complex	1	3	2	3	2	4
	$432,$	$[xy, yz, xz]$	3	1		1		1	
	$43m,$	$x^2+y^2+z^2$	1	1		0		1	
$m3m$	$(x^2-y^2)/2, (\sqrt{3}/2)(z^2-\frac{1}{3}r^2)$ $[xy, yz, xz]$	2 3	1 1	3	1	2	1	3	

* Pairs of functions in a square bracket form a two-dimensional irreducible representation. Pairs of functions in a curly bracket form a real two-dimensional representation which is reducible to complex one-dimensional representations. The numbers of magnetoelastic constants refer to terms coupling strains to spin operators of degree zero and two only.

and Gd, the elastic Hamiltonian for certain hexagonal groups is given explicitly in Sec. 4, Eq. (4.1).

We turn now to the one-ion terms in the magneto-elastic Hamiltonian. We explicitly consider only the lowest-order contributions, which are linear in strain components and of zero and second degree in spin components; terms linear in spin components are excluded because they are not symmetric under time reversal. Higher order terms are fully analogous to the lowest order terms and will be discussed generally below. Again

there are six spin operators of zero and second degree for a single ion, these being $(S^x)^2+(S^y)^2+(S^z)^2=S(S+1)$, $[(S^z)^2-\frac{1}{3}S(S+1)]$, $[(S^x)^2-(S^y)^2]$, $\frac{1}{2}[S^xS^y+S^yS^x]$, $\frac{1}{2}[S^yS^z+S^zS^y]$, and $\frac{1}{2}[S^xS^z+S^zS^x]$. The antisymmetric products such as $[S^xS^y-S^yS^x]=iS^z$ are of first degree rather than of second degree because of the spin commutation relations. The six symmetric spin operators transform isomorphically with the strains, or with the spherical harmonics, as shown in Table I. In fact, these spin operators are linear combinations of the spherical

tensor operators \mathcal{Y}_l^m , which are the operator analogs of the spherical harmonics. The isomorphism between the one-ion spin operators and the classical polynomials (or between the spherical harmonics and the spherical tensor operators) will provide the basic tool of our symmetry analysis.

To obtain the fully symmetric magnetoelastic coupling terms, we form the scalar invariant of the elastic functions and the spin operators belonging to the same representation. Thus for the tetragonal point group the two-dimensional representation with basis functions $[yz, xz]$ permits the coupling terms $\tilde{B}[\frac{1}{2}(S^y S^z + S^z S^y)\epsilon_{yz} + \frac{1}{2}(S^x S^z + S^z S^x)\epsilon_{xz}]$, where \tilde{B} is a phenomenological magnetoelastic coupling constant.

We note that the particular *site* symmetry of a given spin may be lower than the symmetry of \mathcal{G} . Thus the coupling of a given spin to the strain field may contain terms of lower symmetry than the fully symmetric terms above. The sum of such terms over all ions in the unit cell must be fully symmetric, but term-by-term the symmetry may be lower. However, all such terms give no contribution to the free energy in first order, for their average in the unperturbed density operator vanishes term-by-term. Hence these terms make no contribution to the magnetostriction and need not be written explicitly.

Unlike the elastic case, the spin operator corresponding to \mathcal{Y}_0^0 is simply a constant. This reduces the number of magnetoelastic coupling constants relating to the product of fully symmetric basis functions. The number of one-ion magnetoelastic coupling constants for each point group is listed in Columns 7 and 8 of Table II.

The case of complex representations again warrants special comment. Consider the case in which $(zy+ixz)$ and $(yz-ixz)$ each support a one-dimensional representation. Then the two independent magnetoelastic-coupling terms are $(\epsilon_{yz}+i\epsilon_{xz})(S_{yz}+iS_{xz})^*$ and $(\epsilon_{yz}-i\epsilon_{xz})(S_{yz}-iS_{xz})^*$, where we employ the notation $S_{yz} \equiv \frac{1}{2}[S^y S^z + S^z S^y]$, and similarly for S_{xz} . Each of these terms can be multiplied by a complex constant, but the self-adjoint property of the Hamiltonian requires one of these constants to be the complex conjugate of the other. Thus there are two arbitrary real constants. Equivalently, we can take the two real combinations $(\epsilon_{yz}S_{yz} + \epsilon_{xz}S_{xz})$ and $(\epsilon_{yz}S_{xz} - \epsilon_{xz}S_{yz})$; each is to be multiplied by a phenomenological coupling constant. Hence the complex representations are fully effective in forming the magnetoelastic Hamiltonian, whereas they were not in forming the elastic Hamiltonian. This fact is reflected in the numbers of magnetoelastic coupling constants listed in Table II. Such tables have, of course, been given by many authors.^{5,6}

To summarize, let $S_i^{\Gamma, j}(i=1, 2, \dots, n)$ be the spin functions which form a basis for the n -dimensional rep-

resentation Γ , different sets being distinguished by $j=1, 2$. Then the one-ion contributions H_{me}^I to the magnetoelastic Hamiltonian are

$$H_{me}^I = - \sum_f \sum_{\Gamma} \sum_{j, j'} \tilde{B}_{jj'}^{\Gamma}(f) \sum_i \epsilon_i^{\Gamma, j} S_i^{\Gamma, j'}(f) + \tilde{H}_{me}^I, \quad (2.4)$$

where $S_i^{\Gamma, j'}(f)$ refers to the spin operators of the ion at site f , and the summation over f extends over all ions in the crystal. The magnetoelastic coupling constant $\tilde{B}_{jj'}^{\Gamma}(f)$ may be a function of the ionic position if all ions are not equivalent. Finally, \tilde{H}_{me}^I contains all terms which are of lower symmetry term-by-term.

With the isomorphisms of Table I, the one-ion magnetoelastic Hamiltonians can be read directly from Table II. As a specific example, and for purposes of application, H_{me}^I is given explicitly for hexagonal point groups in Sec. 4, Eq. (4.11).

Finally, we discuss the two-ion magnetoelastic Hamiltonian H_{me}^{II} . The spin function analogous to $\frac{1}{2}[S^x S^y + S^y S^x]$ is $\frac{1}{2}[S_f^x S_g^y + S_g^x S_f^y]$, and similarly for the five remaining spin functions listed in Column 4 of Table I. These six functions are symmetric in the interchange of the site labels. In addition, there are three antisymmetric functions, such as $\frac{1}{2}[S_f^x S_g^y - S_g^x S_f^y]$. These may also couple to the strains, but their average in the unperturbed density operator (which is symmetric under interchange of sites) vanishes, and we need not consider them explicitly. Obviously, the discussion now parallels the single-ion case. Summarizing, let $S_i^{\Gamma, j}(f, g)$, ($i=1, 2, \dots, n$) be the set of two-ion spin functions (symmetric in the ion labels f and g) which form the basis of the n -dimensional representation Γ ; different sets are distinguished by $j=1, 2$. Then the two-ion contribution to the magnetoelastic Hamiltonian

$$H_{me}^{II} = - \sum_{(f, g)} \sum_{\Gamma} \sum_{j, j'} \tilde{D}_{jj'}^{\Gamma}(f, g) \times \sum_i \epsilon_i^{\Gamma, j} S_i^{\Gamma, j'}(f, g) + \tilde{H}_{me}^{II}. \quad (2.5)$$

The first summation is over all distinct ion pairs (f, g) . The constants $\tilde{D}_{jj'}^{\Gamma}(f, g)$ are phenomenological two-ion magnetoelastic coupling constants. The term \tilde{H}_{me}^{II} contains all terms which have lower symmetry term-by-term, and it also contains all terms which are antisymmetric under the interchange of the site labels.

Again the explicit form of H_{me}^{II} for hexagonal point groups is given in Sec. 4, Eq. (4.12). For other groups, H_{me}^{II} is easily read directly from Table II.

The final term in the Hamiltonian is the anisotropy energy H_a . For all but the cubic groups, there are fully symmetric terms which are of second degree in spin operators. These are the one-ion term $\frac{1}{2}\sqrt{3}[(S_f^z)^2 - \frac{1}{3}S(S+1)]$, and the two-ion term $\frac{1}{2}\sqrt{3}[S_f^z S_g^z - \frac{1}{3}\mathbf{S}_f \cdot \mathbf{S}_g]$; the remaining two-ion fully symmetric term $\mathbf{S}_f \cdot \mathbf{S}_g$ is spherically symmetric and therefore does not appear as an anisotropic term. Terms of fourth degree in spin

⁵ H. B. Huntington, *Solid State Phys.* **7**, 246 (1958).

⁶ R. S. Krishnan, *Progress in Crystal Physics* (Interscience Publishers, Inc., New York, 1960).

operators can be read from Table II by taking products of second-degree basis functions belonging to the same irreducible representation. These fourth-degree terms are the complete spin analogue of the elastic Hamiltonian.

3. EQUILIBRIUM STRAINS

The free energy, as given in Eq. (2.2), is now observed to be the sum of contributions arising separately from each irreducible representation of the point group \mathcal{G} .

$$F = F_m + \langle H_a \rangle + \sum_{\Gamma} F^{\Gamma}, \quad (3.1)$$

where

$$F^{\Gamma} = \frac{1}{2} \sum_{jj'} c_{jj'}^{\Gamma} \sum_i \epsilon_i^{\Gamma,j} \epsilon_i^{\Gamma,j'} - \sum_{jj'f} \tilde{B}_{jj'}^{\Gamma}(f) \sum_i \epsilon_i^{\Gamma,j} \langle \mathcal{S}_i^{\Gamma,j'}(f) \rangle - \sum_{jj'(f,g)} \tilde{D}_{jj'}^{\Gamma}(f,g) \sum_i \epsilon_i^{\Gamma,j} \langle \mathcal{S}_i^{\Gamma,j'}(f,g) \rangle. \quad (3.2)$$

The equilibrium values of $\epsilon_i^{\Gamma,j}$, designated as $\bar{\epsilon}_i^{\Gamma,j}$,

$$\begin{aligned} \bar{\epsilon}_i^{\Gamma,1} = & (\Delta^{\Gamma})^{-1} \sum_f [c_{22}^{\Gamma} \tilde{B}_{11}^{\Gamma}(f) - c_{12}^{\Gamma} \tilde{B}_{21}^{\Gamma}(f)] \langle \mathcal{S}_i^{\Gamma,1}(f) \rangle \\ & + (\Delta^{\Gamma})^{-1} \sum_f [c_{22}^{\Gamma} \tilde{B}_{12}^{\Gamma}(f) - c_{12}^{\Gamma} \tilde{B}_{22}^{\Gamma}(f)] \langle \mathcal{S}_i^{\Gamma,2}(f) \rangle + (\Delta^{\Gamma})^{-1} \sum_{(f,g)} [c_{22}^{\Gamma} \tilde{D}_{11}^{\Gamma}(f,g) - c_{12}^{\Gamma} \tilde{D}_{21}^{\Gamma}(f,g)] \langle \mathcal{S}_i^{\Gamma,1}(f,g) \rangle \\ & + (\Delta^{\Gamma})^{-1} \sum_{(f,g)} [c_{22}^{\Gamma} \tilde{D}_{12}^{\Gamma}(f,g) - c_{12}^{\Gamma} \tilde{D}_{22}^{\Gamma}(f,g)] \langle \mathcal{S}_i^{\Gamma,2}(f,g) \rangle, \quad (3.5) \end{aligned}$$

where

$$\Delta^{\Gamma} = c_{11}^{\Gamma} c_{22}^{\Gamma} - c_{12}^{\Gamma} c_{21}^{\Gamma}. \quad (3.6)$$

The solution for $\bar{\epsilon}_i^{\Gamma,2}$ is obtained from Eq. (3.5) merely by interchanging the labels 1 and 2. Specific examples are given in Eqs. (4.13)–(4.25), and in Eqs. (4.32)–(4.35).

