be pointed out, however, that the theoretical result was obtained considering direct interactions involving only nearest-neighbor magnetic atoms in a diamagnetic matrix. The induced moments on the host-metal Pt atoms would increase the extent of the short-range interaction and decrease the critical concentration. A fit of the linear part of the C.V. curve to the 2–8 at.% part of the experimental curve gives a value for the exchange coupling constant $J=0.5$ eV, which is somewhat high.

ACKNOWLEDGMENTS

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Magnetic Phase Equilibrium in Chromium-Substituted Calcium Ferrite*,†

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The structure of $CaFe_2O_4$ has orthorhombic symmetry (space group D_{2h}^{16}-*Pnam*) and is characterized by Fe–O–Fe–O chains within which the Fe–O–Fe bond angle is ~130°. These chains are cross-linked by means of Fe–O–Fe bonds in which the angle is ~99°. The compounds $Ca(Cr_xFe_{1-x})_2O_4$, with $0\leq x\leq 0.5$, have been found, by means of neutron measurements, to exhibit two magnetic structures in each of which the chains are internally antiferromagnetic, with spins alternating $+-+-$ along a chain. In one structure the chains are linked ferromagnetically through the 99° bonds, with magnetic symmetry *Pn′a′m*, and in the second they are antiferromagnetically coupled, corresponding to the space group *Pna′m*. A phase diagram has been constructed showing both single-phase regions and a region in which the two phases exist in equilibrium. Transition temperatures as well as the temperature dependence of magnetic moments and phase concentration have been determined as a function of chromium content. The problem posed by the coexistence, at equilibrium, of two magnetic phases belonging to a single crystal structure is discussed.

INTRODUCTION

In this paper we present the results of a systematic study of the magnetic structures occurring in the compounds $Ca(Cr_xFe_{1-x})_2O_4$ for $0\leq x\leq 0.5$. It is proposed that in certain broad temperature and composition ranges, two distinct magnetic phases coexist in thermal equilibrium. This phenomenon has not, to our knowledge, been previously reported in the literature. In the course of preparing this work for publication, we have received several communications[1] reporting work in other laboratories on unsubstituted $CaFe_2O_4$. All groups agree on the magnetic structure of $CaFe_2O_4$ at low temperatures, but only Watanabe *et al.*[1] confirm our observation of a second magnetic phase at higher temperatures. The case of $CaFe_2O_4$ is discussed in greater detail below in the section devoted to the pure compound.

CRYSTAL STRUCTURE

The crystal structure of $CaFe_2O_4$ was first studied by Bertaut, Blum, and Magnano,[2] who also reported the isomorphism with β-$CaCr_2O_4$, and further established by the detailed determinations of Hill, Peiser, and Rait[3] and of Decker and Kasper.[4] The compound is orthorhombic and the coordination of oxygen atoms around iron is approximately octahedral. Following Decker and Kasper, the space group is D_{2h}^{16}-*Pnam* with $a_0=9.230\pm0.012$ Å, $b_0=10.705\pm0.014$ Å, $c_0=3.024\pm0.004$ Å, and all atoms are in position

$$4(c):\quad \pm(x,y,\tfrac{1}{4};\tfrac{1}{2}+x,\tfrac{1}{2}-y,\tfrac{1}{4}).$$

The structure is shown in (001) projection in Fig. 1. Iron atoms are distributed in staggered Fe–O–Fe–O–··· chains (heavy lines of Fig. 1) with Fe–O–Fe bond angle approximately 130°. These chains are cross-linked by means of Fe–O–Fe bonds in which the angle is about 99°.

SAMPLE PREPARATION

Samples were prepared in a variety of ways to insure that the observed phenomena were not accidentally

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‡ Short accounts of this work were presented at the Seventh International Congress of the International Union of Crystallography, Moscow, 1966, and at the Twelfth Annual Conference on Magnetism and Magnetic Materials, Washington, D. C., 1966.

[1] Y. Allain, B. Boucher, P. Imbert, and M. Perrin, Compt. Rend. **263**, 9 (1966); E. F. Bertaut, J. Chappert, A. Apostolov, and V. Semenov, Bull. Soc. Franc. Mineral. Crist. **89**, 206 (1966); H. Watanabe, H. Yamauchi, M. Ohashi, M. Sugimoto, T. Okada, and M. Fukase, J. Phys. Soc. Japan **22**, 939 (1967).

