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Model of Exchange-Inversion Magnetization*

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A thermodynamic theory is given of a class of magnetic crystals which transform from ferromagnetic to antiferromagnetic states as the temperature is varied. Applications are suggested to $Mn_{2-x}Cr_xSb$ and to crystals having the nickel arsenide type structure. It is shown that the exchange magnetoelastic energy is often important in such transformations and leads to an additional interaction energy of the form $(\mathbf{S}_A\cdot\mathbf{S}_B)^2$ in the effective spin Hamiltonian. It is suggested that one of the exchange constants goes linearly through zero near a critical value of some lattice coordinate characterizing the transition. There are important differences in the behavior of compact and noncompact antiferromagnetic lattices, under the assumption of nearest-neighbor interactions between sublattices. A triangular array is treated, such as might arise in crystal structures of the NiAs type.

MAGNETIC crystals are believed to exist which, without benefit of major crystallographic rearrangements, transform from ferromagnetic F (or ferrimagnetic) to antiferromagnetic AF structures as the temperature is varied. Among the numerous examples we mention only three: MnAs[1] and Dy[2] are believed to have a transition from F to AF, and Cr-modified Mn_2Sb[3] definitely has a transition from AF to F with increasing temperature, which Jaep[4] has pointed out is a first-order transition. Such transitions (which have been aptly called[3] exchange-inversion transitions) pose a theoretical problem because they are not expected to occur, as far as we know, within the framework of pure molecular field theory with temperature-independent interactions. There are, however, numerous other ways in which such transitions may occur, and several explanations have been suggested by Néel,[5] Smart,[6] Pratt,[7] and Liu *et al.*[8] In the present paper we examine the consequences of another specific phenomenological model which can give rise to such transitions. Our model has elements in common with the models of Néel and of Smart, and it appears to provide a physical justification for an unusual interaction postulated by Liu *et al.*, but the new model is different from all of these. Our model should be viewed only as one possible model applicable to certain substances; for other substances it may be inapplicable. It leads to a number of results which appear qualitatively to resemble features observed in numerous substances.

We suppose, to start with, that the magnetic structure may be decomposed into two identical lattices A and B, each tightly coupled by exchange within itself and each having a net magnetic moment at all temperatures below the Néel or Curie temperature. The magnetic structure of the substances of interest to us will not always permit a decomposition into only two sublattices, with the property that all the nearest neighbors of the atoms on one sublattice lie on the second sublattice; in particular, we shall have to make an important modification in order to treat NiAs-type structures with metal ions in a simple hexagonal arrangement within closely stacked layers. Similarly, we assume to start with that the ordered states have colinear magnetic structures, but some of the features of our model may be reproduced in canted or spiral structures.

Our central special assumption is that the exchange coupling between the two lattices is a linear function of some one configurational coordinate or lattice parameter and crosses zero at a particular critical value, say a_c, of this parameter. One could, as an alternate assumption, suppose that the exchange between the two lattices is a linear function of the temperature and crosses zero at some temperature T_c, in the neighborhood of which the ferromagnetic/antiferromagnetic transition occurs. The two formulations of the basic assumptions would be equivalent if the temperature coefficient of the parameter a were constant over the whole temperature range of interest, but there may be large magnetic effects on the expansion coefficient da/dT which destroy its constancy. It is essential to take into account the variation of da/dT. We will arrange to have most of the magnetic expansion properties come out of the model, but we feed in the usual lattice thermal expansion. We select the first formulation, rather than correct the second for expansion changes. It is certainly an *ad hoc* assumption to

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[1] L. F. Bates, Phil. Mag. **8**, 714 (1929); C. Guillaud, thesis, Strasbourg, 1943 (unpublished); J. phys. radium **12**, 223 (1951). There is equally persuasive evidence, as C. P. Bean has pointed out (private communication) that the transition is from ferromagnetism to paramagnetism. Bean has proposed an ingenious explanation of how such a first-order F/P transition may occur. See also G. E. Bacon and R. Street, Nature **175**, 518 (1955).

