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Effective Magnetic Anisotropy and Magnetostriction of Monocrystals

PHILIP K. BALTZER
RCA Laboratories, Radio Corporation of America, Princeton, New Jersey

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The effective magnetic anisotropy energies associated with the domain theory are derived to second order for cubic crystals. These effective anisotropy energies are expressed in terms of the intrinsic anisotropy for an undeformed crystal, the magnetostriction, and the elastic moduli. Also, in the process of deriving the effective anisotropy energies to second order, the expression for the magnetostriction of a cubic crystal is expanded to sixth order in the direction cosines for the magnetization. The interrelation between the effective anisotropy in domains and domain walls is studied and its influence upon the domain configuration suggested.

I. INTRODUCTION

THE magnetic anisotropy of an undeformed monocrystal will be defined as the *intrinsic* magnetic anisotropy. The effective anisotropy of a monocrystal, which has been permitted to deform freely due to magnetostriction and/or deformed by an applied stress, is the sum of the intrinsic anisotropy and contributions from the magnetostriction and/or the applied stress. The effective anisotropy of a saturated monocrystal is the effective *domain* anisotropy and is the only effective anisotropy energy which can be directly measured. The intrinsic and *domain-wall* anisotropy energies can not be directly measured and must be determined from the measured effective domain anisotropy, the magnetostriction, and the elastic moduli.

Other workers have derived the effective domain anisotropy expression to the first order.[1,2] Experimental data on many materials indicate the anisotropy energies must be expressed at least to the second order. Hence the main purpose of this paper is to derive and study the effective anisotropy energy expressions to the second order. The domain and the domain-wall anisotropy energies are interdependent through the intrinsic anisotropy and magnetostriction. The interrelation between domain and domain-wall anisotropy energies is shown to have a profound influence upon the magnetic domain configuration in a crystal and hence also upon its macroscopic properties.

The second-order terms in the expression describing the anisotropy energies are sixth order in the magnetization direction cosines. Therefore, the magnetostriction must also be expressed to sixth order in the magnetization direction direction cosines. Since existing expressions for the magnetostriction are inadequate, a new and more general expression has been derived. The sixth-order magnetostriction expression, which has been derived, conveniently reduces to existing lower order expressions and in addition is independent of the nature of the magnetic anisotropy.

II. MAGNETOSTRICTION

The spontaneous magnetostriction of an unconstrained cubic monocrystal at a fixed temperature can be expressed as a series expansion in the direction cosines α_i and β_i for the directions of magnetization and measurement respectively. The direction cosines are referred to the cubic crystallographic axes. Only the terms of even order in the α_i and β_i are nonzero because of the cubic symmetry. The magnetostriction can be expressed to second, fourth, or sixth order in the α_i with two, five, or nine constants respectively. Second- and fourth-order expressions have already been derived[1] which are satisfactory except for the dependence of the fourth-order expression upon the magnetic anisotropy. The zero reference for the existing fourth-order expression, although arbitrary, is defined as the strain for the special domain configuration of an equal volume of domains magnetized along *each of the equivalent easy directions of magnetization*, e.g., the $\langle 111\rangle$ directions in nickel and the $\langle 100\rangle$ in iron. Thus, in cases where the anisotropy changes the direction of easy magnetization with temperature or composition, the magnetostriction for the same variations does not have the same zero reference. A sixth-order expression has already been derived but it does not conveniently reduce to the existing lower order expressions, and in addition it involves ten constants.[3]

The required sixth-order expression for describing the magnetostriction has been obtained by a straightforward extension of the method used by Becker and Döring to determine the fourth-order expression; see

TABLE I. Five-constant magnetostriction data.

Material	$h_1\times10^6$	$h_2\times10^6$	$h_3\times10^6$	$h_4\times10^6$	$h_5\times10^6$
78% Ni-Fe (quenched)[a]	13.7	2.6	−0.3	1.1	−0.1
78% Ni-Fe (slow cooled)[a]	20.9	2.8	1.7	−1.4	−0.2
Nickel[a]	−68.8	−36.5	−2.8	−7.5	7.7
Magnetite (Fe_3O_4)[b]	−24.5	123.3	−0.4	−4.76	−20.1

[a] R. M. Bozorth and R. W. Hamming, Phys. Rev. **89**, 865 (1953).
[b] L. R. Bickford, Phys. Rev. **99**, 1210 (1955).

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[1] R. Becker and W. Döring, *Ferromagnetismus* (Verlag Julius Springer, Berlin, 1939), p. 145.

[2] C. Kittel, Revs. Modern Phys. **21**, 541 (1949).

[3] R. Vautier, Ann. phys. **9**, 322 (1954). The three constants h_3, h_5, and h_6 of Vautier's expression can be replaced by two constants.

Appendix A. It is

$$
\begin{aligned}
\delta l/l = {} & h_1(\alpha_1^2\beta_1^2+\alpha_2^2\beta_2^2+\alpha_3^2\beta_3^2-\tfrac{1}{3})\\
& +2h_2(\alpha_1\alpha_2\beta_1\beta_2+\alpha_2\alpha_3\beta_2\beta_3+\alpha_1\alpha_3\beta_1\beta_3)\\
& +h_3(S-\tfrac{1}{5})\\
& +h_4(\alpha_1^4\beta_1^2+\alpha_2^4\beta_2^2+\alpha_3^4\beta_3^2+\tfrac{2}{3}S-\tfrac{1}{3})\\
& +2h_5(\alpha_1\alpha_2\alpha_3^2\beta_1\beta_2+\alpha_2\alpha_3\alpha_1^2\beta_2\beta_3+\alpha_1\alpha_3\alpha_2^2\beta_1\beta_3) \qquad (1)\\
& +h_6(\alpha_1^6\beta_1^2+\alpha_2^6\beta_2^2+\alpha_3^6\beta_3^2+S-P-\tfrac{1}{3})\\
& +2h_7(\alpha_1\alpha_2\alpha_3^4\beta_1\beta_2+\alpha_2\alpha_3\alpha_1^4\beta_2\beta_3+\alpha_1\alpha_3\alpha_2^4\beta_1\beta_3)\\
& +h_8(P-1/105)\\
& +2h_9(\alpha_1^3\alpha_2^3\beta_1\beta_2+\alpha_2^3\alpha_3^3\beta_2\beta_3+\alpha_1^3\alpha_3^3\beta_1\beta_3),
\end{aligned}
$$

where

$$S=\alpha_1^2\alpha_2^2+\alpha_2^2\alpha_3^2+\alpha_1^2\alpha_3^2, \quad P=\alpha_1^2\alpha_2^2\alpha_3^2.$$

The zero reference of Eq. (1) has been defined as the strain for the special domain configuration of an equal volume of domains magnetized along *all crystallographic directions* and therefore is independent of the magnetic anisotropy. Also the first five constants of Eq. (1) correspond directly with those of the existing fourth-order expression.