[2] E. F. Bertaut, P. Blum, and G. Magnano, Compt. Rend. **241**, 757 (1955); Bull. Soc. Franc. Mineral. Crist. **79**, 536 (1956).

[3] P. M. Hill, H. S. Peiser, and J. R. Rait, Acta Cryst. **9**, 981 (1956).

[4] B. F. Decker and J. S. Kasper, Acta Cryst. **10**, 332 (1957).

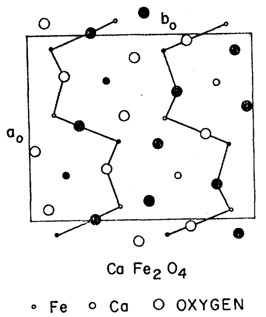

FIG. 1. (001) projection of the $CaFe_2O_4$ structure. Open and closed circles refer to atoms at $z=\frac{1}{4}$ and $\frac{3}{4}$, respectively. Fe–O–Fe–O–··· chains are indicated by heavy connecting lines.

produced by an unknown peculiarity of the method of synthesis. In the case of $CaFe_2O_4$, an intimate mixture of $CaCO_3$ and Fe_2O_3 was heated for 24 h at 900°C in a flux of anhydrous $CaCl_2$. After furnace-cooling to room temperature, the flux was leached away with water, leaving a product consisting of red needles. The compound was also prepared by direct melting of an equimolar mixture of $CaCO_3$ and Fe_2O_3 at 1250°C in a platinum crucible. In a third method, solid-state reaction of $CaCO_3$ and Fe_2O_3 was employed. The starting materials were ground and fired in air at 1000°C. The procedure of grinding and firing was repeated four times and followed by slow cooling in air after the last firing. The Cr-substituted samples were prepared both by direct melting and by solid-state reaction. In the latter case the reacted material was quenched from 1000°C and annealed in vacuum to prevent oxidation of chromium.

MAGNETIC STRUCTURE

Two different magnetic structures occur in the $Ca(Cr_xFe_{1-x})_2O_4$ system for $0\leq x\leq 0.5$. They are given in Fig. 2 and Table I. The *A* structure belongs to magnetic space group *Pn′a′m*, in which the *n* glide perpendicular to the *a* axis and the *a* glide normal to the *b* axis are antisymmetry elements. The *B* structure belongs to *Pna′m*, in which only the *a* glide is an antielement. Atoms lie in the mirror planes normal to the *c* axis and the spins therefore point along *c* in both structures. The *A* structure is most easily observed in pure $CaFe_2O_4$ at low temperatures and is readily confirmed by comparison of calculated and observed intensities given in Table II. The *B* structure is characteristic of compositions for which $x\geq 0.20$. Calculated and observed intensities for the 20% composition are given in Table III. Additional confirmation of the *B* structure is provided by the fact that the model predicts a large number of magnetic absences, in agreement with experiment.

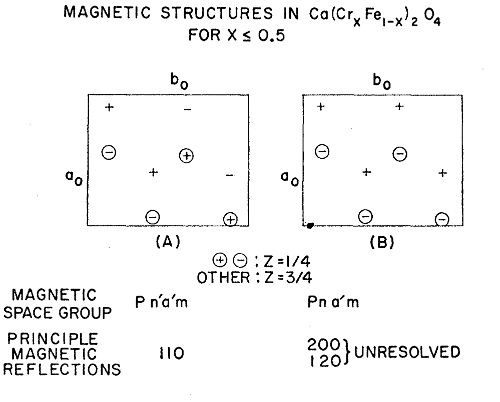

FIG. 2. Spin configurations for the *A* and *B* structures.

TABLE I. Spin assignments in structures *A* and *B*.

Atomic position[a]	*A*[b]	*B*[b]
$x_1, y_1, \frac{1}{4}$	+	−
$\bar{x}_1, \bar{y}_1, \frac{3}{4}$	+	+
$\frac{1}{2}-x_1, \frac{1}{2}+y_1, \frac{3}{4}$	+	+
$\frac{1}{2}+x_1, \frac{1}{2}-y_1, \frac{1}{4}$	+	−
$x_2, y_2, \frac{1}{4}$	−	−
$\bar{x}_2, \bar{y}_2, \frac{3}{4}$	−	+
$\frac{1}{2}-x_2, \frac{1}{2}+y_2, \frac{3}{4}$	−	+
$\frac{1}{2}+x_2, \frac{1}{2}-y_2, \frac{1}{4}$	−	−

[a] Atomic parameters according to Decker and Kasper [see Ref. 4]: $x_1=0.433$, $y_1=0.610$; $x_2=0.420$, $y_2=0.108$.