Again the special cases of complex representations merit special attention. Consider the first hexagonal type, for which $\{yz, xz\}$ form a pair of complex one-dimensional representations. Then, suppressing various indices and summations,

$$F^{\Gamma} = \frac{1}{2} c [\epsilon_{xz}^2 + \epsilon_{yz}^2] - \tilde{B}^1 \epsilon_{xz} \langle \mathcal{S}_{xz} \rangle - \tilde{B}^2 \epsilon_{yz} \langle \mathcal{S}_{yz} \rangle \quad (3.7)$$

plus two-ion terms. Thus each of the real strains in a pair such as $\{\epsilon_{xz}, \epsilon_{yz}\}$ can be considered as independent and obeys the result given in Eq. (3.4). The sole effect of the reducibility to complex representations is the restriction that both ϵ_{xz} and ϵ_{yz} have the same elastic constant. Similarly, the case of two degenerate complex representations (encountered only in the first trigonal set) gives two one-dimensional pairs, each of which corresponds to Eq. (3.5).

We now turn our attention to the dependence of the spin averages on the direction of the applied field. The unperturbed Hamiltonian H_m is assumed to have a spherically symmetric component (arising from ex-

minimize F^{Γ} . Differentiating F^{Γ} with respect to $\epsilon_i^{\Gamma,j}$,

$$\begin{aligned} \sum_{j'} c_{jj'}^{\Gamma} \bar{\epsilon}_i^{\Gamma,j'} = & \sum_{j',f} \tilde{B}_{jj'}^{\Gamma}(f) \langle \mathcal{S}_i^{\Gamma,j'}(f) \rangle \\ & + \sum_{j',(f,g)} \tilde{D}_{jj'}^{\Gamma}(f,g) \langle \mathcal{S}_i^{\Gamma,j'}(f,g) \rangle. \quad (3.3) \end{aligned}$$

Two cases of interest arise; that in which j' takes only the single-value unity, and that in which j' takes two values. The only cases in which there are more than two basis sets corresponding to the same irreducible representation are the fully symmetric representations of the triclinic, monoclinic, and orthorhombic groups, for which a trivial extension is required.

For those cases in which j takes only a single value, it can be suppressed in the notation, and Eq. (3.3) becomes

$$\begin{aligned} \bar{\epsilon}_i^{\Gamma} = & (c^{\Gamma})^{-1} \sum_f \tilde{B}^{\Gamma}(f) \langle \mathcal{S}_i^{\Gamma}(f) \rangle \\ & + (c^{\Gamma})^{-1} \sum_{(f,g)} \tilde{D}^{\Gamma}(f,g) \langle \mathcal{S}_i^{\Gamma}(f,g) \rangle. \quad (3.4) \end{aligned}$$

For those cases in which j takes two values, Eqs. (3.3) are easily solved, giving

change interactions) plus a term of cylindrical symmetry arising from the external field. This latter term is described entirely, for our purposes, by specifying the direction α of the net magnetization. We consequently seek the dependence of the spin averages on the components $(\alpha_x, \alpha_y, \alpha_z)$ of α . It will be recalled that the coordinate axes are fixed in the crystal so that $\alpha_x, \alpha_y, \alpha_z$ describe the orientation of the magnetization relative to the crystallographic axes.

Consider first a one-ion average $\langle \mathcal{S}_i^{\Gamma,j}(f) \rangle$. The spin operators are linear combinations of spherical tensor operators \mathcal{Y}_l^m , as indicated in Table I. Hence

$$\langle \mathcal{S}_i^{\Gamma,j}(f) \rangle = \sum_m a_{i\Gamma}^{j,m} \langle \mathcal{Y}_l^m \rangle. \quad (3.8)$$

We re-express the spherical tensor operators in a rotated (ξ, η, ζ) coordinate system, with the ζ axis along α . Let the spherical tensors in this new coordinate system be distinguished by a tilde. Then

$$\mathcal{Y}_l^m = \sum_{m'} \langle \tilde{Y}_l^{m'} | Y_l^m \rangle \tilde{\mathcal{Y}}_l^{m'}, \quad (3.9)$$

where we have used the isomorphism between spherical tensor operators and spherical harmonics to identify the expansion coefficients. Taking the average value of both sides of Eq. (3.9), in the density operator with azimuthal

symmetry about α , it is clear that only the $m'=0$ term remains

$$\langle \mathcal{Y}_l^m \rangle = \langle \tilde{Y}_l^0 | Y_l^m \rangle \langle \tilde{\mathcal{Y}}_l^0 \rangle. \quad (3.10)$$

Furthermore,

$$\langle \tilde{Y}_l^0 | Y_l^m \rangle = Y_l^m(\alpha), \quad (3.11)$$

where $Y_l^m(\alpha)$ is the spherical harmonic whose arguments θ and ϕ are those of the magnetization direction α relative to the crystal axes. Collecting these results,

$$\langle \mathcal{S}_i^{\Gamma,j}(f) \rangle = \langle \tilde{\mathcal{Y}}_l^0 | \sum_n a_{i\Gamma_j^l, m} Y_l^m(\alpha) \rangle \quad (3.12)$$

or

$$\langle \mathcal{S}_i^{\Gamma,j}(f) \rangle = \langle \tilde{\mathcal{Y}}_l^0 | K_i^{\Gamma,j}(\alpha) \rangle, \quad (3.13)$$

where $K_i^{\Gamma,j}(\alpha)$ is the same function of $\alpha_x, \alpha_y, \alpha_z$ as $\mathcal{S}_i^{\Gamma,j}(f)$ is of S_f^x, S_f^y, S_f^z . That is, $K_i^{\Gamma,j}$ is the classical function of $\alpha_x, \alpha_y, \alpha_z$ which is isomorphic with $\mathcal{S}_i^{\Gamma,j}$ in the sense of Table I. Recalling that the \mathcal{Y}_l^m are normalized with respect to the trace operation, we can express (3.13) in a form which is independent of this definition:

$$\langle \mathcal{S}_i^{\Gamma,j}(f) \rangle = \frac{1}{(\text{tr } 1)^{1/2}} K_i^{\Gamma,j}(\alpha), \quad \text{for } l=0, \quad (3.14)$$

$$\langle \mathcal{S}_i^{\Gamma,j}(f) \rangle = \frac{\langle (S^z)^2 - \frac{1}{3}S(S+1) \rangle}{\{\text{tr}[(S^z)^2 - \frac{1}{3}S(S+1)]^2\}^{1/2}} K_i^{\Gamma,j}(\alpha), \quad \text{for } l=2. \quad (3.15)$$

For simplicity, we have written z in place of ζ in the spin averages. It is quite clear that the result above depended entirely on the isomorphism between the one-spin operators and the classical polynomials, whose transformation properties, in turn, are determined by the spherical harmonics. This isomorphism holds also for the two-spin operators, so that we find, in analogy with Eqs. (3.14) and (3.15),

$$\langle \mathcal{S}_i^{\Gamma,j}(f, g) \rangle = \frac{\langle \mathbf{S}_f \cdot \mathbf{S}_g \rangle}{\{\text{tr}(\mathbf{S}_f \cdot \mathbf{S}_g)^2\}^{1/2}} K_i^{\Gamma,j}(\alpha), \quad \text{for } l=0, \quad (3.16)$$

$$\langle \mathcal{S}_i^{\Gamma,j}(f, g) \rangle = \frac{\langle S_f^z S_g^z - \frac{1}{3} \mathbf{S}_f \cdot \mathbf{S}_g \rangle}{\{\text{tr}[S_f^z S_g^z - \frac{1}{3} \mathbf{S}_f \cdot \mathbf{S}_g]^2\}^{1/2}} K_i^{\Gamma,j}(\alpha), \quad \text{for } l=2. \quad (3.17)$$

We now obtain the final form of our general result. If the representation Γ is supported by only a single set of basis functions, then [from Eqs. (3.4), (3.14)–(3.17)]

$$\bar{\epsilon}_i^{\Gamma} = \lambda^{\Gamma}(T, H) K_i^{\Gamma}(\alpha), \quad (3.18)$$

whereas, if Γ is supported by two different bases,

$$\begin{aligned} \bar{\epsilon}_i^{\Gamma,1} &= \lambda_{11}^{\Gamma}(T, H) K_i^{\Gamma,1}(\alpha) + \lambda_{12}^{\Gamma}(T, H) K_i^{\Gamma,2}(\alpha), \\ \bar{\epsilon}_i^{\Gamma,2} &= \lambda_{21}^{\Gamma}(T, H) K_i^{\Gamma,1}(\alpha) + \lambda_{22}^{\Gamma}(T, H) K_i^{\Gamma,2}(\alpha). \end{aligned} \quad (3.19)$$

Here $\lambda_{jj'}^{\Gamma}$ absorbs all the magnetoelastic coupling constants, elastic constants, and spin correlation functions. These λ 's are therefore functions of the temperature and of the magnitude of the applied field. They play the role of the macroscopic phenomenological magnetostriction coefficients. Before examining their temperature and field dependence, we note that Eqs. (3.18) and (3.19) can be read directly from Tables I and II. In particular, we consider the totally symmetric direct product of strain functions from Column 2 and bilinear direction cosines from Column 5 of Table I, combining these as dictated by Table II. If $\epsilon_i^{\Gamma,j}$ and $K_i^{\Gamma,j}(\alpha)$ are the functions which are paired in this way, then the equilibrium value of $\bar{\epsilon}_i^{\Gamma,j}$ are given by Eqs. (3.18) and (3.19).

The magnetostriction constant λ^{Γ} of Eq. (3.18) is given by

$$\begin{aligned} \lambda^{\Gamma}(T, H) &= (c^{\Gamma})^{-1} \sum_f B^{\Gamma}(f; T, H) \\ &\quad + (c^{\Gamma})^{-1} \sum_{(f, \theta)} D^{\Gamma}(f, g; T, H), \end{aligned} \quad (3.20)$$

whereas the magnetostriction constants of Eq. (3.19) are

$$\begin{aligned} \lambda_{jj'}^{\Gamma}(T, H) &= (\Delta^{\Gamma})^{-1} \sum_f [c_{j\bar{j}}^{\Gamma} B_{jj'}^{\Gamma}(f; T, H) - c_{j\bar{j}}^{\Gamma} B_{\bar{j}j'}^{\Gamma}(f; T, H)] \\ &\quad + (\Delta^{\Gamma})^{-1} \sum_{(f, \theta)} [c_{j\bar{j}}^{\Gamma} D_{jj'}^{\Gamma}(f, g; T, H) - c_{j\bar{j}}^{\Gamma} D_{\bar{j}j'}^{\Gamma}(f, g; T, H)], \end{aligned} \quad (3.21)$$

where we use the notation \bar{j} ("not j ") to denote $\bar{j}=2$ if $j=1$, and vice versa. Also $\lambda^{\Gamma} \equiv \lambda_{11}^{\Gamma,1}$, $B^{\Gamma} \equiv B_{11}^{\Gamma,1}$, and $D^{\Gamma} \equiv D_{11}^{\Gamma,1}$, the superfluous indices being omitted for convenience in Eq. (3.20).