[2] F. Trombe, Compt. rend. **221**, 19 (1945); **236**, 591 (1953). J. F. Elliott, S. Legvold, and F. H. Spedding, Phys. Rev. **94**, 1143 (1954).

[3] T. J. Swoboda, W. H. Cloud, T. A. Bither, M. S. Sadler, and H. S. Jarrett, Phys. Rev. Letters **4**, 509 (1960).

[4] W. F. Jaep, du Pont Engineering Department (private communication).

[5] L. Néel, Compt. rend. **242**, 1824 (1956); Izvest. Akad. Nauk S.S.S.R. Ser. Fiz. **21**, 890 (1957) [translation: Bull. Acad. Sciences U.S.S.R. **21**, 889 (1957)].

[6] J. S. Smart, Phys. Rev. **90**, 55 (1953).

[7] G. W. Pratt, Jr., Phys. Rev. **108**, 1233 (1957).

[8] S. H. Liu, D. R. Behrendt, S. Legvold, and R. H. Good, Jr., Phys. Rev. **116**, 1464 (1959).

suppose that one exchange constant vanishes at some accessible value of a lattice parameter—one suggestion[9] is that the superexchange and indirect exchange interactions accidentally cancel at this value. The materials cited are all metallic conductors, and the spatial dependence of the exchange interactions offers possibilities for accidents, such as that experimentalists will discover materials in which cancellations of two interactions occur. By varying the temperature and by forming solid solutions, it is not unusual to cover a 0.1 A range in lattice parameter with a given crystal—if the exchange integral crosses zero at one point at random in an appropriate 2 A range, one might argue, partly facetiously, that there is a 1:20 chance that a new magnetic crystal will display a F/AF transition.

The mathematical treatment is elementary. We do not include magnetocrystalline anisotropy, because this is not central to the present model; anisotropy can easily be added where it is known. We wish, however, to include specifically the effects of the strain dependence of the isotropic exchange energy—what Néel[10] has called the *exchange magnetostriction.* This makes a more important contribution to the energy than previously recognized; for example, in MnAs the volume change at the possible F/AF transition is about 2%; the associated elastic energy will be of the order of 10^8–10^9 ergs/cm^3, which is comparable with the interlattice exchange energy. This is appreciably larger than the usual run of anisotropy energies, and in this circumstance the exchange magnetostriction will dominate at the transition, rather than the anisotropy energy. In $Mn_{1.96}Cr_{0.04}Sb$ the deformation at the AF/F transition is 0.6%; the transition here appears to set in near a fixed value of the c-lattice parameter. The Cr content, by contracting the lattice, appears chiefly to influence the temperature at which the critical lattice parameter is reached, but other alloying constituents may have more important direct effects on the interlattice coupling, so that the size of an ion is not the only criterion of its effect on the transition.

Much larger strains and strain-energy densities than these are found in magnetic crystals subject to Jahn-Teller deformations: Such deformations have been discussed by Goodenough, McClure, Dunitz, Orgel, Wojtowicz, Finch, Sinha, and others in connection with transition metal compounds, particularly cupric and manganite oxides and ferrites. The crystals often exhibit a first-order tetragonal/cubic transition. The deformations around individual ion sites are associated with the removal of orbital degeneracy, and the strain is coupled to the orbital motion. The greater the splitting of the degeneracy, the greater the quenching of the spin-orbit coupling. The quenching tends to weaken (in general) the coupling between magnetization direction and strain. The argument here does not mean that Jahn-Teller orbital situations do not have fairly high magnetocrystalline anisotropy and associated magnetostriction, for indeed they do, but the argument suggests that the purely anisotropic magnetostrictive part of the Jahn-Teller energy may not be as large as the exchange magnetoelastic energy, except perhaps in quite special situations. An anisotropic magnetostrictive deformation of 10^{-3} is generally considered to be extremely high, but it is lower than the exchange magnetostriction which is the central theme of the present paper. Thus, that part of the Jahn-Teller strain which is connected with spin direction may not be very important.