[b] Spins parallel to *c* axis.

The salient feature of our observation is that for certain composition and temperature ranges, the complete sets of reflections corresponding to both the *A* and *B* structures occur simultaneously. No lines are observed which do not belong to either the *A* or *B* sets. One example of this behavior, and perhaps the most striking, is given in Fig. 3, where the intensities of the principal magnetic reflections are given as a function of temperature for the 2.5% compound. As seen from the diagram, the *B* structure appears at about 190°K. At approximately 170°K, lines corresponding to the *A* structure make their appearance and the two sets of lines persist down to 4.2°K. An increase in the intensities of the *A* lines is accompanied by a corresponding decrease in the *B* lines. This is most clearly seen at low temperature, but is equally true at the high-temperature end when the Brillouin dependence of the moment is taken into account. One notes also that the behavior with temperature is ***reversible*** on heating and cooling, as indicated by the open and solid symbols of the figure.

TABLE II. Magnetic intensities for $CaFe_2O_4$ at 4.2°K (*A* structure).

hkl	Calculated[a]		Observed
110		11 430	11 630
210		1790	1670
130		640	600
011		70	0
230	1060		
		1140	1210
111	80		

[a] $\mu_{Fe}=4.26\mu_B$, spin direction parallel to *c* axis.

TABLE III. Relative intensities of $Ca(Cr_{0.2}Fe_{0.8})_2O_4$ at 4.2°K (*B* structure).

hkl	Calculated intensity Nuclear	Magnetic[a]	Total	Observed intensity
200 120	1602	7533	9135	9081
220	159	81	240	235
040 320 021	2120	58	2178	2172
201 121 140	1531	378	1909	1966

[a] $\langle\mu\rangle = 3.75\mu_B$, spin direction parallel to *c* axis.

Whenever the *A* or *B* structures are found to occur alone, calculations based on the observed relative intensities require the spins to lie along the *c* axis. In the "mixed" region, the relative intensities of the *A* reflections as well as those of the *B* reflections remain the same as for the "pure" structures, suggesting very strongly that two phases exist and that the spins of each structure remain pointed along the *c* axis. The constancy of the relative intensities immediately rules out the otherwise attractive possibility of a canted spin model in which the *A* reflections arise from one component of the spin and the *B* reflections from another. Canted models permitted by the magnetic space groups derived from *Pnam* fail to explain the data. However, this does not entirely eliminate canted structures since the symmetry might be lower than that determined by x rays.

More conclusive evidence against the existence of a single-phase structure which could account for the simultaneous presence of the *A* and *B* reflections, is obtained from the following calculation, which assumes only that the moments of all iron atoms are substantially equal in magnitude. (This assumption is certainly reasonable from a chemical point of view and is borne out by the Mössbauer measurements reported in Ref. 1.) We suppose that the spin on each atom in the unit cell is arbitrarily oriented. From the magnetic absences one obtains a number of relations between the spin components on different sites which greatly limit the number of possible models.[5] These models were tested directly by computing the relative intensities of the observed reflections. All single-phase models allowed by the absent reflections failed to give even a qualitative fit with the data.

TWO-PHASE MODEL

We are thus led to the conclusion that the mixed region is one in which two distinct magnetic phases coexist. The relative amounts of the phases vary with temperature in a way which depends on chromium content. In all cases, however, the variation is reversible with temperature, indicating that the two phases are in equilibrium. A good check on the model is provided by the variation of moment with temperature. On the two-phase model, the average moment at a given temperature is given by the expression

$$\mu^2 = C_A I(110) + C_B I(200+120),$$

where C_A and C_B are the reciprocals of the calculated (110) and (200+120) intensities for unit moment and I refers to observed absolute intensities obtained by normalization to the nuclear scattering, for which the atomic parameters of Decker and Kasper[4] were used. Despite the pronounced variation of phase composition with temperature, indicated in Fig. 3 for 2.5% Cr, the moment varies smoothly with temperature, deviating from Brillouin behavior in a way that is characteristic of most antiferromagnetic compounds [see Fig. 4]. Similar behavior is found for all other chromium compositions investigated. We have assumed in the foregoing that the Néel temperature of the system corresponds to the first appearance of magnetic ordering. Separate Néel points, given by the temperatures at which the individual phases first appear, do not give a good account of the data, inasmuch as large deviations from Brillouin behavior are required.