Theoretically all nine constants of Eq. (1) could be experimentally determined by extension of the method now used to obtain the first five constants. The h_i are obtained by the inversion of a strain matrix, which is made up of a sufficient number of independent strain measurements. However, the present experimental techniques used to make the strain measurements introduce errors which make the determination of the constants h_4 and h_5 very uncertain. Since the constants h_6 to h_9 would be expected to be smaller than the first five, determination of all nine constants does not seem feasible using present experimental techniques. Nevertheless, all nine constants will be retained to ascertain the role of the higher order terms on the anisotropy energies. Existing five-constant data are listed in Table I to provide a comparison between various materials and a basis for following calculations.

The most familiar representation of magnetostriction is the two-constant expression,

$$
\begin{aligned}
\delta l/l = {} & \tfrac{3}{2}\lambda_{100}(\alpha_1^2\beta_1^2+\alpha_2^2\beta_2^2+\alpha_3^2\beta_3^2-\tfrac{1}{3})\\
& +3\lambda_{111}(\alpha_1\alpha_2\beta_1\beta_2+\alpha_2\alpha_3\beta_2\beta_3+\alpha_1\alpha_3\beta_1\beta_3), \qquad (2)
\end{aligned}
$$

where

$$\lambda_{100}=\tfrac{2}{3}h_1, \quad \lambda_{111}=\tfrac{2}{3}h_2, \quad h_3 \text{ to } h_9=0.$$

Almost all existing magnetostriction data on monocrystals consist only of the two constants λ_{100} and λ_{111}. Two-constant data for several materials have been listed in Table II.

When $h_3, \cdots, h_9 \neq 0$, Eq. (2) is not a valid representation and the measured constants, λ_{100} and λ_{111}, are not unique. Therefore, since the constants h_3 to h_9 have not been determined for most materials, the two constants λ_{100} and λ_{111} and Eq. (2) must be used with caution. Most experimental techniques, used to obtain λ_{100} and λ_{111}, exploit the symmetry of Eq. (2) with respect to the directions of magnetization and measurement (i.e., symmetry with respect to the direction cosines α_i and β_i, respectively). Inspection of Eq. (1) shows that such symmetry does not hold for higher order expressions. Hence, if h_3 to $h_9 \neq 0$, the evaluation of λ_{100} and λ_{111} will differ according to whether the direction of magnetization or measurement is kept constant. It can easily be shown, by using the data in Table I, that the evaluation of the two constants for nickel or magnetite could vary by 10%, depending upon the method of measurement.

TABLE II. Two-constant magnetostriction data.

Material	$\lambda_{100}\times 10^6$	$\lambda_{111}\times 10^6$
Iron	+19.5	−18.8
Nickel	−46	−25
Fe_3O_4[a]	−19.4	+86.4
$Ni_{0.8}Fe_{2.2}O_4$[b]	−36	−4
$CoFe_2O_4$[b]	−515	+45
$Co_{0.8}Fe_{2.2}O_4$[c]	−590	+120
$Co_{0.3}Zn_{0.2}Fe_{2.2}O_4$[c]	−210	+110
$Co_{0.3}Mn_{0.4}Fe_{2.0}O_4$[c]	−200	+65
$Mn_{0.98}Fe_{1.86}O_4$[c]	−35	−1
$Mn_{0.6}Zn_{0.1}Fe_{2.1}O_4$[c]	−14	14

[a] B. A. Calhoun, Technical Report No. 68, Laboratory for Insulation Research, Massachusetts Institute of Technology, July, 1953 (unpublished).

[b] R. M. Bozorth and J. G. Walker, Phys. Rev. **88**, 1209 (1952).

[c] Bozorth, Tilden, and Williams, Phys. Rev. **99**, 1788 (1955).

III. EFFECTIVE DOMAIN ANISOTROPY ENERGY

The intrinsic magnetic anisotropy energy, i.e., that for an undeformed monocrystal, may be expressed in the form

$$U=K_1S+K_2P, \tag{3}$$

where S and P, functions of the magnetization direction cosines, have already been defined for Eq. (1). An undeformed crystal is one which has not been permitted to deform either due to magnetostriction or externally applied stresses. Although the undeformed state is virtually impossible to obtain, it is a useful concept and is the defined reference state for describing the anisotropy energy for any other state of strain.

When magnetic measurements are made no external stresses are usually applied and the sample is allowed to deform freely due to magnetostriction. The effective anisotropy energy for a saturated monocrystal under no constraints may be expressed by

$$U_d^0=(K_1)_{\text{eff}}S+(K_2)_{\text{eff}}P, \tag{4}$$

which has the same form as Eq. (3). It should be noted that Eq. (4) expresses the effective *domain* anisotropy since a saturated monocrystal is by definition a single domain. The effective anisotropy constants of Eq. (4) are, however, not equal to the corresponding constants of Eq. (3) since the total magnetoelastic energies of an unconstrained monocrystal vary with the direction of magnetization. The anisotropy contributions from the magnetoelastic and elastic energies have been derived in Appendix B. The resulting expressions for the effective constants of Eq. (4) are

$$(K_1)_{\mathrm{eff}}=K_1+(C_{11}-C_{12})\left(h_1^2+\frac{7}{3}h_1h_4-h_1h_6-h_4h_6\right)-2C_{44}h_2^2+3(C_{11}+2C_{12})\left(\frac{h_3^2}{5}+\frac{h_3h_8}{105}\right), \quad (5)$$

$$(K_2)_{\mathrm{eff}}=K_2-3(C_{11}-C_{12})h_1h_4+12C_{44}h_2h_5+3(C_{11}+2C_{12})\left(\frac{h_3h_8}{5}+\frac{h_8^2}{105}\right). \quad (6)$$