The *effective magnetostrictive coupling coefficients* are given by

$$\begin{aligned} B_{jj'}^{\Gamma}(f; T, H) &= 0, & \text{if } \Gamma = \Gamma_{\alpha} \text{ and } j' = 1 \\ &= \bar{B}_{jj'}^{\Gamma}(f) \mathcal{E}_f(T, H), & \text{otherwise,} \end{aligned} \quad (3.22)$$

$$\begin{aligned} D_{jj'}^{\Gamma}(f, g; T, H) &= \bar{D}_{jj'}^{\Gamma}(f, g) \mathcal{E}_{f\theta}(T, H), & \text{if } \Gamma = \Gamma_{\alpha} \text{ and } j' = 1 \\ &= \bar{D}_{jj'}^{\Gamma}(f, g) \mathcal{E}_{f\theta}(T, H), & \text{otherwise,} \end{aligned} \quad (3.23)$$

where $\epsilon^{\alpha,1}$ is always taken as the volume dilatation ($\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}$).

The one-ion and two-ion longitudinal correlation functions, and the two-ion isotropic correlation function are

defined by

$$\mathfrak{L}_f(T, H) = \frac{\langle (S_f^z)^2 - \frac{1}{3}S(S+1) \rangle}{\{\text{tr}[(S_f^z)^2 - \frac{1}{3}S(S+1)]\}^{1/2}} = \left(\frac{(2S+3)!}{5!(2S-2)!} \right)^{1/2} \langle (S_f^z)^2 - \frac{1}{3}S(S+1) \rangle, \quad (3.24)$$

$$\mathfrak{L}_{f_0}(T, H) = \frac{\langle S_f^z S_{\theta}^z - \frac{1}{3}\mathbf{S}_f \cdot \mathbf{S}_{\theta} \rangle}{\{\text{tr}[S_f^z S_{\theta}^z - \frac{1}{3}\mathbf{S}_f \cdot \mathbf{S}_{\theta}]\}^{1/2}} = \frac{3\sqrt{3}\langle S_f^z S_{\theta}^z - \frac{1}{3}\mathbf{S}_f \cdot \mathbf{S}_{\theta} \rangle}{\sqrt{2}S(S+1)(2S+1)}, \quad (3.25)$$

$$\mathfrak{g}_{f_0}(T, H) = \frac{\langle \mathbf{S}_f \cdot \mathbf{S}_{\theta} \rangle}{\{\text{tr}(\mathbf{S}_f \cdot \mathbf{S}_{\theta})^2\}^{1/2}} = \frac{\sqrt{3}\langle \mathbf{S}_f \cdot \mathbf{S}_{\theta} \rangle}{S(S+1)(2S+1)}. \quad (3.26)$$

The temperature and field dependence of all effective magnetostrictive coupling coefficients, and hence of all magnetostriction constants, is characterized entirely by the three correlation functions $\mathfrak{L}_f(T, H)$, $\mathfrak{L}_{f_0}(T, H)$, and $\mathfrak{g}_{f_0}(T, H)$. The isotropic correlation function $\mathfrak{g}_{f_0}(T, H)$ enters only in the discussion of fully symmetric strains ($\Gamma = \Gamma_{\alpha}$); all less-symmetric strains are associated only with longitudinal correlation functions.

The volume dilatation $\epsilon^{\alpha,1}$ is the only fully symmetric strain for the cubic point groups. The corresponding magnetostriction constant [Eq. (3.20)] contains two-ion contributions only [cf., Eq. (3.22)]. For all noncubic point groups, the volume dilatation is degenerate at least with $\epsilon^{\alpha,2} = (\sqrt{3}/2)[\epsilon_{zz} - \frac{1}{3}\epsilon^{\alpha,1}]$. The resulting temperature dependence arises from a linear combination of longitudinal and isotropic correlation functions.

The anisotropy energy which arises from the term of degree l in spin operators similarly has the temperature dependence of $\langle \mathfrak{Y}_l^0 \rangle$.

Finally, the one-ion magnetoelastic coefficient, arising from higher degree magnetoelastic terms, first order in strains and l th degree in spin, has the temperature dependence of $\langle \mathfrak{Y}_l^0 \rangle$. The two-ion coefficient of the same degree has the temperature dependence of $\langle \mathfrak{Y}_l^0(f, g) \rangle$, where $\mathfrak{Y}_l^0(f, g)$ is the two-ion operator isomorphic with $\mathfrak{Y}_l^0(f)$.

Adding a superscript l to $\tilde{B}_{jj'}^{\Gamma}$ to indicate the degree of the spin operators associated with it, we summarize:

$$\begin{aligned} B_{jj'}^{\Gamma, l}(f; T, H) &= 0, & \text{if } \Gamma = \Gamma_{\alpha} \text{ and } j' = 1 \text{ (i.e., if } l=0) \\ &= \tilde{B}_{jj'}^{\Gamma, l}(f) \langle \mathfrak{Y}_l^0 \rangle, & \text{otherwise;} \end{aligned} \quad (3.27)$$

and, similarly,

$$\begin{aligned} D_{jj'}^{\Gamma, l}(f, g; T, H) &= \tilde{D}_{jj'}^{\Gamma, l}(f, g) \langle \mathfrak{Y}_l^0(f, g) \rangle = \tilde{D}_{jj'}^{\Gamma}(f, g) \mathfrak{g}_{f_0}(T, H), & \text{if } l=0 \text{ (i.e., } \Gamma = \Gamma_{\alpha} \text{ and } j' = 1) \\ &= \tilde{D}_{jj'}^{\Gamma}(f, g) \mathfrak{L}_{f_0}(T, H), & \text{if } l=2 \\ &= \tilde{D}_{jj'}^{\Gamma, l}(f, g) \langle \mathfrak{Y}_l^0(f, g) \rangle, & \text{in general.} \end{aligned} \quad (3.28)$$

We shall illustrate these results for hexagonal crystals in the following section and then consider various approximate calculations of the correlation functions in subsequent sections.

Finally, we note that the magnetostrictive coefficients $\lambda_{jj'}^{\Gamma}(T, H)$ are closely related to, but not identical to, the conventional magnetostrictive coefficients. The latter are defined as follows: Let $\delta l/l$ be the fractional change in length of the crystal, measured in the direction $(\beta_x, \beta_y, \beta_z)$, when the magnetization is in the direction $(\alpha_x, \alpha_y, \alpha_z)$. Again this quantity must be fully symmetric, so that $\delta l/l$ can be read from Table I by taking the direct product of the bilinear α functions (Column 3) with the bilinear β functions. The independent constants in this biquadratic expression are the conventional magnetostrictive coefficients. This is essentially the method used by Döring and Simon.³ Alternatively, we can calculate $\delta l/l$ directly by⁷

$$\delta l/l = \sum_{\mu, \nu} \bar{\epsilon}_{\mu\nu} \beta_{\mu} \beta_{\nu} \quad (\mu, \nu = x, y, z) \quad (3.29)$$

and expressing the $\bar{\epsilon}_{\mu\nu}$ in terms of the symmetry strains

⁷ R. Becker and W. Döring, *Ferromagnetismus* (Julius Springer-Verlag, Berlin, 1939).

$\bar{\epsilon}_i^{\Gamma, j}$, and these in turn in terms of α by Eq. (3.19), one obtains the relation between the two types of magnetostrictive coefficients. This relationship is illustrated in the following section.

We note in passing that the hexagonal and cubic systems each have two symmetry types, only one of which is commonly familiar. Thus the hexagonal point groups treated above (622 , $6mm$, $\bar{6}m2$, and $6/mmm$) have six magnetostriction constants, whereas the remaining hexagonal point groups (6 , $\bar{6}$ and $6/m$) have eight magnetostriction constants (of degree zero and two in the direction cosines of the magnetization). Similarly, the common cubic groups (432 , $\bar{4}3m$, and $m\bar{3}m$) have three magnetostriction constants, whereas the cubic point groups 23 and $m\bar{3}$ have four magnetostriction constants.³ As a matter of interest, the particularization of Eq. (3.29) to the cubic point groups 23 and $m\bar{3}$ is given in Eq. (4.36) below.

4. PARTICULARIZATION TO HEXAGONAL AND CUBIC SYSTEMS

To illustrate the general formalism, and to facilitate application to particular systems, we first indicate the

specific form taken by the theory in the special case of a hexagonal system.

For the second type of hexagonal symmetry (point groups 622 , $6mm$, $6m2$, and $6/mmm$), the elastic Hamiltonian is

$$H_e = \frac{1}{2}c_{11}^\alpha(\epsilon^{\alpha,1})^2 + c_{12}^\alpha\epsilon^{\alpha,1}\epsilon^{\alpha,2} + \frac{1}{2}c_{22}^\alpha(\epsilon^{\alpha,2})^2 + \frac{1}{2}c^\gamma[(\epsilon_1^\gamma)^2 + (\epsilon_2^\gamma)^2] + \frac{1}{2}c^\epsilon[(\epsilon_1^\epsilon)^2 + (\epsilon_2^\epsilon)^2], \quad (4.1)$$

where the symmetry strains are related to the Cartesian strains by

$$\epsilon^{\alpha,1} = \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}, \quad (4.2)$$

$$\epsilon^{\alpha,2} = (\sqrt{3}/2)[\epsilon_{zz} - \frac{1}{3}\epsilon^{\alpha,1}], \quad (4.3)$$

$$\epsilon_1^\gamma = \frac{1}{2}[\epsilon_{xx} - \epsilon_{yy}], \quad \epsilon_2^\gamma = \epsilon_{xy}, \quad (4.4)$$

$$\epsilon_1^\epsilon = \epsilon_{yz}, \quad \epsilon_2^\epsilon = \epsilon_{zx}, \quad (4.5)$$

and where the symmetry elastic constants are related to the conventional Cartesian elastic constants by

$$c_{11}^\alpha = \frac{1}{3}[2c_{11} + 2c_{12} + 4c_{13} + c_{33}], \quad (4.6)$$

$$c_{12}^\alpha = (2/3\sqrt{3})[-c_{11} - c_{12} + c_{13} + c_{33}], \quad (4.7)$$

$$c_{22}^\alpha = (2/3)c_{11} + (2/3)c_{12} - (8/3)c_{13} + (4/3)c_{33}, \quad (4.8)$$

$$c^\gamma = 2[c_{11} - c_{12}], \quad (4.9)$$

$$c^\epsilon = 4c_{44}. \quad (4.10)$$

The one-ion magnetoelastic Hamiltonian is

$$H_{me}^I(f) = -\bar{B}_{12}^\alpha\epsilon^{\alpha,1}(\sqrt{3}/2)[(S_f^z)^2 - \frac{1}{3}S(S+1)] - \bar{B}_{22}^\alpha\epsilon^{\alpha,2}(\sqrt{3}/2)[(S_f^z)^2 - \frac{1}{3}S(S+1)] - \bar{B}^\gamma\{\epsilon_1^\gamma\frac{1}{2}[(S_f^x)^2 - (S_f^y)^2] + \epsilon_2^\gamma\frac{1}{2}[S_f^x S_f^y + S_f^y S_f^x]\} - \bar{B}^\epsilon\{\epsilon_1^\epsilon\frac{1}{2}[S_f^y S_f^z + S_f^z S_f^y] + \epsilon_2^\epsilon\frac{1}{2}[S_f^x S_f^z + S_f^z S_f^x]\}, \quad (4.11)$$

and the two-ion magnetoelastic Hamiltonian is

$$H_{me}^{II}(f,g) = -\bar{D}_{11}^\alpha\epsilon^{\alpha,1}\mathbf{S}_f \cdot \mathbf{S}_g - \bar{D}_{12}^\alpha\epsilon^{\alpha,1}(\sqrt{3}/2)[S_f^z S_g^z - \frac{1}{3}\mathbf{S}_f \cdot \mathbf{S}_g] - \bar{D}_{21}^\alpha\epsilon^{\alpha,2}\mathbf{S}_f \cdot \mathbf{S}_g - \bar{D}_{22}^\alpha\epsilon^{\alpha,2}(\sqrt{3}/2)[S_f^z S_g^z - \frac{1}{3}\mathbf{S}_f \cdot \mathbf{S}_g] - \bar{D}^\gamma\{\epsilon_1^\gamma\frac{1}{2}[S_f^x S_g^x - S_f^y S_g^y] + \epsilon_2^\gamma\frac{1}{2}[S_f^x S_g^y + S_f^y S_g^x]\} - \bar{D}^\epsilon\{\epsilon_1^\epsilon\frac{1}{2}[S_f^y S_g^z + S_f^z S_g^y] + \epsilon_2^\epsilon\frac{1}{2}[S_f^x S_g^z + S_f^z S_g^x]\}. \quad (4.12)$$