We have used the term "magnetic phase" to describe an extended region characterized by a single magnetic structure. The two-phase model assumes that this

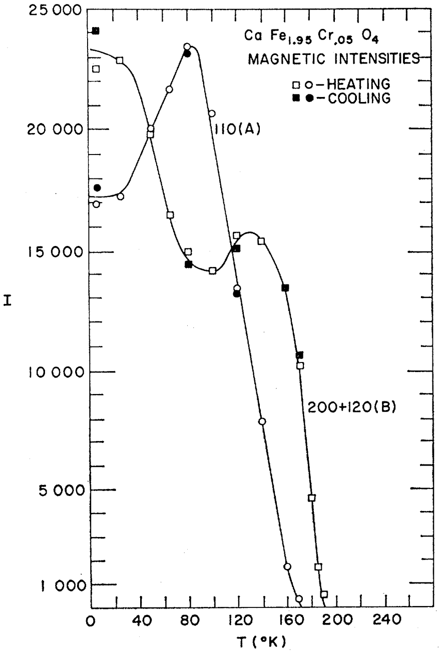

FIG. 3. Temperature dependence of the principal magnetic reflections of the *A* and *B* structures for $Ca(Cr_{0.025}Fe_{0.975})_2O_4$.

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[5] Define $\mathbf{K}_{hkl} = \Sigma_i \boldsymbol{\kappa}_i \exp(hx_i + ky_i + lz_i)$, where $\boldsymbol{\kappa}_i$ is a unit vector parallel to the spin at site *i*. Then, if $\mathbf{e}$ is the scattering vector, $F_{hkl}^2 = |\mathbf{K}_{hkl}|^2 - (\mathbf{e}\cdot\mathbf{K}_{hkl})^2 = (\mathbf{e}\times\mathbf{K}_{hkl})^2$. A magnetic absence, for which $F_{hkl}^2 = (\mathbf{e}\times\mathbf{K}_{hkl})^2 = 0$, implies that $K_{okl}^x = 0$ if (*okl*) vanishes; $K_{hol}^y = 0$ for (*hol*) absent; and $K_{hko}^z = 0$ for (*hko*) absent.

region is as least as large as the coherent scattering domain, and thus, that the two phases scatter incoherently. If, on the other hand, the single-phase regions are small compared to the domain of coherence, the effective structure factor becomes $F = xF_A + (1-x)F_B$, where x is the fraction of phase A, and the moment is no longer given by the simple expression presented above. This model is, however, untenable, since in the case of $CaFe_2O_4$, the derived dependence of moment on temperature exhibits an anomolous "bump," and in the 2.5% Cr compound the moment rises to $6\mu_B$ at 4.2°K.

MAGNETIC PHASE DIAGRAM

Using the two-phase model, the temperature dependence of the phase composition is readily obtained from the observed variation of the magnetic intensities of the A and B phases. The results are summarized in Fig. 5, where the fraction of the A phase is displayed as a function of temperature and chromium content. From this data a phase diagram has been constructed as shown in Fig. 6. The diagram shows that the Néel temperature represents a transition entirely to the B phase. For compositions less than about 20% Cr, the A phase makes its appearance at a well-defined temperature T_1. Further lowering of the temperature results in growth of the A phase and a corresponding decrease in the concentration of B. The boundary indicated by T_2 is not sharp, but encloses a region in which the B phase is essentially absent. The concentration of the B phase at helium temperatures increases with Cr concentration and for compositions between 20 and 50%, it is stable at all temperatures below T_N. Diffraction patterns for the 20–50% range show evidence of magnetic disorder at helium temperatures which increases with Cr content. Beyond 50% there is no long-range order at 4.2°K until the vicinity of β-$CaCr_2O_4$ is reached. The structure of this compound appears to be complex and is currently under investigation.