If, however, a Jahn-Teller deformation *transition* should occur below the F/P or AF/P transition temperature, then the accompanying change in atom spacing might be enough to cause a F/AF transition purely as a side effect of the JT first-order transition. Here P denotes a paramagnetic phase. We would expect to find such combined F/AF–JT transformations, but it is not clear that any have been identified at present. Their thermodynamic treatment would require an extension of the theory below, with the introduction of new variables. In the crystals treated in the present paper, it appears that exchange magnetostriction can plausibly provide the necessary driving force for the observed deformation, as will emerge below, with values of $(\partial J/\partial e)/J \sim 10$, where J is the exchange integral and e the strain. It is not possible without further experimental measurements tested against the present theory to make an unambiguous assignment of responsibility for the F/AF transitions. One may note that in a Jahn-Teller transition one would expect in general both the c and a lattice parameters to change discontinuously at the transition; this is indeed observed, but not in our materials.

One should note further that indirect spin-spin coupling by phonons will cause the appearance of terms in the free energy of the form $M_{Az}^2 M_{Bz}^2$, etc. Such terms may have roughly the same effect on a *magnetic* transition as the $(\mathbf{M}_A \cdot \mathbf{M}_B)^2$ terms which, as we show below, arise from the exchange magnetoelastic energy. The phonon spin-spin coupling will be important when the Jahn-Teller effect is important—that is, when the magnetocrystalline anisotropy is high. First-order transformations in this circumstance have been considered by Néel. Our present paper is not directly applicable to such substances.

EXCHANGE MAGNETOELASTIC ENERGY

We assume that the interlattice exchange energy of a specimen of volume V can be written as

$$-\rho(a-a_c)V\mathbf{M}_A \cdot \mathbf{M}_B$$

where a is the relevant lattice parameter and a_c is the value at which the interlattice exchange interaction

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[9] This suggestion emerged in a discussion with Dr. H. S. Jarrett of du Pont; see also work cited in footnote 3.

[10] L. Néel, Bull. soc. franç. minéral. crist. 77, 257 (1954); Smart, footnote 5.

changes sign; ρ denotes $\partial\alpha/\partial a$, where α is the molecular field constant connecting the sublattice magnetizations $\mathbf{M}_A$ and $\mathbf{M}_B$. We have no *a priori* knowledge of the sign of ρ, which may be positive or negative, according to the substance.

If we may neglect the intrinsic dependence of the sublattice magnetization on the parameter a, the parts of the free energy at zero pressure which involve a are, to the lowest relevant order,

$$F=\tfrac{1}{2}RV(a-a_T)^2-\rho(a-a_c)V\mathbf{M}_A\cdot\mathbf{M}_B, \tag{1}$$

where R is equal to the appropriate elastic stiffness constant divided by a^2; here a_T is the equilibrium value of a at temperature T for the orientation $\mathbf{M}_A\perp\mathbf{M}_B$. We shall not, in the interest of simplicity, extend the model to yield the temperature dependence of $M=|\mathbf{M}_A|=|\mathbf{M}_B|$, but shall take this as determined by experiment and assumed to be independent of the relatively weak interlattice interaction.

The equilibrium value of a is given by

$$(\partial F/\partial a)_T\cong RV(a-a_T)-\rho V\mathbf{M}_A\cdot\mathbf{M}_B=0. \tag{2}$$

Here we have neglected higher order effects. Thus we have

$$a=a_T+(\rho/R)(\mathbf{M}_A\cdot\mathbf{M}_B). \tag{3}$$

In the molecular field approximation $a=a_T$ in the paramagnetic region. The term in $\mathbf{M}_A\cdot\mathbf{M}_B$ gives the thermal expansion or contraction resulting from the intrinsic decrease of sublattice magnetization with increasing temperature. The same term also gives the change in the lattice parameter when the orientation of $\mathbf{M}_A$ relative to $\mathbf{M}_B$ is changed. Thus the difference in a at constant temperature between the ferromagnetic and antiferromagnetic states is

$$\Delta a=a_{\mathrm{F}}-a_{\mathrm{AF}}=2\rho M^2/R. \tag{4}$$

The sign of $a_{\mathrm{F}}-a_{\mathrm{AF}}$ determines the sign of ρ.