The equilibrium strains are then given by [Eqs. (3.18)–(3.19)]

$$\bar{\epsilon}^{\alpha,1} = \lambda_{11}^\alpha K^{\alpha,1}(\boldsymbol{\alpha}) + \lambda_{12}^\alpha K^{\alpha,2}(\boldsymbol{\alpha}) = \lambda_{11}^\alpha + \lambda_{12}^\alpha(\sqrt{3}/2)[\alpha_z^2 - \frac{1}{3}], \quad (4.13)$$

$$\bar{\epsilon}^{\alpha,2} = \lambda_{22}^\alpha K^{\alpha,1}(\boldsymbol{\alpha}) + \lambda_{22}^\alpha K^{\alpha,2}(\boldsymbol{\alpha}) = \lambda_{21}^\alpha + \lambda_{22}^\alpha(\sqrt{3}/2)[\alpha_z^2 - \frac{1}{3}], \quad (4.14)$$

$$\bar{\epsilon}_1^\gamma = \lambda^\gamma K_1^\gamma(\boldsymbol{\alpha}) = \lambda^\gamma\frac{1}{2}[\alpha_x^2 - \alpha_y^2], \quad (4.15)$$

$$\bar{\epsilon}_2^\gamma = \lambda^\gamma K_2^\gamma(\boldsymbol{\alpha}) = \lambda^\gamma\alpha_x\alpha_y, \quad (4.16)$$

$$\bar{\epsilon}_1^\epsilon = \lambda^\epsilon K_1^\epsilon(\boldsymbol{\alpha}) = \lambda^\epsilon\alpha_y\alpha_z, \quad (4.17)$$

$$\bar{\epsilon}_2^\epsilon = \lambda^\epsilon K_2^\epsilon(\boldsymbol{\alpha}) = \lambda^\epsilon\alpha_x\alpha_z, \quad (4.18)$$

where [Eqs. (3.20)–(3.26)]

$$\lambda_1^\alpha = (1/\Delta^\alpha) \sum_{(f,\theta)} [c_{22}^\alpha \bar{D}_{11}^\alpha(f,g) - c_{12}^\alpha \bar{D}_{21}^\alpha(f,g)] \mathcal{G}_{f\theta}(T,H), \quad (4.19)$$

$$\lambda_{21}^\alpha = (1/\Delta^\alpha) \sum_{(f,\theta)} [c_{11}^\alpha \bar{D}_{21}^\alpha(f,g) - c_{22}^\alpha \bar{D}_{11}^\alpha(f,g)] \mathcal{G}_{f\theta}(T,H), \quad (4.20)$$

$$\lambda_{12}^\alpha = (1/\Delta^\alpha) \sum_f [c_{22}^\alpha \bar{B}_{12}^\alpha(f) - c_{12}^\alpha \bar{B}_{22}^\alpha(f)] \mathcal{L}_f(T,H) + (1/\Delta^\alpha) \sum_{(f,\theta)} [c_{22}^\alpha \bar{D}_{12}^\alpha(f,g) - c_{12}^\alpha \bar{D}_{22}^\alpha(f,g)] \mathcal{L}_{f\theta}(T,H), \quad (4.21)$$

$$\lambda_{22}^\alpha = (1/\Delta^\alpha) \sum_f [c_{11}^\alpha \bar{B}_{22}^\alpha(f) - c_{21}^\alpha \bar{B}_{12}^\alpha(f)] \mathcal{L}_f(T,H) + (1/\Delta^\alpha) \sum_{(f,\theta)} [c_{11}^\alpha \bar{D}_{22}^\alpha(f,g) - c_{21}^\alpha \bar{D}_{12}^\alpha(f,g)] \mathcal{L}_{f\theta}(T,H), \quad (4.22)$$

$$\lambda^\gamma = (1/c^\gamma) \sum_f \bar{B}^\gamma(f) \mathcal{L}_f(T,H) + (1/c^\gamma) \sum_{(f,\theta)} \bar{D}^\gamma(f,g) \mathcal{L}_{f\theta}(T,H), \quad (4.23)$$

$$\lambda^\epsilon = (1/c^\epsilon) \sum_f \bar{B}^\epsilon(f) \mathcal{L}_f(T,H) + (1/c^\epsilon) \sum_{(f,\theta)} \bar{D}^\epsilon(f,g) \mathcal{L}_{f\theta}(T,H), \quad (4.24)$$

and

$$\Delta^\alpha = c_{11}^\alpha c_{22}^\alpha - (c_{12}^\alpha)^2. \quad (4.25)$$

Finally, the fractional change in length measured in a direction \mathfrak{B} (with direction cosines $\beta_x, \beta_y, \beta_z$) is [Eq. (3.29)]

$$\delta l/l = [\frac{1}{3}\bar{\epsilon}^{\alpha,1} - \frac{2}{3}\bar{\epsilon}^{\alpha,2} + \epsilon_1^\gamma]\beta_x^2 + [\frac{1}{3}\bar{\epsilon}^{\alpha,1} - \frac{2}{3}\bar{\epsilon}^{\alpha,2} - \epsilon_1^\gamma]\beta_y^2 + [\frac{4}{3}\bar{\epsilon}^{\alpha,2} + \frac{1}{3}\bar{\epsilon}^{\alpha,1}]\beta_z^2 + 2\bar{\epsilon}_2^\gamma\beta_x\beta_y + 2\bar{\epsilon}_1^\epsilon\beta_y\beta_z + 2\bar{\epsilon}_2^\epsilon\beta_x\beta_z \quad (4.26)$$

or

$$\begin{aligned} \delta l/l = & \frac{1}{3}\lambda_{11}^\alpha(T, H) + (1/2\sqrt{3})\lambda_{12}^\alpha(T, H)(\alpha_z^2 - \frac{1}{3}) + 2\lambda_{21}^\alpha(T, H)(\beta_z^2 - \frac{1}{3}) \\ & + \sqrt{3}\lambda_{22}^\alpha(T, H)(\alpha_z^2 - \frac{1}{3})(\beta_z^2 - \frac{1}{3}) + 2\lambda^\gamma(T, H)\{\frac{1}{4}(\alpha_x^2 - \alpha_y^2)(\beta_x^2 - \beta_y^2) + \alpha_x\alpha_y\beta_x\beta_y\} \\ & + 2\lambda^\epsilon(T, H)\{\alpha_y\alpha_z\beta_y\beta_z + \alpha_x\alpha_z\beta_x\beta_z\}. \end{aligned} \quad (4.27)$$

This equation establishes the relation between our magnetostriction coefficients and the conventional ones [in which the numerical coefficients in Eq. (4.27) are absorbed into the λ 's].

The reader is cautioned that our definition of λ_{ij}^α differs slightly from that adopted in the companion paper by Clark, De Savage, and Bozorth⁴, although the definitions of λ^γ and λ^ϵ do agree. The relation between our coefficients and those of Clark, De Savage, and Bozorth (which appear in the right-hand members of the equations below) are

$$\lambda_{11}^\alpha = 2\lambda_1^{\alpha,0} + \lambda_2^{\alpha,0} + 2\lambda_1^{\alpha,2} + \lambda_2^{\alpha,2}, \quad (4.28)$$

$$(\sqrt{3}/2)\lambda_{12}^\alpha = 2\lambda_1^{\alpha,2} + \lambda_2^{\alpha,2}, \quad (4.29)$$

$$2\lambda_{21}^\alpha = -\lambda_1^{\alpha,0} + \lambda_2^{\alpha,0}, \quad (4.30)$$

$$\sqrt{3}\lambda_{22}^\alpha = -\lambda_1^{\alpha,2} + \lambda_2^{\alpha,2}. \quad (4.31)$$

As mentioned at the end of the preceding section, there are certain hexagonal groups ($6, \bar{6}, 6/m$) and certain cubic groups ($23, m\bar{3}$) which have more than the accustomed number of magnetostriction constants. The method outlined above leads to the following expressions for the 23 and $m\bar{3}$ cubic groups

$$\epsilon^\alpha = \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz} = \lambda^\alpha, \quad (4.32)$$

$$\epsilon_1^\gamma = (1/2\sqrt{3})[2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy}] = \lambda_1^\gamma(\sqrt{3}/2)(\alpha_z^2 - \frac{1}{3}) + \lambda_2^\gamma\frac{1}{2}(\alpha_x^2 - \alpha_y^2), \quad (4.33)$$

$$\epsilon_2^\gamma = \frac{1}{2}[\epsilon_{xx} - \epsilon_{yy}] = -\lambda_2^\gamma(\sqrt{3}/2)(\alpha_z^2 - \frac{1}{3}) + \lambda_1^\gamma\frac{1}{2}(\alpha_x^2 - \alpha_y^2), \quad (4.34)$$

$$\epsilon_1^\epsilon = \epsilon_{yz} = \lambda^\epsilon\alpha_y\alpha_z; \quad \epsilon_2^\epsilon = \epsilon_{xz} = \lambda^\epsilon\alpha_x\alpha_z; \quad \epsilon_3^\epsilon = \epsilon_{xy} = \lambda^\epsilon\alpha_x\alpha_y, \quad (4.35)$$

and

$$\begin{aligned} \delta l/l = & \frac{1}{3}\lambda^\alpha + \frac{1}{2}\lambda_1^\gamma[3(\alpha_z^2 - \frac{1}{3})(\beta_z^2 - \frac{1}{3}) + (\alpha_x^2 - \alpha_y^2)(\beta_x^2 - \beta_y^2)] \\ & + (\sqrt{3}/2)\lambda_2^\gamma[(\alpha_x^2 - \alpha_y^2)(\beta_z^2 - \frac{1}{3}) - (\alpha_z^2 - \frac{1}{3})(\beta_x^2 - \beta_y^2)] + 2\lambda^\epsilon[\alpha_x\alpha_y\beta_x\beta_y + \alpha_y\alpha_z\beta_y\beta_z + \alpha_x\alpha_z\beta_x\beta_z]. \end{aligned} \quad (4.36)$$

5. THEORIES OF THE SINGLE-ION SPIN FUNCTIONS: DYSPROSIUM

As is well known, the low temperature behavior of the spin averages is related to the low-temperature behavior of the magnetization. Van Vleck⁸ has shown that, at sufficiently low temperatures in ferromagnets,

$$\begin{aligned} \langle \mathcal{Y}_l^0(f; T, H) \rangle / \langle \mathcal{Y}_l^0(f; 0, 0) \rangle \\ = \langle \mathcal{Y}_l^0(f, g; T, H) \rangle / \langle \mathcal{Y}_l^0(f, g; 0, 0) \rangle \\ = [m(T, H)]^{l(l+1)/2}. \end{aligned} \quad (5.1)$$

This power law was applied by Kittel and Van Vleck⁹ to the magnetostriction coefficients. The result in Eq. (5.1) is an immediate consequence¹⁰ of the Wigner-Eckart theorem for the matrix elements of spherical tensor operators. When particularized to the spin functions of direct interest to us, it states

$$\mathcal{J}_{f\theta}(T, H) / \mathcal{J}_{f\theta}(0, 0) = m^0(T, H) = 1, \quad T \ll T_c, \quad (5.2)$$

$$\begin{aligned} \mathcal{L}_f(T, H) / \mathcal{L}_f(0, 0) = \mathcal{L}_{f\theta}(T, H) / \mathcal{L}_{f\theta}(0, 0) \\ = m^3(T, H), \quad T \ll T_c. \end{aligned} \quad (5.3)$$

Unfortunately, this $[l(l+1)/2]$ -power law is rather a weak theorem; it states only that the coefficients in the leading term ($T^{3/2}$) in the series expansions of both sides of the equation are equal, whereas even the $T^{5/2}$ terms may be different.