The K_1 and K_2 are the anisotropy constants defined by Eq. (3), the h_1 to h_9 are the magnetostriction coefficients defined by Eq. (1), and the C_{11}, C_{12}, and C_{44} are the usual elastic moduli for a cubic crystal. When the higher order magnetostriction coefficients are zero, Eqs. (5) and (6) reduce to the simpler first-order expressions derived by others.[1,2]

Since an unconstrained monocrystal is allowed to deform freely to a lower energy state, it has been argued by some[4] that always $|(K_1)_{\mathrm{eff}}|<|K_1|$. It will be shown subsequently, however, that for both magnetite and cobalt-zinc ferrite $|(K_1)_{\mathrm{eff}}|>|K_1|$. These results for magnetite and cobalt-zinc ferrite are not anomalous since the concept derived above is based on a fallacious argument. The fallacy is that the reduction in the *total* energy produced by a free deformation is *anisotropic*. Although the *total* energy of the crystal is always lowered by permitting the free deformation, the *anisotropy* of the total energy may either be increased or decreased. Therefore, the intrinsic anisotropy constants K_1 and K_2 of Eq. (3) may be either greater or smaller than the measured effective constants and must be calculated from Eqs. (5) and (6).

In order to calculate the intrinsic anisotropy constants from Eqs. (5) and (6), the elastic moduli must be known. The elastic moduli C_{11}, C_{12}, and C_{44} describe the elastic deformation of a cubic monocrystal under a given stress. When these moduli are measured for magnetic materials it is essential that strains, such as could be produced by magnetostriction and/or ionic ordering, should not occur during the period of measurement. The influence of the magnetostriction can be removed by maintaining the sample in a saturating field, thus fixing the magnetic state during the period of measurement. The elimination of the influence of ionic ordering however is practically impossible. Fine and Kenney[5] were so concerned about the influence of the order-disorder transformation of magnetite at 120°K that they were not willing to calculate even the room temperature moduli from their data. The influence of magnetostriction upon the determination of elastic moduli has been recognized for some time and called the "ΔE effect." Despite this fact, most existing data on the elastic constants of magnetic materials have been obtained *without regard for the inelastic strains produced by magnetostriction.* Thus, at present we must be content to use such data that are available; see Table III.

The intrinsic anisotropy constants of Eq. (3) can be calculated from Eqs. (5) and (6). Using the data in Tables I, II, and III, the measured anisotropy constants of Eq. (4) for some materials have been compared in Table IV with the calculated intrinsic constants. The intrinsic constants are significantly different from the reported effective constants.

IV. EFFECTIVE DOMAIN-WALL ANISOTROPY

Most magnetic monocrystals have a magnetic domain configuration in which domains of a given saturation magnetization are separated from each other by transition regions called domain walls. The volume of a domain wall is so small compared to that for the adjacent domains that the elastic state within a domain wall is dictated by the deformations of the adjacent domains. Hence the rotation of magnetic moment through a domain wall, from one domain to the other, must be accomplished under the constraint of an essentially fixed elastic state, within the domain wall. The general calculation of the effective anisotropy energy for a fixed elastic deformation is quite complex. However, the problem is greatly simplified for certain special cases. Since the magnetostriction of the domains is an even function of the direction of magnetization [see Eq. (1)], the magnetostriction of antiparallel domains is the same. Thus, in the case of 180° domain walls, the elastic deformation is a constant across the wall thickness. In other than 180° domain walls, the deformation must be considered a function of the distance through the wall. Only the effective anisotropy for a 180° domain wall (i.e., constant deformation) will be calculated.

The deformation existent within a 180° domain wall is considered to correspond to the magnetostrictive deformation of the adjacent domains when the magnetization in these domains is defined by the direction cosines ζ_i, referred to the cubic crystal lattice. The anisotropy energy, U_w, within a 180° domain wall associated with the rotation of the magnetic moment, defined by the

TABLE III. Elastic moduli.

Material	$C_{11}\times10^{-12}$ (ergs/cc)	$C_{12}\times10^{-12}$ (ergs/cc)	$C_{44}\times10^{-12}$ (ergs/cc)
Fe_3O_4[a]	2.7	1.08	0.987
$Co_{0.32}Zn_{0.22}Fe_{2.2}O_4$[b]	2.66	1.53	0.78
Nickel[c]	2.50	1.60	1.185
Iron[d]	2.41	1.46	1.12

[a] M. S. Doraiswami, Proc. Indian Acad. Sci. **25A**, 413 (1947).
[b] McSkimin, Williams, and Bozorth, Phys. Rev. **95**, 616 (1954).
[c] Bozorth, Mason, McSkimin, and Walker, Phys. Rev. **75**, 1954 (1949).
[d] R. Kimura and K. Ohno, Sci. Repts. Tohoku Univ. **23**, 359 (1934).

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[4] H. Shenker, Naval Ordnance Laboratory Report 3858, February 8, 1955 (unpublished).

[5] M. E. Fine and N. T. Kenney, Phys. Rev. **94**, 1573 (1954).

TABLE IV. Anisotropy constants in units of 10^4 ergs/cc.

Material	Effective-measured $(K_1)_{\text{eff}}$	Effective-measured $(K_2)_{\text{eff}}$	Intrinsic-calculated (5-constant magnetostriction) K_1	Intrinsic-calculated (5-constant magnetostriction) K_2	Intrinsic-calculated (2-constant magnetostriction) K_1	Intrinsic-calculated (2-constant magnetostriction) K_2
Iron	42	15	...	...	42.1	15
Nickel	−4.26[a]	1.09[a]	−4.48	1.7	−4.35	1.09
Fe_3O_4	−11[b]	...	−8.0	...	−8.0	...
$Co_{0.3}Zn_{0.2}Fe_{2.2}O_4$	150[c]	...	...	...	143	...
$Mn_{0.98}Fe_{1.86}O_4$	−2.8[d]	0.2±0 4[d]	...	...	−3 1[f]	0.2±0.4[f]
$Ni_{0.8}Fe_{2.2}O_4$	−3.9[e]	...	...	...	−4.2[f]	...