We now substitute (3) in (1), obtaining

$$F/V=-(\rho^2/2R)(\mathbf{M}_A\cdot\mathbf{M}_B)^2-\rho(a_T-a_c)(\mathbf{M}_A\cdot\mathbf{M}_B). \tag{5}$$

We see that if $\rho(a_T-a_c)$ is positive the interaction is ferromagnetic: It is the sign of $\rho(a_T-a_c)$ and not of $\rho(a-a_c)$ that determines the effective sign of the interaction.

If φ is the angle between $\mathbf{M}_A$ and $\mathbf{M}_B$, we see that the energy density (5) involves

$$\cos^2\varphi=\tfrac{1}{2}(1+\cos 2\varphi), \tag{6}$$

in addition to the usual $\cos\varphi$ dependence of the exchange energy. A term in the free energy in the cosine of twice the angle was put forward simply as a postulate by Liu *et al.*[8] in discussing dysprosium; we have found in Eq. (5) one explanation of the origin of such a term. Our result suggests that there is no necessary connection between the temperature dependences of the $\cos\varphi$ and $\cos 2\varphi$ terms. The $\cos 2\varphi$ dependence should not be confused with the $\cos(\varphi/2)$ dependence found by Anderson and Hasegawa[11] for the Zener double exchange interaction. Terms in a spin Hamiltonian having the form $(\mathbf{S}_1\cdot\mathbf{S}_2)^2$ may arise in the way we have indicated.

The condition $\partial F/\partial\varphi=0$ for an extremum has several solutions; the minimum has $\sin\varphi=0$, so that

$$F/V=-(\rho^2/2R)M^4\pm\rho M^2(a_T-a_c), \tag{7}$$

with one sign corresponding to ferromagnetic order and the other to antiferromagnetic order. There occurs a first-order phase transition between the two states at a temperature T_0 such that

$$a_T=a_c. \tag{8}$$

We observe that a_T, not a, enters the condition for the transition temperature. At this temperature the actual values of a for the two states will differ by the amount given in Eq. (4), with a_c half-way in between. We have assumed the sublattice magnetization M does not change on passing through the transition.

The term in $\cos^2\varphi$ in (5) acts as a potential barrier separating the ferromagnetic and antiferromagnetic states and may cause a temperature hysteresis at the transition. The instability criterion for an extremum is

$$\partial^2F/\partial\varphi^2=V(\rho^2M^4/R)\cos 2\varphi+V\rho(a_T-a_c)M^2\cos\varphi\leqq 0. \tag{9}$$

Setting $\cos\varphi=\pm1$, instability occurs when

$$a_T-a_c=\pm\rho M^2/R, \tag{10}$$

suggesting that the temperature hysteresis—the difference between the temperatures at which the transition occurs on warming and on cooling—may be as great as that determined by

$$\Delta a_T=2\rho M^2/R, \tag{11}$$

or, if the Grüneisen relation is applicable,

$$(\gamma C_L/a_0R)\Delta T=2\rho M^2/R, \tag{12}$$

where C_L is the lattice heat capacity per unit volume and γ is the Grüneisen constant. The result (11) must not be confused with (4), which gives the difference in a between the two states at the temperature T_0 at which they are in equilibrium.

One must bear in mind that the width of the temperature hysteresis may often be much less than (12) suggests; the width (in temperature) may even be essentially zero. The point is that the phase of lowest free energy may be able to nucleate and to grow at smaller temperature differences than (12). This fact is well known in connection with order-disorder transformations of the first order in alloys, where often no hysteresis is observed. In antiferromagnetics, however, we frequently do observe the magnetic hysteresis connected

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[11] P. W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955); P.-G. de Gennes, Phys. Rev. **118**, 141 (1960).

with the flopping field $\sim(2H_E H_A)^{\frac{1}{2}}$. Without a detailed study, we really do not know what to expect by way of temperature hysteresis in the present problem. The presence of nucleation centers will reduce the hysteresis, so that the purer specimens may show more hysteresis.