In a separate publication, H. Callen and S. Shtrikman¹¹ show that a wide range of theories of ferromagnetism predict a universal relationship between $\langle \mathcal{Y}_l^0(f; T, H) \rangle$ and $m(T, H)$, for all temperatures. These theories include all "renormalized collective-excitation" theories—that is, all theories which describe the ferromagnet in terms of collective excitations, while permitting the frequency of an excitation to depend upon the presence of other excitations. Spin-wave theory is in this class, as are the random-phase approximation^{12,13} and other Green's function theories.¹⁴ A trivial example of such theories is molecular-field theory, which is equivalent to a spin-wave model with all spin-wave frequencies degenerate (analogous to the Einstein model of vibrational modes).

The dependence of $\langle \mathcal{Y}_2^0(f; T, H) \rangle$ and $\langle \mathcal{Y}_4^0(f; T, H) \rangle$

¹¹ H. B. Callen and S. Shtrikman, *Solid State Commun.* (to be published).

¹² S. V. Tyablikov, *Ukr. Mat. Zh.* **11**, 287 (1959).

¹³ R. Tahir-Kheli and D. ter Haar, *Phys. Rev.* **127**, 88 (1962).

¹⁴ H. B. Callen, *Phys. Rev.* **130**, 890 (1963).

⁸ J. H. Van Vleck, *J. Phys. Radium* **20**, 128 (1959).

⁹ C. Kittel and J. H. Van Vleck, *Phys. Rev.* **118**, 1231 (1960).

¹⁰ H. B. Callen and E. Callen (to be published).

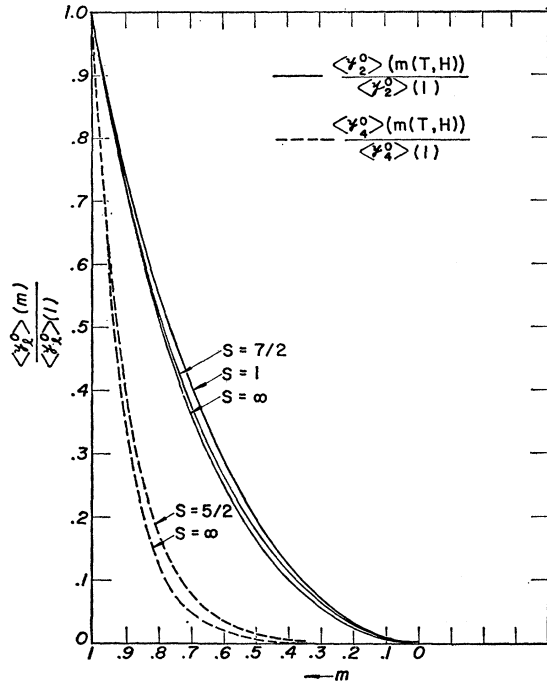


FIG. 1. Magnetization dependence of spherical tensors $\langle \mathcal{Y}_l^0(S) \rangle$ for various degrees l and spins S . From Wolf (Ref. 15) and Callen and Callen (Ref. 16).

on $m(T, H)$ has been calculated by W. P. Wolf¹⁵ for several spin values, by molecular-field theory. Also the present authors have calculated $\langle \mathcal{Y}_l^0(f; T, H) \rangle$ as a function of $m(T, H)$ for general l but infinite spin.¹⁶ As remarked above, these calculations are in fact of much greater generality than the molecular-field theory on which they are nominally based.

The results of Wolf and of Callen and Callen are shown in Fig. 1. As expected, the results for moderate spin rapidly converge toward the results for infinite spin; the relevant parameter is the number of discrete azimuthal levels $(2S+1)$ over which summations are carried. As the infinite-spin case is expressible in closed form, it is particularly convenient and, in most cases, it is of quite sufficient accuracy for practical applications. For infinite spin we have¹⁶

$$\langle \mathcal{Y}_l^0(f; T, H) \rangle / \langle \mathcal{Y}_l^0(f; 0, 0) \rangle = \hat{I}_{l+1/2}(x), \quad (5.4)$$

where $\hat{I}_{l+1/2}$ is the ratio of the hyperbolic Bessel function of order $(l+\frac{1}{2})$ to the hyperbolic Bessel function of order $\frac{1}{2}$; $\hat{I}_{l+1/2}(x) = I_{l+1/2}(x)/I_{1/2}(x)$. The argument x is to be considered as a parameter to be expressed in terms of the magnetization by inversion of the relationship

$$m(T, H) = \langle \mathcal{Y}_1^0(f; T, H) \rangle / \langle \mathcal{Y}_1^0(f; 0, 0) \rangle = \hat{I}_{3/2}(x) = \coth x - 1/x. \quad (5.5)$$

¹⁵ W. P. Wolf, Phys. Rev. **108**, 1152 (1957).

¹⁶ E. R. Callen and H. B. Callen, J. Phys. Chem. Solids **16**, 310 (1960).

It will be noted that $\hat{I}_{3/2}(x)$ is the familiar Langevin function, and analogously $\hat{I}_{l+1/2}(x)$ can be considered as a "higher-order Langevin function." Equation (5.4) was first given by Keffer.¹⁷

In the molecular field theory, the significance of x is

$$x = \beta\mu(h+H), \quad (5.6)$$

where $\beta = 1/k_B T$, μ is the magnetic moment per ion, H is the external field, and h is an effective molecular field which is simply proportional to $m(T, H)$. However, we again stress that Eqs. (5.4) and (5.5) have greater generality than molecular-field theory, and that, in general, x does not have the significance of Eq. (5.6). From the formal point of view, x is simply defined as a function of $m(T, H)$ by Eq. (5.5), and $m(T, H)$ is considered either to be given by an independent calculation or to be taken from experiment.

To illustrate the application of the above results, we first consider the paramagnetic region ($T > T_c$), where $m(T, H)$ is small. Then, from Eq. (5.5), we conclude that x is small, and

$$m(T, H) = \frac{1}{3}x + \dots \quad (5.7)$$

We then recall that

$$\hat{I}_{l+1/2}(x) = [1/(2l+1)!!]x^l + \dots, \quad x \ll 1, \quad (5.8)$$

whence

$$\hat{I}_{l+1/2}(x) \simeq 3^l m^l(T, H) / (2l+1)!!, \quad m \ll 1, \quad (5.9)$$

and, in particular,

$$\begin{aligned} \mathcal{L}_f(T, H) / \mathcal{L}_f(0, 0) &= \hat{I}_{5/2}(x) = (9/15)m^2(T, H) \\ &= (9\chi^2(T)/15M_0^2)H^2, \quad T \gg T_c. \end{aligned} \quad (5.10)$$

Here $(2l+1)!!$ denotes $1 \times 3 \times 5 \cdots (2l+1)$ and $\chi(T)$ is the susceptibility.

Below T_c , it is convenient to expand $m(T, H)$ and x around their zero-field values, $m(T, 0)$ and x_0 . For this purpose, we recall the recurrence relations

$$\begin{aligned} \frac{d}{dx} \hat{I}_{l+1/2}(x) &= \frac{l}{2l+1} \hat{I}_{l-1/2}(x) \\ &+ \frac{l+1}{2l+1} \hat{I}_{l+3/2}(x) - \hat{I}_{3/2}(x) \hat{I}_{l+1/2}(x) \end{aligned} \quad (5.11)$$

and

$$\hat{I}_{l+3/2}(x) = \hat{I}_{l-1/2}(x) - [(2l+1)/x] \hat{I}_{l+1/2}(x). \quad (5.12)$$

In particular, we find

$$\begin{aligned} \frac{\mathcal{L}_f(T, H)}{\mathcal{L}_f(0, 0)} &= \hat{I}_{5/2}(x) = \hat{I}_{5/2}(x_0) \\ &+ \frac{d\hat{I}_{5/2}(x_0)}{dx_0} \frac{dx_0}{dm(T, 0)} \frac{dm(T, 0)}{dH} H + \dots \end{aligned} \quad (5.13)$$

¹⁷ F. Keffer, Phys. Rev. **100**, 1692 (1955).

$$= 1 - \frac{3m(T,0)}{x_0} - \frac{3}{x_0} \frac{3m(T,0) - x_0[1 - m^2(T,0)]}{2m(T,0) - x_0[1 - m^2(T,0)]} \times \frac{\chi(T)}{M_0} H + \dots, \quad (5.14)$$

where x_0 is to be eliminated by the relation

$$m(T,0) = \coth x_0 - (1/x_0). \quad (5.15)$$

If $m(T,0)$ and $\chi(T)$ are known from experiment, this relation determines the temperature and field dependence of $\mathcal{L}_f(T, H)$. However, if $\chi(T)$ is not known empirically, we can make the further approximation of taking $\chi(T)$ from molecular-field theory. Then

$$\frac{\mathcal{L}_f(T, H)}{\mathcal{L}_f(0,0)} = 1 - \frac{3m(T,0)}{x_0} + \frac{1}{x_0} \frac{\mu H}{kT_c} + \dots \quad (5.16)$$

Finally, we note the simplification of these equations at very low temperature. For small T (large x),

$$\hat{I}_{l+1/2}(x) = 1 - [l(l+1)/2x] + \dots \quad (5.17)$$

and

$$m = \hat{I}_{3/2}(x) = 1 - (1/x) + \dots, \quad (5.18)$$

whence

$$\hat{I}_{l+1/2}(x) = 1 - [l(l+1)/2](1-m) + \dots \simeq m^{l(l+1)/2}, \quad (5.19)$$

corroborating the $[l(l+1)/2]$ -power law.

Clark, DeSavage, and Bozorth⁴ analyze in detail the field and temperature dependences of the magnetoelastic strains in dysprosium metal. Their measurements extend over the ferromagnetic, antiferromagnetic, and paramagnetic phases. In the intermediate phase, the antiferromagnetic spiral structure is suppressed by a sufficiently large magnetic field in the basal plane, to cause ferromagnetic alignment. Below the Neel temperature of 178°K, magnetic anisotropy restricts the magnetization to the basal plane, and only the λ^γ coefficient can be measured. Figure 2 shows this coefficient, at fixed field, as a function of temperature, from just above the Curie temperature (85°K), far into the paramagnetic region. Over this interval, λ^γ varies by four orders of magnitude, but it obeys the single-ion theory throughout. The saturation magnetostriction follows the theoretical temperature dependence, and the "forced" field-dependent part is linear in field below T_N , quadratic above, and with the single-ion temperature dependence everywhere. Clearly the two-ion term of Eq. (4.23) is not contributing, in this case. In their paper, Clark, DeSavage, and Bozorth show that the shear magnetostriction λ^ϵ also obeys the single-ion theory through the paramagnetic range in which it can be measured. On the other hand, their measurements of the volume strain and c -axis elongation do not follow the one-ion theory, as one would expect. However, because of the aniso-

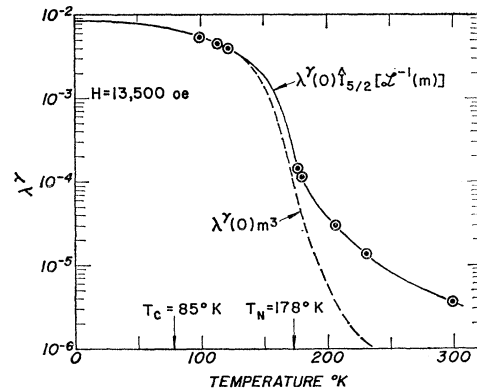


FIG. 2. Temperature dependence of magnetostriction coefficient λ^γ of dysprosium. From Clark, DeSavage, and Bozorth (Ref. 4).

tropic susceptibility, Clark, DeSavage, and Bozorth do not separate these particular one- and two-ion strains, hence we cannot apply to their data the analysis of the two-ion terms to which we now turn.