[a] Y. Nakamura, J. Phys. Soc. Japan **10**, 937 (1955).
[b] L. R. Bickford, Phys. Rev. **78**, 449 (1950).
[c] R. M. Bozorth *et al.*, Phys. Rev. **99**, 1788 (1955).
[d] J. F. Dillon, Jr., *e. al.*, Phys. Rev. **100**, 750 (1955).
[e] R. M. Bozorth *et al.*, Phys. Rev. **99**, 1898 (1955).
[f] In lieu of experimental data, the elastic constants have been estimated to be $(C_{11}-C_{12})=C_{44}=10^{12}$ ergs/cc.

direction cosines α_i, has been derived in Appendix C:

$$\begin{aligned}U_w=&\{K_1-3(C_{11}+2C_{12})h_3[h_3(S_0-\tfrac{1}{5})+h_8(P_0-1/105)]\}S\\&+\{K_2-3(C_{11}+2C_{12})h_8[h_3(S_0-\tfrac{1}{5})+h_8(P_0-1/105)]\}P\\&-(C_{11}-C_{12})h_1^2[\alpha_1^2\xi_{11}+\alpha_2^2\xi_{22}+\alpha_3^2\xi_{33}-\tfrac{1}{3}w]\\&-4C_{44}h_2^2[\alpha_1\alpha_2\xi_{12}+\alpha_2\alpha_3\xi_{23}+\alpha_1\alpha_3\xi_{13}]\\&-(C_{11}-C_{12})h_1h_4[\alpha_1^4\xi_{11}+\alpha_2^4\xi_{22}+\alpha_3^4\xi_{33}+w(\tfrac{2}{3}S-\tfrac{1}{3})]\\&-4C_{44}h_2h_5[\alpha_1\alpha_2\alpha_3^2\xi_{12}+\alpha_2\alpha_3\alpha_1^2\xi_{23}+\alpha_1\alpha_3\alpha_2^2\xi_{13}]\\&-(C_{11}-C_{12})h_1h_6[\alpha_1^6\xi_{11}+\alpha_2^6\xi_{22}+\alpha_3^6\xi_{33}+w(S-P-\tfrac{1}{3})]\\&-4C_{44}h_2h_7[\alpha_1\alpha_2\alpha_3^4\xi_{12}+\alpha_2\alpha_3\alpha_1^4\xi_{23}+\alpha_1\alpha_3\alpha_2^4\xi_{13}]\\&-4C_{44}h_2h_9[\alpha_1^3\alpha_2^3\xi_{12}+\alpha_2^3\alpha_3^3\xi_{23}+\alpha_1^3\alpha_3^3\xi_{13}],\end{aligned}\tag{7}$$

where

$$\xi_{ii}=\frac{1}{h_1}[h_1\zeta_i^2+h_4\zeta_i^4+h_6\zeta_i^6],$$

$$\xi_{ij}=\frac{1}{h_2}[h_2\zeta_i\zeta_j+h_5\zeta_i\zeta_j\zeta_k^2+h_7\zeta_i\zeta_j\zeta_k^4+h_9\zeta_i^3\zeta_j^3],$$

$$w=\frac{1}{h_1}[h_1-h_4(2S_0-1)-h_6(3S_0-3P_0-1)],$$

$$S_0=\zeta_1^2\zeta_2^2+\zeta_2^2\zeta_3^2+\zeta_1^2\zeta_3^2,$$

$$P_0=\zeta_1^2\zeta_2^2\zeta_3^2.$$

As will be shown later, the form of Eq. (7) is quite similar to the expression for describing the influence of an externally applied linear stress. Thus, the gross influence of the magnetic domains upon the domain wall may be interpreted as an equivalent stress parallel to the domain magnetization, which tends to align the magnetization within the wall parallel to that in the adjacent domains.

In most materials the domains are magnetized along either ⟨100⟩ or ⟨111⟩ directions depending upon the domain anisotropy. Eq. (7) is greatly simplified for either of these special cases; the corresponding expressions for h_6 to h_9 equal zero are

Domain magnetization along ⟨100⟩

$$\zeta_1=1,\quad \zeta_2=\zeta_3=0,$$

$$\begin{aligned}U_w=&\left[K_1+\frac{3(C_{11}+2C_{12})}{5}h_3^2\right]S+K_2P\\&-(C_{11}-C_{12})(h_1^2+h_1h_4)(\alpha_1^2-\tfrac{1}{3})\\&-(C_{11}-C_{12})(h_1h_4+h_4^2)(\alpha_1^4+\tfrac{2}{3}s-\tfrac{1}{3}).\end{aligned}\tag{8}$$

Domain magnetization along ⟨111⟩

$$\zeta_1=\zeta_2=\zeta_3=1/\sqrt{3},$$

$$\begin{aligned}U_w=&\left[K_1-\frac{2(C_{11}+2C_{12})}{5}h_3^2\right]S+K_2P\\&-4C_{44}\left(\frac{h_2^2}{3}+\frac{h_2h_5}{9}\right)(\alpha_1\alpha_2+\alpha_2\alpha_3+\alpha_1\alpha_3)\\&-4C_{44}\left(\frac{h_2h_5}{3}+\frac{h_5^2}{9}\right)(\alpha_1\alpha_2\alpha_3^2+\alpha_2\alpha_3\alpha_1^2+\alpha_1\alpha_3\alpha_2^2).\end{aligned}\tag{9}$$

The lack of cubic symmetry in the domain-wall anisotropy energy is the main feature which makes the domain and the domain-wall anisotropy energies different. The constants of Eq. (9) may be calculated for nickel and magnetite by using the data in Tables I, III, and IV. The constants for the noncubic terms are approximately $K_1/10$ for both materials.

The first-order form of Eq. (7), obtained by letting $K_2=0$, $h_{i\geq 3}=0$, $h_1=\frac{3}{2}\lambda_{100}$, and $h_2=\frac{3}{2}\lambda_{111}$, is simply

$$\begin{aligned}U_w=&K_1S-(9/4)(C_{11}-C_{12})\lambda_{100}^2(\alpha_1^2\zeta_1^2+\alpha_2^2\zeta_2^2+\alpha_3^2\zeta_3^2-\tfrac{1}{3})\\&-9C_{44}\lambda_{111}^2(\alpha_1\alpha_2\zeta_1\zeta_2+\alpha_2\alpha_3\zeta_2\zeta_3+\alpha_1\alpha_3\zeta_1\zeta_3).\end{aligned}\tag{10}$$

It should be noted that the second or third terms of Eq. (10) go to zero when the domain magnetization is along a ⟨111⟩ or ⟨100⟩ direction respectively. Therefore usually only one of the last terms predominates in a given material. The coefficients for Eq. (10) have been calculated for several materials and tabulated in Table V. As noted by Kittel, the magnetostrictive contribution to the effective domain-wall anisotropy is small for the metals iron and nickel. However, in the magnetic oxides this contribution can be quite large, as for Fe_3O_4 and $Co_{0.3}Zn_{0.2}Fe_{2.2}O_4$, or very small as in the case of $Mn_{0.98}Fe_{1.86}O_4$.