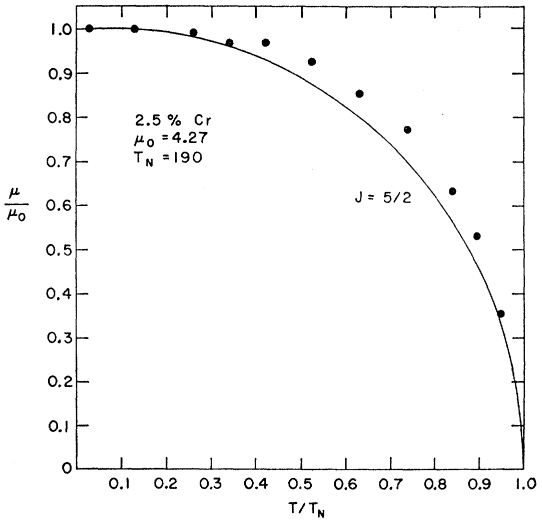

FIG. 4. Variation of moment with temperature for $Ca(Cr_{0.025}Fe_{0.975})_2O_4$. The solid curve is the Brillouin function for spin $\frac{5}{2}$.

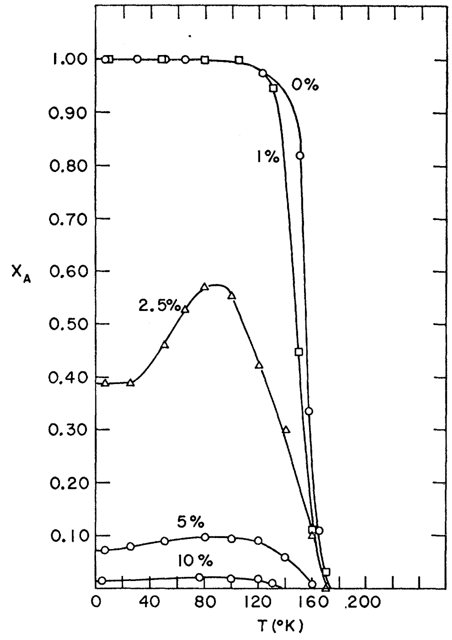

FIG. 5. Fraction of the A phase as a function of temperature. Individual curves are labelled according to the percentage of chromium.

The role of chromium in this system appears to be quite remarkable; relatively small amounts inhibit the complete transformation of the B phase to the A phase. A 10% aluminum-substituted compound, by contrast, behaves very much like pure $CaFe_2O_4$ with a reduced moment.

MAGNETIC MOMENT

The magnitude of the average moment observed at 4.2°K is given in Table IV and is seen to decrease progressively with increase of chromium content. These values are obtained by normalizing the magnetic scattering to the nuclear scattering and are probably subject to several percent error because of uncertainties in the atomic parameters. Systematic errors may also

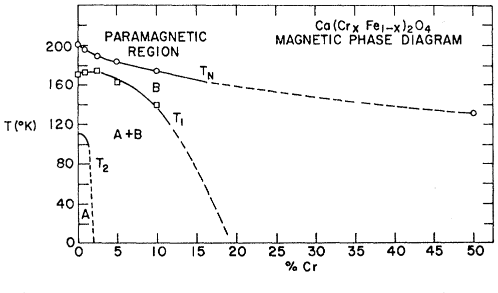

FIG. 6. Magn etic phase diagram for the system $Ca(Cr_xFe_{1-x})_2O_4$.

TABLE IV. Magnetic moment versus chromium content in $Ca(Cr_xFe_{1-x})_2O_4$.

x	μ (expt.)	Calculated iron moment (a) $\mu_{Cr}=+1.00$	(b) $\langle\mu_{Cr}\rangle=0$	(c) $\mu_{Cr}=-1.00$
0	4.26±0.10	4.26	4.26	4.26
0.01	4.30	4.33	4.34	4.35
0.025	4.26	4.34	4.37	4.40
0.05	4.13	4.29	4.35	4.40
0.10	3.96	4.29	4.40	4.51
0.20	3.75	4.44	4.69	4.94
0.33	2.85	3.78	4.27	4.77

arise, particularly for higher chromium concentrations, if these parameters change with composition. Nevertheless, the general trend can be accounted for with constant iron and chromium moments as shown in the column labeled (a) in Table IV. This calculation assumes that chromium enters the lattice with the same net-spin orientation as the iron it replaces. If the reverse is true, the iron moment must increase with addition of chromium, as indicated by the sample calculation of column (c). In the calculation of column (b), the chromium moment is assumed to have arbitrary magnitude but to be directed as often parallel as antiparallel to the iron that is replaced. Clearly, the data cannot provide a detailed description of the behavior of the individual moments without further assumptions or additional information.