6. ISOTROPIC CORRELATION FUNCTION; ANOMALOUS THERMAL EXPANSION AND VOLUME MAGNETOSTRICTION

In the following two sections, we shall discuss two approximate calculations of the isotropic correlation function $\mathcal{G}_{f\theta}(T, H)$. However, we first recall the observable magnetostriction components which depend upon this correlation function; these are the fully symmetric strains $\bar{\epsilon}^{\alpha,j}$. For cubic crystals, there is only one such strain, the volume dilatation, and its field and temperature dependence is entirely dictated by $\mathcal{G}_{f\theta}(T, H)$. For all other crystal symmetries, both the volume dilatation $\bar{\epsilon}^{\alpha,1}$ and $\bar{\epsilon}^{\alpha,2} = \frac{2}{3}[\bar{\epsilon}_{zz} - \frac{1}{3}\bar{\epsilon}^{\alpha,1}]$ are fully symmetric, and hence each is a linear combination of $\mathcal{G}_{f\theta}(T, H)$ and of the longitudinal spin functions \mathcal{L}_f and $\mathcal{L}_{f\theta}$:

$$\bar{\epsilon}^{\alpha,1} = \delta V/V = \lambda_{11}^\alpha(T, H) + \lambda_{12}^\alpha(T, H)(\sqrt{3}/2)(\alpha_z^2 - \frac{1}{3}), \quad (6.1)$$

$$\bar{\epsilon}^{\alpha,2} = (\sqrt{3}/2)(\bar{\epsilon}_{zz} - \frac{1}{3}\bar{\epsilon}^{\alpha,1}) = \lambda_{21}^\alpha(T, H) + \lambda_{22}^\alpha(T, H)(\sqrt{3}/2)(\alpha_z^2 - \frac{1}{3}), \quad (6.2)$$

where, as in Eqs. (4.19)–(4.22), λ_{11}^α and λ_{21}^α depend only on $\mathcal{G}_{f\theta}(T, H)$, whereas λ_{12}^α and λ_{22}^α depend on \mathcal{L}_f and $\mathcal{L}_{f\theta}$:

$$\lambda_{11}^\alpha(T, H) = (1/\Delta^\alpha) \sum_{(f,\theta)} [c_{22}^\alpha \bar{D}_{11}^\alpha(f, g) - c_{12}^\alpha \bar{D}_{21}^\alpha(f, g)] \mathcal{G}_{f\theta}(T, H), \quad (6.3)$$

$$\lambda_{21}^\alpha(T, H) = (1/\Delta^\alpha) \sum_{(f,\theta)} [c_{11}^\alpha \bar{D}_{21}^\alpha(f, g) - c_{22}^\alpha \bar{D}_{11}^\alpha(f, g)] \mathcal{G}_{f\theta}(T, H). \quad (6.4)$$

The two terms of Eqs. (6.1) or (6.2) can be distinguished experimentally. Thus the volume dilatation

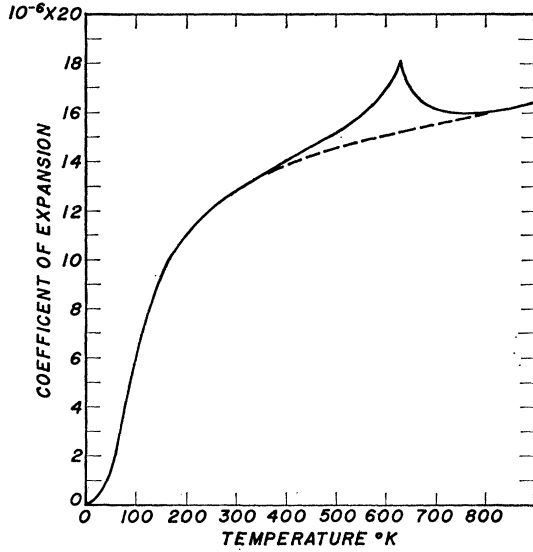


FIG. 3. Thermal expansion coefficient of nickel. The dashed curve represents the normal Gruneisen behavior. From Nix and MacNair (Ref. 18).

can be measured as a function of the magnetization direction α , and the average over all directions can be determined as a function of temperature. This *isotropic component* of the volume dilatation will be denoted by $\bar{\epsilon}_{\text{isotr}}^{\alpha,1}$ or $(\delta V/V)_{\text{isotr}}$. Consequently, for *all* crystal symmetries,

$$(\delta V/V)_{\text{isotr}} = \lambda_{11}^{\alpha}(T, H) \quad (6.5)$$

and, similarly,

$$\bar{\epsilon}_{\text{isotr}}^{\alpha,2} = \lambda_{21}^{\alpha}(T, H). \quad (6.6)$$

In fact, the isotropic component of the volume dilatation is simply the anomalous thermal expansion coefficient, or the magnetic contribution to the thermal expansion coefficient. Thus

$$\alpha_{\text{magnetic}} = \frac{1}{V} \left(\frac{\delta V}{\delta T} \right)_{\text{isotr}} = \frac{d\lambda_{11}^{\alpha}(T, H)}{dT}. \quad (6.7)$$

In Fig. 3, we show the thermal expansion coefficient of nickel¹⁸ and, for comparison, the Gruneisen behavior typical of a nonmagnetic material. The difference of the two curves is α_{magnetic} , and it is seen that this difference peaks at the Curie temperature where $\mathcal{G}_{f\theta}(T, 0) \sim \langle \mathbf{S}_f \cdot \mathbf{S}_\theta \rangle$ is strongly temperature-dependent. Integrating α_{magnetic} from infinite temperature down to temperature T gives $(\delta V/V)_{\text{isotr}} = \lambda_{11}^{\alpha}(T, 0)$. In nickel, this dilatation at 0°K is about 10^{-4} , whereas the other magnetostriction coefficients are of the order of 10^{-5} .

In 1921, Chevenard¹⁹ observed that in some metals the anomalous volume dilatation $(\delta V/V)_{\text{isotr}}$ is approximately proportional to $m^2(T, 0)$, below T_c . This is, of course, just the result expected by molecular-field

theory. However, the relationship between $m^2(T, 0)$ and $(\delta V/V)_{\text{isotr}}$ is not a very satisfactory one. Whereas $m^2(T, 0)$ vanishes at T_c , the anomalous volume dilatation falls at T_c to about 28% of its zero temperature value, and it then maintains appreciable values in the paramagnetic region to about $1.2T_c$. This is consistent with our identification of $(\delta V/V)_{\text{isotr}}$ as proportional to the correlation function $\langle \mathbf{S}_f \cdot \mathbf{S}_\theta \rangle$, which is known²⁰ to persist well above T_c .

In a completely analogous manner, the c/a ratio of a uniaxial crystal will change with temperature, with a pronounced dependence in the vicinity of the Curie temperature. The isotropic part (that part independent of magnetization direction) is given by Eqs. (6.6) and (6.4) and is determined by $\mathcal{G}_{f\theta}(T, H)$.

At constant temperature, a change in the magnitude of the applied field also changes $\mathcal{G}_{f\theta}(T, H)$. The resultant change in $(\delta V/V)_{\text{isotr}}$ is the *isotropic forced volume magnetostriction*. The analogous change in the z -axis dilatation $\bar{\epsilon}_{\text{isotr}}^{\alpha,2}$ is also an isotropic forced magnetostriction.

Thus, to recapitulate, λ^{α} for cubic crystals and both λ_{11}^{α} and λ_{21}^{α} for all other crystals, depend on the isotropic correlation function $\mathcal{G}_{f\theta}(T, H)$. They determine the isotropic volume dilatation and the isotropic linear strain $\frac{1}{2}\sqrt{3}[\bar{\epsilon}_{zz} - \frac{1}{3}(\delta V/V)]$. The spontaneous temperature dependence of $\mathcal{G}_{f\theta}(T, H)$ thereby determines the anomalous thermal (volume) expansion coefficient α_{magnetic} and the isotropic, anomalous, thermal, z -axis expansion. And, finally, the magnetic field dependence of $\mathcal{G}_{f\theta}(T, H)$ determines the isotropic forced volume magnetostriction and the isotropic forced z -axis dilatation.

7. CLUSTER THEORY OF $\mathcal{G}_{f\theta}(T, H)$; EuO AND EuS: GADOLINIUM

To calculate $\mathcal{G}_{f\theta}(T, H)$, we must adopt a particular model. Unfortunately, the simplest theory, molecular-field theory, is inadequate for this purpose. In fact, $\mathcal{G}_{f\theta}(T, H)$ reduces to $m^2(T, H)$ in molecular-field theory, and for $H=0$ it therefore vanishes at the Curie temperature. However, the value of $\mathcal{G}_{f\theta}(T_c, 0)/\mathcal{G}_{f\theta}(0, 0)$ has been obtained by high-temperature series extrapolation for nearest-neighbor models,²⁰ and it has the very appreciable value of 0.596 for spin $\frac{1}{2}$, at the Curie temperature. Hence we must have recourse to an approximation more powerful than molecular-field theory.

In another paper,²¹ we have developed a two-spin cluster approximation for ferromagnets with nearest-neighbor and next-nearest-neighbor exchange interactions. We there applied the theory to EuO and EuS, which are cubic ferromagnets with positive nearest-neighbor exchange J_1 and smaller negative next-nearest-neighbor exchange J_2 . Using the exchange constants J_1 and J_2 suggested by Charap and Boyd²² (on the basis of a spin-wave analysis of low-temperature

¹⁸ F. C. Nix and D. MacNair, Phys. Rev. **60**, 597 (1941).

¹⁹ P. Chevenard, Comptes Rend. **172**, 1655 (1921).

²⁰ C. Domb and M. F. Sykes, Phys. Rev. **128**, 168 (1962).

²¹ H. B. Callen and E. Callen, Phys. Rev. **136**, A1675 (1964).

²² S. H. Charap and E. L. Boyd, Phys. Rev. **133**, A811 (1964).

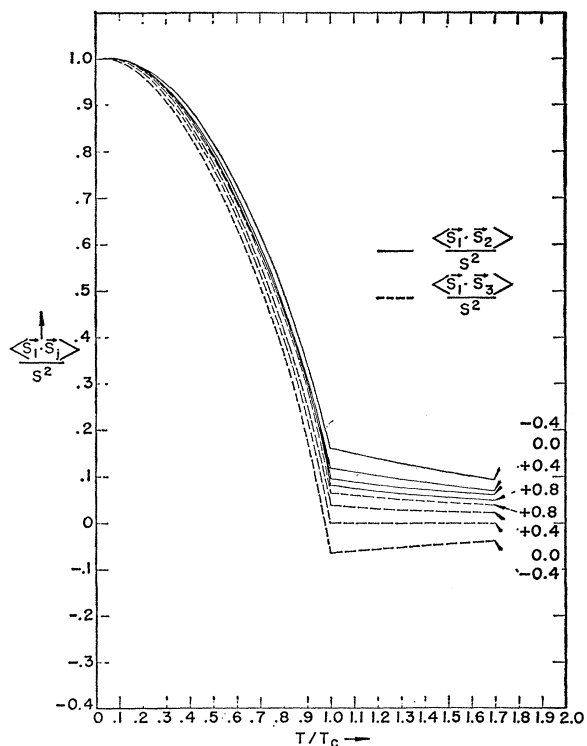


FIG. 4. Nearest and next-neighbor isotropic correlation functions for various values of J_2/J_1 calculated by the cluster theory (Ref. 21).

data), the cluster theory predicts $T_c = 16.92^\circ\text{K}$ for EuS, whereas the observed value is 16.52°K . The theoretical specific heat is also in excellent agreement with the observed²³ λ -like anomaly at the Curie temperature, particularly in the ferromagnetic region (below T_c). This agreement attests to the success of the cluster theory in predicting the isotropic correlation function $\mathcal{S}_{fg}(T, H) \sim \langle \mathbf{S}_f \cdot \mathbf{S}_g \rangle$ on which the magnetic energy depends. The results of the cluster theory are shown in Fig. 4, where we give $\langle \mathbf{S}_f \cdot \mathbf{S}_g \rangle$ for nearest neighbors and for next-nearest-neighbors, for various ratios J_2/J_1 of exchange constants.