TABLE V. Effective domain-wall anisotropy constants, in units of 10^4 ergs/cc.

Material	K_1	$-(9/4)(C_{11}-C_{12})$ $\times\lambda_{100}^2$	$-9C_{44}\lambda_{111}^2$
Iron	$+42.1$	-0.08^a	-0.09
Nickel	4.35	-0.43	-0.17^a
Fe_3O_4	-8.0	-0.14	-1.7^a
$Co_{0.3}Zn_{0.2}Fe_{2.2}O_4$	$+143$	-11^a	-2.1
$Mn_{0.98}Fe_{1.86}O_4$[b]	-3.1	-0.27	10^{-4} [a]
$Ni_{0.8}Fe_{2.2}O_4$[b]	-4.2	-0.29	-0.03^a

[a] Predominant term resulting from direction of domain magnetization.
[b] Elastic constants approximated: $(C_{11}-C_{12})=C_{44}=10^{12}$ ergs/cc.

V. INTERRELATION BETWEEN THE EFFECTIVE ANISOTROPY IN DOMAINS AND IN DOMAIN WALLS

The effective anisotropies in a domain and in a domain wall depend on the same independent parameters and are therefore interrelated. The magnetic domain configuration and thus also the magnetic properties of a material are grossly influenced by not only the absolute values of the domain and domain-wall anisotropy energies (U_d and U_w) but also by their relative values. The special cases which are the most interesting and also the most illuminating are those for which either of the anisotropy energies is zero and those cases for which certain of the independent parameters are zero. For brevity, only the first-order expressions for U_d and U_w will be used. The first-order expression for U_d is readily obtained from Eqs. (4), (5), and (6) as that given in Eq. (11). The first-order expression for U_w has already been given in Eq. (10).

$$U_d=(K_1)_{\text{eff}}S, \tag{11}$$

where

$$(K_1)_{\text{eff}}=K_1(9/4)[(C_{11}-C_{12})\lambda_{100}^2-2C_{44}\lambda_{111}^2].$$

In the expression for U_d all the terms have the same symmetry and $U_d=0$ if $(K_1)_{\text{eff}}=0$, i.e., if

$$K_1=-(9/4)[(C_{11}-C_{12})\lambda_{100}^2-2C_{44}\lambda_{111}^2]. \tag{12}$$

Substitution of Eq. (12) into the expression for U_w shows that *if U_d is zero then U_w is not necessarily zero.* Since the expression for U_w is comprised of terms each having a different symmetry, U_w can be zero only when each term is separately zero. Therefore, it follows that *if $U_w=0$ then U_d must also be zero.*

If $U_w=0$, then discrete domain walls would not exist and the change in magnetization from one domain to another would be accomplished in a rather incoherent way. The fact that $U_w\neq 0$, even when $U_d=0$, means that the magnetization process can usually be considered one of discrete domain-wall motion in addition to domain rotations. The domain-wall energy density, which is dependent[2] upon U_w, should be minimized to reduce the static and dynamic losses.[6] One should therefore question how U_w may be reduced and what is the corresponding effect on the U_d and the general domain structure.

The reduction of U_w breaks down to the possibilities $K_1=0$, $\lambda_{100}=0$, $\lambda_{111}=0$ or any combination of two of these possibilities (the case of all three being zero has already been considered). When $K_1=0$, U_d depends only upon the magnetostriction coefficients. In fact, $U_d=0$ if

$$(C_{11}-C_{12})\lambda_{100}^2=2C_{44}\lambda_{111}^2; \tag{13}$$

Eq. (13) does not require elastic isotropy $(C_{11}-C_{12}=2C_{44})$ or magnetostrictive isotropy $(\lambda_{100}=\lambda_{111})$, but isotropy of the magnetoelastic energy. If Eq. (13) is fulfilled and $K_1=0$, then U_w may be expressed in a very simple form:

$$U_w=-(9/4)(C_{11}-C_{12})\lambda_{100}^2\cos^2\theta, \tag{14}$$

where θ is the angle between the magnetization in the wall and the magnetization in the adjacent domains.

When the total magnetostrictive contribution to U_w goes to zero, 180° domain walls tend to separate into "90°" domain walls.[2] Therefore, in addition to the possibility of reducing U_w, it is also necessary to establish the conditions which favor 180° or 90° domain walls. When both $\lambda_{100}=0$ and $\lambda_{111}=0$, $U_w=K_1S$ and 90° domain walls will be favored. When either $\lambda_{100}=0$ or $\lambda_{111}=0$, the magnetostrictive contribution to U_w may or may not be zero, depending upon the direction of magnetization in the adjacent domains [see Eq. (10)]. In Table VI the cases favoring the types of domain walls are tabulated for either λ_{100} or $\lambda_{111}=0$.

In cases (a) and (b) of Table VI, the domain anisotropy energy will simply be $U_w=K_1S$ and 90° domain walls will be favored. Both of these cases are nicely illustrated in the system Fe-Ni and have been studied in detail by Bozorth *et al.*[7] It is notable that the response to a magnetic anneal in the system Fe-Ni goes to zero at the compositions for which cases (a) and (b) are fulfilled and thus where 180° domain walls are not favored.

In cases (c) and (d) of Table VI, the domain-wall anisotropy will be expressed as

$$U_w=K_1S-9C_{44}\lambda_{111}^2(\alpha_1\alpha_2\zeta_1\zeta_2+\alpha_2\alpha_3\zeta_2\zeta_3+\alpha_1\alpha_3\zeta_1\zeta_3), \tag{15}$$

$$U_w=K_1S-(9/4)(C_{11}-C_{12})\lambda_{100}^2 \times(\alpha_1^2\zeta_1^2+\alpha_2^2\zeta_2^2+\alpha_3^2\zeta_3^2-\tfrac{1}{3}), \tag{16}$$

respectively. In both cases the U_w will not be sensibly affected by the fact that one of the magnetostrictive

TABLE VI. Influence of magnetostriction on domain wall type.