$CaFe_2O_4$

The behavior of the principal magnetic reflections of the *A* and *B* phases is shown in Fig. 7 for the case of $CaFe_2O_4$ itself. The decrease in intensity with increasing temperature, which arises from the normal decrease of the moment, tends to obscure the presence of the *B* phase. In fact, it would be missed entirely if only the (110) reflection of phase *A* were followed as a function of temperature. The common practice of recording complete patterns at helium, nitrogen, and room temperatures, may have prevented previous observation in other compounds of the phenomenon reported in this paper.

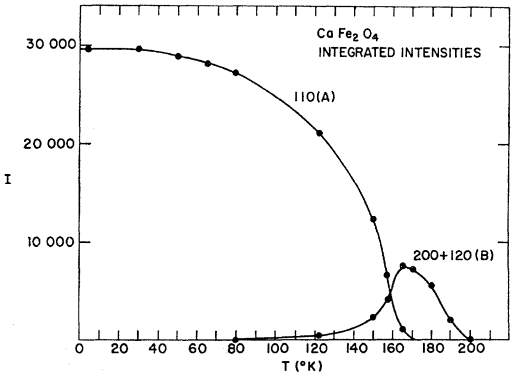

FIG. 7. Temperature dependence of the principal magnetic reflections of the *A* and *B* phases of $CaFe_2O_4$.

Our results indicate a transition to the *B* phase at $T_N=200$°K, appearance of the *A* phase at 170°K, and a moment of $(4.26\pm0.10)\mu_B$. Allain *et al.*[1] do not report the *B* phase, but give a Néel temperature of 180°K based on susceptibility, neutron, and Mössbauer measurements. Their moment of 4.05±0.15 agrees with our result within experimental error. Bertaut *et al.*[1] find $T_N=200$°K from Mössbauer measurements and a moment of 4.44±0.20, but do not report the *B* phase. Watanabe *et al.*,[1] on the other hand, find both the *A* and *B* phases and indicate a temperature region in which the two sets of lines appear simultaneously. They do not, however, establish the existence of a phase equilibrium. Their value of the Néel temperature (285°K) is considerably higher than that assigned by any of the other investigators, and the temperature at which the *A* phase first appears (140°K) is substantially lower than that given in the present paper. They estimate an approximate moment of $4.0\mu_B$ by extrapolation of intensity data from N_2 temperatures.

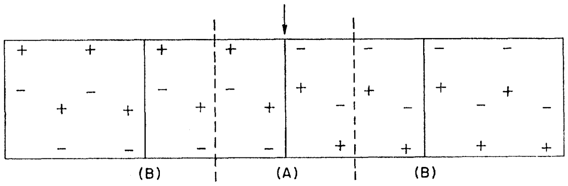

FIG. 8. Boundary (indicated by arrow) formed by two magnetic domains of the *B* phase. The region immediately adjacent to the boundary, enclosed by dashed lines, has the structure of the *A* phase.

DISCUSSION

Decker and Kasper,[4] in their discussion of the $CaFe_2O_4$ structure, suggested that the Me–O–Me–O–··· chains of Fig. 1 (Me≡metal) would be antiferromagnetic with spins alternating along the chain. This is found to be the case in both the *A* and *B* structures and is consistent with observations in spinels and garnets where the bonding is similar. Superexchange calculations indicate that the 180° Cr^{+3}–O–Fe^{+3} interaction is ferromagnetic and thus that chromium would enter the chain with spin parallel to that of its iron neighbors, if this interaction dominates. From the previous discussion of the average moment in the substituted compounds, it is clear that the data are not conclusive on this point. The chains are cross-linked ferromagnetically in the *A* structure, but antiferromagnetically in the *B* structure. The existence of an equilibrium between the two structures leads to the conclusion that this interaction is probably weak. It should be noted, however, that very similar linkages exist in the *c* direction and that these are always ferromagnetic.

The main puzzle, of course, is the existence of an equilibrium. One intuitively expects that one of the two structures to have lowest energy, and thus, except for thermal hysteresis effects which are negligible in this case, that one and only one magnetic phase would be observed at a given temperature. Stability estimates, however, must in principle include surface energy and long-range interactions between the phases. From this point of view the two-phase system may represent a disordered superstructure of A and B.