In applying the cluster theory to the magnetostriction in the europium chalcogenides, it is plausible that $\bar{D}^\alpha(f, g)$ should also be short-ranged. In fact, we might reasonably expect that the magnetostrictive coupling arises by the strain dependence of the exchange interaction: $\bar{D}^\alpha(f, g) = \partial J_{fg} / \partial \epsilon^\alpha$. Accordingly, we tentatively adopt the simplifying assumption that $\bar{D}^\alpha(f, g)$ is non-zero only for nearest and next-nearest neighbors. Then Fig. 4 provides the theoretical prediction of the various effects discussed in the preceding section.

The close analogy between the anomalous thermal expansion coefficient and the magnetic specific heat is

²³ V. L. Moruzzi and D. T. Teaney, *Solid State Commun.* **1**, 127 (1963).

also of interest:

$$\alpha_{\text{magnetic}} = N z_1 \frac{\sqrt{3} \bar{D}^\alpha(1, 2)}{S(S+1)(2S+1)} \frac{d}{dT} \langle \mathbf{S}_1 \cdot \mathbf{S}_2 \rangle + N z_2 \frac{\sqrt{3} \bar{D}^\alpha(1, 3)}{S(S+1)(2S+1)} \frac{d}{dT} \langle \mathbf{S}_1 \cdot \mathbf{S}_3 \rangle, \quad (7.1)$$

$$c_v = N z_1 J_{12} \frac{d}{dT} \langle \mathbf{S}_1 \cdot \mathbf{S}_2 \rangle + N z_2 J_{13} \frac{d}{dT} \langle \mathbf{S}_1 \cdot \mathbf{S}_3 \rangle. \quad (7.2)$$

Here N is the number of ions per unit volume, z_1 is the number of nearest neighbors ($z_1 = 12$), z_2 is the number of next-nearest neighbors ($z_2 = 6$), and ions 2 and 3 are representative nearest and next-nearest neighbors of ion #1. For EuO, J_{13} is very small compared to J_{12} , and it is plausible that only the first terms in Eqs. (7.1) and (7.2) need be retained; in that case, α_{magnetic} and c_v should exhibit the same temperature dependence. In EuS, the second-neighbor exchange is appreciable, but α_{magnetic} and c_v should be compared. In passing, we note that even in nickel, with a long range of interaction, the behaviors of c_v ²⁴ and α_{magnetic} are suggestively similar, as is indicated by comparison of Figs. 3 and 5.

Unfortunately, no data on the forced magnetostriction of the europium chalcogenides are available, but we can note the similarity between our theoretical results and the observed forced volume magnetostriction in gadolinium.

Corner and Hutchinson²⁵ first observed that the forced-volume magnetostriction in gadolinium is linear in field below T_c and quadratic well above T_c , but that the linearity below T_c appears to persist several degrees above T_c . However, the linearity above T_c can only be apparent, for time-reversal symmetry in the paramagnetic state precludes odd powers in the field. Bozorth and Wakiyama²⁶ have confirmed the observations of Corner and Hutchinson and have also measured the isotropic and anisotropic parts of the c -axis forced magnetostriction [the first and second terms of Eq. (6.2), respectively]. Again, both of these are linear in H below T_c , and the anisotropic term is only about 1.5% of the isotropic term. This is in contrast to dysprosium, in which the anisotropic term of the c -axis magneto-

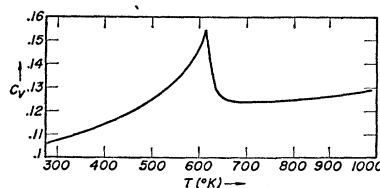


FIG. 5. Specific heat of nickel. From Moser (Ref. 24).

²⁴ H. Moser, *Phys. Z.* **37**, 737 (1936).

²⁵ W. D. Corner and F. Hutchinson, *Proc. Phys. Soc. (London)* **75**, 781 (1960).

²⁶ R. M. Bozorth and T. Wakiyama, *J. Phys. Soc. Japan* **17**, 1669, 1670 (1962); **18**, 97 (1963).

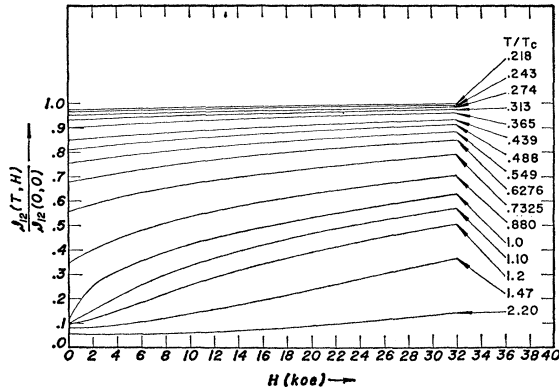


FIG. 6. Magnetic-field dependence of the nearest-neighbor isotropic correlation function for various T/T_c . Calculated by cluster theory (Ref. 21) with nearest-neighbor interactions.

striction is large. In more physical terms, this observation implies that elongation of the c axis of gadolinium alters the isotropic exchange energy ($\bar{D}_{12}^\alpha(f, g)\mathbf{S}_f \cdot \mathbf{S}_g \epsilon^{\alpha, 2}$) but does not introduce appreciable anisotropic exchange [$\bar{D}_{22}^\alpha(f, g)(\sqrt{3}/2)(S_f^z S_g^z - \frac{1}{3}\mathbf{S}_f \cdot \mathbf{S}_g)\epsilon^{\alpha, 2}$] nor lead to one-ion anisotropy terms [$\bar{B}^\alpha(f)(\sqrt{3}/2)[(S_f^z)^2 - \frac{1}{3}S(S+1)]\epsilon^{\alpha, 2}$]. Finally, Coleman and Pavlovic²⁷ and Coleman²⁸ have made comprehensive measurements of the temperature and field dependence of all six magnetostriction coefficients of gadolinium [Eqs. (4.19)–(4.24)]. To summarize, then, all investigators observe that λ_{21}^α , the coefficient of the isotropic part of the c -axis elongation, is linear in field below T_c and quadratic well above T_c , but that the linearity appears to persist several degrees above T_c . We shall now show that, although the magnetostriction of gadolinium apparently arises through the long-range Ruderman-Kittel-Kasuya-Yosida interaction, an analogous pseudolinearity occurs also in a nearest-neighbor model. Again we stress, however, that the pseudolinearity is the sum of even terms ($aH^2 + bH^4 + cH^6 + \dots$) in a series which converges slowly just above T_c ; true linearity above T_c is disallowed by time-reversal symmetry.

In Fig. 6, we show the field dependence of the isotropic correlation function (and therefore of λ_{21}^α) for a nearest-neighbor model, as computed by the two-spin cluster theory. For $T < T_c$, the expected linearity for small fields is clear, as is the expected quadratic dependence for $T \gg T_c$. The curve for $T = 1.10 T_c$ exhibits an apparent linearity, which appears to persist up to perhaps $1.3 T_c$.

Davies²⁹ has also discussed the anomalous pseudolinear field dependence of the forced magnetostriction of gadolinium just above T_c , again using a nearest-neighbor model. His analysis starts with the thermo-

dynamic identity

$$(\partial V / \partial H)_{T, \rho} = -V_0 (\partial M / \partial P)_{T, H}, \quad (7.3)$$

which Davies then writes as

$$\frac{dV}{V_0} = - \left(\frac{\partial M}{\partial J} \right)_{H, T} \left(\frac{\partial J}{\partial T_c} \right) \left(\frac{\partial T_c}{\partial P} \right) dH. \quad (7.4)$$

Davies calculates $(\partial M / \partial J)_{H, T}$ by the constant coupling approximation, takes $\partial J / \partial T_c$ from the same theory, and relies on independent experimental data for $\partial T_c / \partial P$.

To exhibit the relation to our method, we note that

$$m = (1/NS) \sum_j (\text{tr} S_j^z e^{-\beta H} / \text{tr} e^{-\beta H}), \quad (7.5)$$

so that, recalling the form of \mathcal{H} and recalling that $\langle S^z \rangle = 0$ in the paramagnetic range,

$$\partial m / \partial J \sim \sum_{j \neq 0} \langle S_j^z \mathbf{S}_j \cdot \mathbf{S}_0 \rangle. \quad (7.6)$$

In our analysis, the dominant terms in the volume dilatation are

$$\delta V / V = 2 \sum_{(f, g)} \bar{D}_{11}^\alpha(f, g) \langle \mathbf{S}_f \cdot \mathbf{S}_g \rangle. \quad (7.7)$$

And the derivative with respect to the field would be

$$\frac{\partial}{\partial H} \frac{\delta V}{V} \sim 4 \sum_{j(f, g)} \bar{D}_{11}^\alpha(f, g) \langle S_j^z \mathbf{S}_j \cdot \mathbf{S}_g \rangle. \quad (7.8)$$

Thus the correlation functions which appear implicitly in each theory are identical. The above considerations can be extended to second derivatives as well, so that our treatment of the forced magnetostriction in the paramagnetic range is implicitly related to Davies' analysis.

Tonegawa³⁰ has also analyzed the forced magnetostriction and anomalous thermal expansion of gadolinium. He calculates the exchange interaction by the Ruderman-Kittel-Kasuya-Yosida mechanism, and relates the anisotropy of the forced magnetostriction and anomalous thermal expansion to an asphericity of the Fermi surface.

8. SCALAR CORRELATION FUNCTION IN THE PARAMAGNETIC REGION: RANDOM PHASE APPROXIMATION

Although the cluster expansion of Ref. (21) yields scalar correlation functions and a specific heat in extremely close agreement with the measured curve for EuS below T_c , it is less satisfactory in the paramagnetic region, and we turn to the random phase approximation as formulated for general spin by Tahir-Kheli and ter Haar.¹⁴ Their analysis can be cast in the following form.

²⁷ W. E. Coleman and A. S. Pavlovic, Phys. Rev. **135**, A426 (1964).

²⁸ W. E. Coleman, thesis, West Virginia University, Morgantown, West Virginia, 1964 (unpublished).

²⁹ J. T. Davies, Proc. Phys. Soc. (London) **79**, 821 (1962).

³⁰ T. Tonegawa, J. Phys. Soc. Japan **19**, 1168 (1964).