	Conditions favoring 90° domain walls	Conditions favoring 180° domain walls
$\lambda_{100}=0$	(a) $(K_1)_{\text{eff}}>0$, or $K_1>(9/2)C_{44}\lambda_{111}^2$	(c) $(K_1)_{\text{eff}}<0$, or $K_1<(9/2)C_{44}\lambda_{111}^2$
$\lambda_{111}=0$	(b) $(K_1)_{\text{eff}}<0$, or $K_1<-(9/4)(C_{11}-C_{12})\lambda_{100}^2$	(d) $(K_1)_{\text{eff}}>0$, or $K_1>-(9/4)(C_{11}-C_{12})\lambda_{100}^2$

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[6] J. B. Goodenough, Phys. Rev. **95**, 917 (1954), and N. Menyuk and J. B. Goodenough, J. Appl. Phys. **26**, 8 (1955).

[7] R. M. Bozorth, Revs. Modern Phys. **25**, 42 (1953).

coefficients goes through zero. An illustration of case (c) is not known although one does not see why it would not be physically possible. Case (d) is illustrated in the system Fe-Si where 180° domain walls have been observed.[8]

In all the ferrites measured, λ_{100} has always been negative. Hence, the occurrence of $\lambda_{100}=0$ in the ferrites would seem unlikely. The sign of λ_{111} does, however, change sign for the ferrites and can be made zero. Thus, only cases (b) and (d) need be considered for the ferrites. Since $(K_1)_{\text{eff}}$ is usually negative, *90° domain walls will predominate in most ferrites when* $\lambda_{111}=0$. *Only when* $(K_1)_{\text{eff}}$ *is positive will 180° domain walls be favored when* $\lambda_{111}=0$.

VI. INFLUENCE OF APPLIED STRESSES

The influence of externally applied stresses upon the magnetic state may be expressed as a contribution U_σ to the total effective anisotropy energies.

$$\begin{aligned}U_\sigma=&-\sigma h_1(\alpha_1^2\gamma_1^2+\alpha_2^2\gamma_2^2+\alpha_3^2\gamma_3^2-\tfrac{1}{3})\\&-2\sigma h_2(\alpha_1\alpha_2\gamma_1\gamma_2+\alpha_2\alpha_3\gamma_2\gamma_3+\alpha_1\alpha_3\gamma_1\gamma_3)\\&-\sigma h_3(S-\tfrac{1}{5})\\&-\sigma h_4(\alpha_1^4\gamma_1^2+\alpha_2^4\gamma_2^2+\alpha_3^4\gamma_3^2+\tfrac{2}{3}S-\tfrac{1}{3})\\&-2\sigma h_5(\alpha_1\alpha_2\alpha_3^2\gamma_1\gamma_2+\alpha_2\alpha_3\alpha_1^2\gamma_2\gamma_3+\alpha_1\alpha_3\alpha_2^2\gamma_1\gamma_3)\\&-\sigma h_6(\alpha_1^6\gamma_1^2+\alpha_2^6\gamma_2^2+\alpha_3^6\gamma_3^2+S-P-\tfrac{1}{3})\\&-2\sigma h_7(\alpha_1\alpha_2\alpha_3^4\gamma_1\gamma_2+\alpha_2\alpha_3\alpha_1^4\gamma_2\gamma_3+\alpha_1\alpha_3\alpha_2^4\gamma_1\gamma_3)\\&-\sigma h_8(P-1/105)\\&-2\sigma h_9(\alpha_1^3\alpha_2^3\gamma_1\gamma_2+\alpha_2^3\alpha_3^3\gamma_2\gamma_3+\alpha_1^3\alpha_3^3\gamma_1\gamma_3)\end{aligned}\tag{17}$$

U_σ as expressed in Eq. (17) has been derived in Appendix **D**, where the applied stress has been defined as linear with a magnitude σ and direction cosines γ_i. The total effective anisotropy energy expressions for domains and 180° domain walls are

$$U_d^\sigma=U_d^0+U_\sigma,\tag{18}$$

$$U_w^\sigma=U_w^0+U_\sigma,\tag{19}$$

respectively, where U_d^0 and U_w^0 are the respective anisotropy energies for an unconstrained monocrystal.

The first-order expression for U_σ is obtained from Eq. (17) by letting $h_1=\frac{3}{2}\lambda_{100}$, $h_2=\frac{3}{2}\lambda_{111}$, and $h_3,\cdots,h_9=0$:

$$\begin{aligned}U_\sigma=&-\tfrac{3}{2}\sigma\lambda_{100}(\alpha_1^2\gamma_1^2+\alpha_2^2\gamma_2^2+\alpha_3^2\gamma_3^2-\tfrac{1}{3})\\&-3\sigma\lambda_{111}(\alpha_1\alpha_2\gamma_1\gamma_2+\alpha_2\alpha_3\gamma_2\gamma_3+\alpha_1\alpha_3\gamma_1\gamma_3).\end{aligned}\tag{20}$$

The corresponding first-order expressions for U_d^0 and U_w^0 are given in Eqs. (10) and (11). The first-order expressions U_d^σ and U_w^σ may now be used to study the interrelationship between the effective anisotropy in domains and domain wall in the presence of an applied stress. The results obtained are similar to those obtained in Sec. V for zero stress. The most significant difference is that, in general, the presence of an applied stress makes 180° domain walls more favorable. Only rather special stresses will not tend to inhibit the formation of "90°" walls.

VII. SUMMARY

A nine-constant expression has been derived for empirically describing the spontaneous magnetostriction to the sixth order in the direction cosines of the magnetization. This expression is readily reduced to the familiar five- and two-constant expressions. The zero reference usually used for magnetostriction expressions has been replaced by one that does not depend upon the effective anisotropy. The questionable significance of existing two-constant data is also pointed out.

The effective first- and second-order anisotropy coefficients of an *unconstrained* monocrystal have been derived in terms of the intrinsic anisotropy coefficients of an *undeformed* monocrystal, the nine magnetostriction constants, and the elastic moduli. The contribution to the total effective anisotropy from a linear applied stress has been derived to the sixth order.