The relationship between the A and B structures can be simply described in terms of the Me–O–Me–O–··· chains of which they are composed. In the B phase the chains are identical; in the A phase they are reversed. If we consider a boundary parallel to the *a-c* plane between two magnetic domains of the B structure, spins on either side of the boundary are necessarily opposite in sign. The region spanning the boundary, as shown in Fig. 8, has the structure of the A phase. Thus, the A phase is automatically nucleated at domain boundaries of the B phase and, similarly, nuclei of the B phase are generated at domain boundaries of A. If the two-phase configuration results from such a nucleation process, we can offer no explanation at the present time for the growth of these nuclei and the dependence of their ultimate size on temperature and composition.

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Magnetoelastic Behavior of Single-Crystal Europium Oxide. I. Thermal Expansion Anomaly

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The thermal expansivity of a single crystal of EuO was determined in the temperature range 25 to 250°K by a differential-strain-gauge method. The temperature of the peak in the λ curve of expansivity is 69.2°K, in agreement with the specific-heat measurements. After correcting for the normal lattice expansivity using the Grüneisen theory, we observe that the resulting magnetoelastic component of expansivity α_{me} obeys a *magnetic Grüneisen law*, being proportional to the magnetic specific heat C_m over wide ranges of temperature both above and below the λ transition. Europium oxide can therefore be characterized by a temperature-independent "magnetic" Grüneisen constant, $\partial \ln U_m / \partial \ln V = -5.3$, given by $-3\alpha_{\mathrm{me}} C_m^{-1} B_T$, where the isothermal bulk modulus $B_T = 1.07 \times 10^{+12}$ dyn/cm^2. The *lattice* Grüneisen constant, $\partial \ln U_l / \partial \ln V = 1.9$, was similarly derived from the data at temperatures well above the λ anomaly. For U_m, the internal magnetic energy, we also derive the variation with temperature $U_m(T)/U_m(0)$, the variation with pressure $\partial \ln U_m / \partial P = 4.9 \times 10^{-12}$ dyn^{-1} cm^2, and the value $U_m(0) = -4.9 \times 10^8$ erg/cm^3 at 0°K. Comparison with results of other experiments and with theories based on the Heisenberg Hamiltonian is also presented. The model of D. C. Mattis and T. D. Schultz and of E. Pytte is consistent with the observed proportionality between C_m and α_{me}. A more general model proposed by E. R. Callen and H. B. Callen includes magnetoelastic coupling of unequal strengths to first- and second-nearest neighbors. When the second-neighbor interaction is weaker than the first, this model is also consistent with a single effective magnetic Grüneisen constant not only because the model then differs only slightly from a special case of that of Mattis and Schultz and of Pytte, but also because the spin correlation functions $\langle \mathbf{S} \cdot \mathbf{S}' \rangle_{\text{1st neighbor}}$ and $\langle \mathbf{S} \cdot \mathbf{S}' \rangle_{\text{2nd neighbor}}$ appear to be nearly proportional to each other over a wide temperature range.

INTRODUCTION

EUROPIUM oxide is an insulating ferromagnet with S-state Eu^{++} ions situated on cubic face-centered sites of the NaCl-type structure. As such EuO represents a nearly ideal Heisenberg lattice of interacting spins making its fundamental magnetic properties especially interesting to study and relate to predictions of theory. In this work (I) the magnetic thermal expansion anomaly is measured and used for describing that part of the magnetic energy which is isotropic with respect to the direction of the magnetization in the crystal. Subsequently, in II, we shall report on the *induced* isotropic and anisotropic (macroscopic) strains which appear upon application of a magnetic field and also investigate the behavior of the transition anomaly in the presence of applied magnetic fields. Previously, we measured the strength of the first-order term in the free energy that depends upon the direction of the magnetization in the crystal (magnetocrystalline anisotropy) and this was compared with predictions of a theory that treats the interaction of the otherwise isolated Eu^{++} ion with its cubic crystal environment.[1]

The meaning and fundamental usefulness of the thermal expansion anomaly for a ferromagnet is evident

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[1] N. Miyata and B. E. Argyle, Phys. Rev. **157**, 448 (1967).