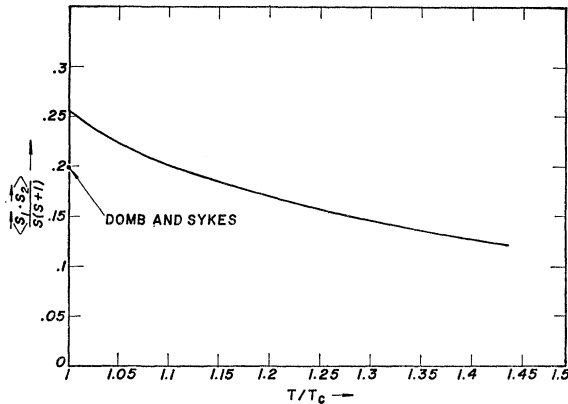


FIG. 7. Nearest-neighbor isotropic correlation function in the paramagnetic region, for $S = \frac{1}{2}$, calculated by random phase approximation. The point represents the high-temperature series extrapolation of Domb and Sykes (Ref. 20).

Let ξ be the susceptibility in units of $2zJ/\mu^2$. Then

$$\langle \mathbf{S}_f \cdot \mathbf{S}_g \rangle / S(S+1) = \tilde{\phi}(\mathbf{R}_{fg}, \xi) / \tilde{\phi}(0, \xi), \quad (8.1)$$

where

$$\tilde{\phi}(\mathbf{R}, \xi) \equiv (1/N) \sum_k \{ e^{-ik \cdot \mathbf{R}} / [1 + \xi(1 - \gamma_k)] \} \quad (8.2)$$

and

$$T/T_c = F(-1) / \xi \tilde{\phi}(0, \xi). \quad (8.3)$$

Here γ_k is the Fourier transform of J_{fg} , in units of zJ , and $F(-1)$ is 1.51638 for simple cubic, 1.39320 for body-centered cubic, and 1.34466 for face-centered cubic.

For each ξ and \mathbf{R}_{fg} we have evaluated $\phi(\mathbf{R}_{fg}, \xi)$ by numerical integration through one octant of the Brillouin zone, on the NOL 7090 computer. Thus Eq. (8.1) gives $\langle \mathbf{S}_f \cdot \mathbf{S}_g \rangle / S(S+1)$ as a function of ξ . Elimination of ξ gives $\langle \mathbf{S}_f \cdot \mathbf{S}_g \rangle / S(S+1)$ as a function of T/T_c . The resultant theoretical curve, for nearest-neighbor exchange and $S = \frac{1}{2}$, is given in Fig. 7. For comparison, we show the value of $\langle \mathbf{S}_f \cdot \mathbf{S}_g \rangle / S(S+1)$ at the Curie temperature, as calculated by Domb and Sykes²⁰ by extrapolation of the high-temperature series expansion. In this latter connection, we note that the random phase approximation gives $\langle \mathbf{S}_f \cdot \mathbf{S}_g \rangle_{T=T_c} = 0.2554 S(S+1)$ for the fcc lattice.

9. TWO-ION LONGITUDINAL CORRELATION FUNCTION $\mathcal{L}_{fg}(T, H)$

The last of the three spin functions which arise in the theory of magnetostriction is the two-ion longitudinal correlation function $\mathcal{L}_{fg}(T, H) \sim \langle S_f^z S_g^z - \frac{1}{3} \mathbf{S}_f \cdot \mathbf{S}_g \rangle$.

It will be recalled, from Eq. (5.1), that this function satisfies the $[\frac{1}{2}l(l+1)]$ -power law at sufficiently low temperatures, whence

$$(3/2S^2) \langle S_f^z S_g^z - \frac{1}{3} \mathbf{S}_f \cdot \mathbf{S}_g \rangle = m^2(T, H), \quad T \ll T_c. \quad (9.1)$$

However, this result applies only to ions f and g which are strongly correlated (by virtue of being reasonably

close together). For ions f and g sufficiently far apart, the spins are independent and

$$(3/2S^2) \langle S_f^z S_g^z - \frac{1}{3} \mathbf{S}_f \cdot \mathbf{S}_g \rangle = m^2(T, H). \quad (9.2)$$

It is of interest to consider briefly the range parameter $R(T)$ which determines the transition from the m^3 to the m^2 behavior. This range is roughly equal to the shortest wavelength of spin wave which is thermally excited at the given temperature:

$$k_B T = \hbar \omega \simeq 2S_z J a^2 k^2 \simeq 2S_z J a^2 (2\pi/R)^2. \quad (9.3)$$

Our range parameter $R(T)$ is the "Debye length" of Horwitz and Mattis,³¹ who show that the exchange interaction between spin pairs at separation R_i is magnetization renormalized for $R_i \gg R(T)$.

The temperature dependence given by Eq. (9.2) for distant neighbors is valid at almost all temperatures. However, the m^3 temperature dependence for near neighbors holds only at low temperature. In the physically interesting range of temperature, we must have recourse to approximation methods.

By an extension of the cluster theory,²¹ we have calculated the two-ion longitudinal correlation function for several spin values and for various ratios of exchange constants J_2/J_1 . These correlation functions for nearest-neighbor and next-nearest-neighbor spins are shown in Fig. 8, as a function of m^2 , assuming $S = \frac{1}{2}$, fcc lattice,

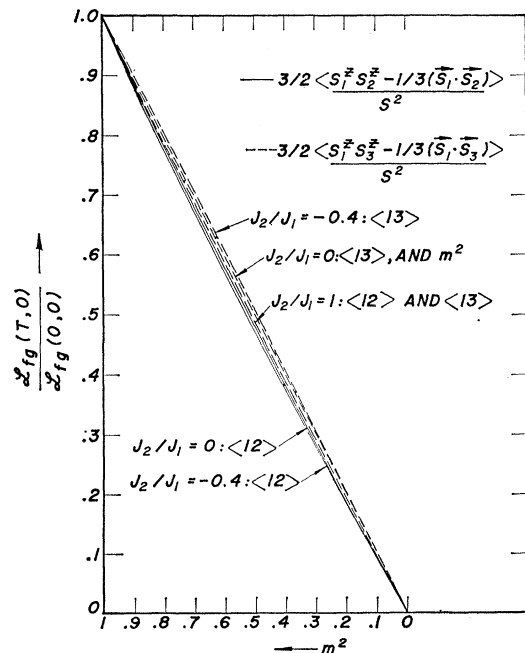


FIG. 8. Nearest- and next-nearest-neighbor longitudinal correlation function versus the square of the magnetization, calculated by cluster theory (Ref. 21), with $S = \frac{1}{2}$ and fcc, and for several ratios J_2/J_1 .

³¹ L. P. Horwitz and D. C. Mattis, Phys. Rev. Letters **10**, 511 (1963).

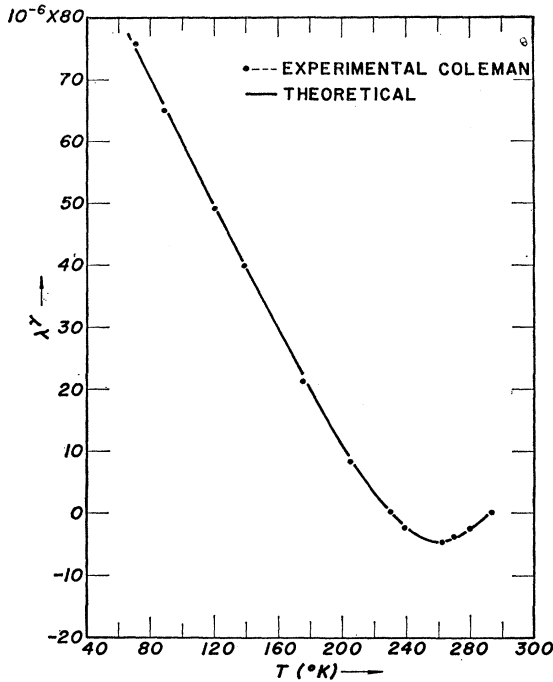


FIG. 9. Temperature dependence of magnetostriction coefficient λ^γ of gadolinium. Experimental data from Coleman (Ref. 28); theoretical curve calculated by Eq. (9.6).

zero magnetic field, and three ratios J_2/J_1 . Curves for other spin values are almost identical to those for $S=7/2$. Although the correlation functions do vary as m^3 at sufficiently low temperature, as required by Eq. (8.1), the range of temperature in which this law is valid is extremely narrow. Over almost the entire temperature range, both the nearest- and next-nearest-neighbor correlation functions vary very closely as m^2 , for all ratios J_2/J_1 . We conclude that, for the purposes of applications, it is sufficient to represent the two-ion longitudinal correlation function by m^2 :

$$\mathcal{L}_{f\theta}(T, H) = \frac{3\sqrt{3}\langle S_f^z S_\theta^z - \frac{1}{3}\mathbf{S}_f \cdot \mathbf{S}_\theta \rangle}{\sqrt{2}S(S+1)(2S+1)} \approx \frac{6^{1/2}S}{(S+1)(2S+1)} m^2(T, H). \quad (9.4)$$

As an illustration of the application of this result, we consider the magnetostriction coefficient λ^γ of gadolinium. The measurements of Coleman²⁸ are shown in Fig.

9, and it is seen that this coefficient changes sign before vanishing at the Curie temperature, in quantitative agreement with the measurements of others.^{26,32,33} The magnetostriction equation used by Coleman is not identical to Eq. (4.27), as Coleman's function transforming as Γ_γ is an admixture of both $l=2$ and $l=4$, whereas our functions are pure $l=2$. However, the magnetoelastic coefficient of the $l=4$ angular dependence presumably is negligibly small, as has been carefully confirmed in dysprosium.⁴ Consequently, Coleman's R_5 coefficient can be associated directly with our λ^γ ; $R_5 = \lambda^\gamma$.

From Eqs. (4.23), (5.10), and (9.4), we have

$$\lambda^\gamma = \left[\left(\frac{(2S+3)!}{5!(2S-2)!} \right)^{1/2} \frac{1}{c^\gamma} \sum_f \bar{B}^\gamma(f) \right] \hat{I}_{5/2}(x) + \left[\frac{6^{1/2}S}{(S+1)(2S+1)} \frac{1}{c^\gamma} \sum_{(f,g)} \bar{D}^\gamma(f,g) \right] m^2(T, H), \quad (9.5)$$

where x is to be expressed in terms of $m(T)$ by Eq. (5.5). The magnetization of gadolinium has been measured by Elliott, Legvold, and Spedding³⁴ and by Nigh, Legvold and Spedding.³⁵ Regarding the bracketed quantities in Eq. (9.5) as adjustable constants, we obtain exact agreement with experiment over the entire range, as shown in Fig. 9, by choosing

$$\lambda^\gamma = 351 \times 10^{-6} \hat{I}_{5/2}(x) - 243 \times 10^{-6} m^2(T, H). \quad (9.6)$$

Tsuya and Clark³⁶ have shown that the real magnetic dipole contribution to the two-ion magnetoelastic coupling is much too small to account for the coefficient of m^2 in Eq. (9.6). Those authors have also estimated³⁷ the coefficient of the $\hat{I}_{5/2}(x)$ term above for the heavy rare earth metals. They have shown that the coefficient of the $\hat{I}_{5/2}(x)$ term in gadolinium can arise from a 4% admixture of a Tb-type wave function into the Gd ground state.

³² K. P. Belov, R. Z. Levitin, S. A. Nikitin, and A. V. Ped'ko, Zh. Eksperim. i Teor. Fiz. **40**, 1562 (1961) [English transl.: Soviet Phys.—JETP **13**, 1096 (1961)].

³³ G. Alstad and S. Legvold, J. Appl. Phys. **35**, 1752 (1964).

³⁴ J. F. Elliott, S. Legvold and F. H. Spedding, Phys. Rev. **91**, 28 (1953).

³⁵ H. E. Nigh, S. Legvold, and F. H. Spedding, Phys. Rev. **132**, 1092 (1963).

³⁶ N. Tsuya and A. E. Clark (private communication).

³⁷ N. Tsuya, A. E. Clark, and R. M. Bozorth, in Proceedings of the International Conference on Magnetism, Nottingham, England, September 1964 (unpublished).