The effective anisotropy for a 180° domain wall has been derived and compared with that for a domain. The interrelation between the effective anisotropy energies in a domain and in a domain wall has been studied, and the conditions favoring the formation of 180° or 90° domain walls determined for the cases when the magnetostriction constants go to zero.

APPENDIX A. MAGNETOSTRICTION OF AN UNCONSTRAINED MONOCRYSTAL

The phenomenological expression for describing the magnetostriction of a monocrystal to sixth order in the magnetization direction cosines, α_i, is derived by extending the method of Becker and Döring[1] to higher order.

The elastic energy, U_e, of a cubic crystal may be expressed as

$$\begin{aligned}U_e=&\tfrac{1}{2}(C_{11}-C_{12})(e_{xx}^2+e_{yy}^2+e_{zz}^2)\\&+\tfrac{1}{2}C_{12}(e_{xx}+e_{yy}+e_{zz})^2+\tfrac{1}{2}C_{44}(e_{xy}^2+e_{yz}^2+e_{zx}^2),\end{aligned}\tag{A1}$$

where the C's are the elastic moduli and the e_{ij} the strain components.

The magnetoelastic coupling energy, U_λ, which may be considered responsible for the phenomenon of magnetostriction, may be expressed in the general form

$$\begin{aligned}U_\lambda=&F_{11}e_{xx}+F_{22}e_{yy}+F_{33}e_{zz}\\&+F_{12}e_{xy}+F_{23}e_{yz}+F_{13}e_{zx},\end{aligned}\tag{A2}$$

where the F_{ij} are functions of the α_i and must have the same invariance to crystal symmetry operations possessed by the corresponding e_{ij}. Therefore it follows that F_{ii} must be an even function of α_i, α_j, and α_k and also be symmetrical in α_j and α_k, which is expressed in general form by

$$\begin{aligned}F_{ii}=&b_0+b_1(\alpha_i^2-\tfrac{1}{3})+b_3S+b_4(\alpha_i^4+\tfrac{2}{3}S-\tfrac{1}{3})\\&+b_6(\alpha_i^6+S-P-\tfrac{1}{3})+b_8P,\end{aligned}\tag{A3}$$

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[8] L. J. Dijkstra and U. M. Martius, Revs. Modern Phys. 25, 146 (1953).

where the b_i's are called the magnetoelastic coupling coefficients. Similarly F_{ij} must be symmetric in α_i and α_j which results in

$$F_{ij}=2b_2\alpha_i\alpha_j+2b_5\alpha_i\alpha_j\alpha_k^2+2b_7\alpha_i\alpha_j\alpha_k^4+2b_9\alpha_i^3\alpha_j^3, \quad \text{for} \quad i\neq j. \tag{A4}$$

Static equilibrium of the crystal requires that

$$\partial(U_\lambda+U_e)/\partial e_{ij}=0, \tag{A5}$$

which results in six independent equations. The explicit dependence of the e_{ij} on the magnetization direction cosines may now be found by solving Eq. (A5) for the e_{ij} and eliminating the F_{ij} by use of Eqs. (A3) and (A4). The resulting expressions for the e_{ij} are

$$e_{ij}=2h_2\alpha_i\alpha_j+2h_5\alpha_i\alpha_j\alpha_k^2+2h_7\alpha_i\alpha_j\alpha_k^4+2h_9\alpha_i^3\alpha_j^3 \quad \text{for} \quad i\neq j, \tag{A6}$$

$$e_{ii}=h_0+h_1(\alpha_i^2-\tfrac{1}{3})+h_3S+h_4(\alpha_i^4+\tfrac{2}{3}S-\tfrac{1}{3})+h_6(\alpha_i^6+S-P-\tfrac{1}{3})+h_8P, \tag{A7}$$

and the corresponding expressions are obtained by cyclic permutations of the α_i.

The h_i of Eqs. (A6) and (A7) are the magnetostriction constants, which are related to the magnetoelastic coupling coefficients in the following manner:

$$\begin{aligned} h_0&=-b_0/(C_{11}+2C_{12}), & h_1&=-b_1/(C_{11}-C_{12}),\\ h_2&=-b_2/C_{44}, & h_3&=-b_3/(C_{11}+2C_{12}),\\ h_4&=-b_4/(C_{11}-C_{12}), & h_5&=-b_5/C_{44},\\ h_6&=-b_6/(C_{11}-C_{12}), & h_7&=-b_7/C_{44},\\ h_8&=-b_8/(C_{11}+2C_{12}), & h_9&=-b_9/C_{44}. \end{aligned} \tag{A8}$$

The strain of a monocrystal in the direction defined by the direction cosines β_i may be expressed by

$$\frac{\delta l}{l}=\sum_{i,j} e_{ij}\beta_i\beta_j. \tag{A9}$$

The measured strain may be completely described with respect to an arbitrary zero reference. A special magnetic domain configuration has been defined for a zero reference, namely that an equal volume of domains are magnetized in all crystallographic directions. Hence, suitable averaging of Eqs. (A6) and (A7) for the zero reference and substitution into Eq. (A9) yields

$$h_0+h_3/5+h_8/105=0. \tag{A10}$$

Finally, substitution of Eqs. (A6), (A7), and (A10) into Eq. (A9) gives the desired expression for describing the magnetostriction as Eq. (1) in the text.

APPENDIX B. EFFECTIVE ANISOTROPY ENERGY OF AN UNCONSTRAINED MONOCRYSTAL

The total energy dependent upon the direction of the spontaneous magnetization may be expressed in the following form:

$$U_{\text{tot}}=U_k+U_\lambda+U_e. \tag{B1}$$

The U_k is defined as the anisotropy energy for an undistorted crystal which for a cubic crystal may be expressed to the sixth order in the α_i as

$$U_k=K_1S+K_2P. \tag{B2}$$

The elastic energy and magnetoelastic coupling energy, U_e and U_λ, are given in Eqs. (A1) and (A2) as functions of the F_{ij} and e_{ij}. Substitution of Eqs. (A3), (A4), (A6), (A7), (A8), and (A10) into Eqs. (A1) and (A2) and retention of terms up to sixth order in the α_i yields

$$\begin{aligned} U_\lambda+U_e=\Big[&(C_{11}-C_{12})(h_1^2+\frac{7}{3}h_1h_4-h_4h_6)\\ &-2C_{44}h_2^2+3(C_{11}+2C_{12})\left(\frac{h_3^2}{5}+\frac{h_3h_8}{105}\right)\Big]S\\ &-3\Big[(C_{11}-C_{12})h_1h_4+12C_{44}h_2h_5\\ &-3(C_{11}+2C_{12})\left(\frac{h_3h_8}{5}+\frac{h_8^2}{105}\right)\Big]P. \end{aligned} \tag{B3}$$

Using Eqs. (B2) and (B3), the Eq. (B1) for the total energy may be expressed as Eqs. (4), (5), and (6) in the text.

APPENDIX C. EFFECTIVE ANISOTROPY ENERGY WITHIN A 180° DOMAIN WALL

The case of constant deformation in a crystallite is the first-order approximation to the condition existent with 180° domain wall. The distortion is dictated by the distortion in the adjacent domains. The distortion will be taken as that consistent with the direction of magnetization defined by the direction cosines, ζ_i, *in the adjacent domains*. The direction of magnetization *within the domain wall* will be defined by the usual direction cosines, α_i. Considering the magnetization as rotating through a domain wall, the direction cosines ζ_i may therefore be considered the initial values of the α_i.

Since the state of strain of the 180° domain wall is independent of the direction of magnetization within the wall, the elastic energy is not a function of the direction of magnetization and will not contribute to the effective anisotropy energy. The effective anisotropy energy for a 180° domain wall is the sum of the anisotropy of the undistorted crystal, U_k, and the magnetoelastic energy, U_λ:

$$U_w=U_k+U_\lambda. \tag{C1}$$

U_k is the intrinsic anisotropy energy defined by Eq. (B2). U_λ, the magnetoelastic coupling energy, is given by Eq. (A2) where it should be noted that the strain components e_{ij} are now constants. The constant e_{ij} may be expressed in terms of the domain magnetization by replacing the α_i of Eqs. (A6) and (A7) by the corresponding initial values ζ_i. Substitution of the constant e_{ij} together with Eqs. (A3), (A4), (A8), and (A10) into Eq. (A2) yields the form of U_λ for final substitution into Eq. (C1) to give the desired expression for U_w as Eq. (7) in the text.

APPENDIX D. MAGNETIC ANISOTROPY RESULTING FROM AN APPLIED STRESS

The elastic strain components e_{ij}^σ resulting from the application of a linear stress are

$$e_{ii}^\sigma = \frac{\sigma\gamma_i^2}{C_{11}-C_{12}} - \frac{C_{12}\sigma}{(C_{11}-C_{12})(C_{11}+2C_{12})}, \qquad \text{(D1)}$$

$$e_{ij}^\sigma = \frac{\sigma\gamma_i\gamma_j}{C_{44}} \quad \text{for} \quad i\neq j,$$

where the applied stress is defined by the magnitude σ and the direction cosines γ_i. Since the e_{ij}^σ do not depend upon the magnetization, the only contribution to the magnetic anisotropy energy is through the magnetoelastic coupling energy U_λ^σ,

$$U_\lambda^\sigma = U_\lambda^0 + U_\sigma. \qquad \text{(D2)}$$

U_λ^0 is the magnetoelastic coupling energy for zero applied stress used in Appendixes A, B, and C. U_σ is the total contribution to the magnetic anisotropy energy due to the applied stress which, by analogy with Eq. (A2), may be expressed as

$$U_\sigma = F_{11}e_{xx}^\sigma + F_{22}e_{yy}^\sigma + F_{33}e_{zz}^\sigma + F_{12}e_{xy}^\sigma + F_{23}e_{yz}^\sigma + F_{13}e_{zx}^\sigma. \qquad \text{(D3)}$$

Substitution of Eqs. (A3), (A4), (A8), (A10), and (D1) into Eq. (D3) finally gives U_σ as an explicit function of the magnetization direction cosines α_i and the applied stress in Eq. (17) in the text.

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Anomalous Variation of Band Gap with Composition in Zinc Sulfo- and Seleno-Tellurides

S. Larach, R. E. Shrader, and C. F. Stocker
RCA Laboratories, Radio Corporation of America, Princeton, New Jersey

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A monotonic variation of band gap with composition occurs for many binary solid solutions. Of some Group II–Group VI systems, ZnS-ZnSe shows this type of variation of band gap with composition, whereas ZnSe-ZnTe, ZnS-ZnTe show an anomalous minimum in a plot of band gap *versus* composition of the solid solution.

INTRODUCTION

Some measurements of the variation of band-gap-energy with composition in isomorphous series of two-component solid solutions have been reported. Gisolf[1] has investigated the ZnS-CdS system, Johnson and Christian,[2] the Ge-Si system, and Folberth,[3] Group III–Group V materials. The results seemed to confirm a postulate that intermediate members of a two-component series have band-gap energies intermediate to those of the extreme members of the series. The present work reports results which show that although the systems ZnS-ZnSe follows the above postulate, the systems ZnS-ZnTe and ZnSe-ZnTe do not.

EXPERIMENTAL

Synthesis of Materials

Phosphor-grade zinc chalcogenides were used through out the work. Powder mixtures of the pure ingredients (in the desired molar proportions) were dry ball-milled for six hours, to insure homogeneity of mixing. The materials were then transferred to silica boats, and crystallized in an atmosphere of purified nitrogen at 900°C. The materials were cooled under nitrogen. Phosphor-type purity and precautions were maintained throughout the synthesis.

Analysis

X-ray diffraction studies were carried out using a North American Philips diffractometer, with a copper target and nickel filter, to obtain monochromatic 1.54 A radiation.

Chemical quantitative analyses of tellurium in solid solution were carried out by an electrometric titration method developed by Dr. M. C. Gardels of these laboratories.[4]

Reflection Spectra

In the absence of single crystals for direct absorption measurements, the diffuse reflectance of the micro-

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[1] J. H. Gisolf, Physica 6, 84 (1939).

[2] E. R. Johnson and S. M. Christian, Phys. Rev. 95, 560 (1954).

[3] O. G. Folberth, Z. Naturforsch. 10a, 502 (1955).

[4] Method to be published elsewhere.