PRESSURE DEPENDENCE OF THE TRANSITION TEMPERATURE

We want to treat the effect of hydrostatic pressure on the transition temperature between ferro- and antiferromagnetism without going into the geometry (for any particular crystal) of the coordinate we have denoted by a. We shall simply assume for the present that $-pV(da/a)$ is the element of work done on the substance by the pressure p in causing the change da. Then, at the first-order transition, the Clausius-Clapeyron equation gives us

$$\frac{dT_0}{dp}=-\frac{V\Delta a/a}{\Delta(\partial F/\partial T)_p}=\frac{\Delta V}{\Delta S}, \tag{13}$$

where now F is the Gibbs free energy. Using (4) and (7),

$$\frac{dT_0}{dp}=\frac{2\rho M^2/Ra}{2\rho M^2(\partial a_T/\partial T)_p}=\frac{1}{aR(\partial a_T/\partial T)_p}. \tag{14}$$

With the Grüneisen relation for the lattice thermal expansivity, we have

$$dT_0/dp\approx 1/\gamma C_L, \tag{15}$$

where C_L is the lattice heat capacity per unit volume and γ is the Grüneisen constant for the crystal direction under consideration. This specific model actually yields that expression for dT_0/dp which has often been used as an empirical rule in other phase transitions. We must emphasize that $\partial a_T/\partial T$ may contain some magnetic effects as well as the usual phonon anharmonic effects. The magnetic effects included will be those which do not change sign at the F/AF transition.

MAGNETIC FIELD DEPENDENCE OF THE TRANSITION TEMPERATURE

The Clausius-Clapeyron equation becomes

$$(\partial T_0/\partial H)_p=-\Delta(MV)/\Delta S\cong 2MV/\Delta(\partial F/\partial T)_p, \tag{16}$$

recalling the definition of M as the magnetization of *one* sublattice. Then

$$(\partial T_0/\partial H)_p=-1/\rho M(\partial a_T/\partial T)_p, \tag{17}$$

or, using (14),

$$(\partial T_0/\partial H)_p=-(aR/\rho M)(\partial T_0/\partial p)_H. \tag{18}$$

We can also obtain (18) from the thermodynamic relation

$$(\partial T_0/\partial H)_p=-(\partial T_0/\partial p)_H(\partial p/\partial H)_{T_0}, \tag{19}$$

where

$$(\partial p/\partial H)_{T_0}=-\Delta(\partial F/\partial H)_{p,T_0}/\Delta(\partial F/\partial p)_{H,T_0}=V\Delta M/\Delta V=Ra/\rho M, \tag{20}$$

in agreement with (18).

It is not always easy to pick a reliable value for $(\partial T_0/\partial H)_p$ from the experimental magnetization curves at various temperatures.

GENERALIZATION FOR NiAs STRUCTURE

In Cr-modified $\mathrm{Mn_2Sb}$ it is known[3] that $\Delta a=a_{\mathrm{F}}-a_{\mathrm{AF}}$ is positive so that, according to (4), ρ is positive. Actually our parameter a for this crystal must be the c lattice parameter, as it is the c parameter which changes discontinuously at the AF/F transition. It is reasonable to take the thermal expansivity $\partial a_T/\partial T$ as positive, and this is compatible with the lattice parameter data on $\mathrm{Mn_2Sb}$. Thus, below T_0 we have $\rho(a_T-a_c)$ negative, which leads, according to (5), to antiferromagnetism below T_0 and ferromagnetism above, in agreement with observation. Further, the observed sign of $(\partial T_0/\partial p)_H$ is positive and that of $(\partial T_0/\partial H)_p$ is negative, in conformity with (15) and (18). We shall touch on the quantitative situation later, but the qualitative situation is not incompatible with our model, with the A and B lattices composed of alternate sets of layers normal to the c axis of the crystal.

In MnAs we know[1] that Δa is also positive, so that one would expect, just as above, that the antiferromagnetic state is stable at low temperatures. This is contrary to observation. Further, the observed value[12] of $(\partial T_0/\partial p)_H$ is negative, equal to -0.012 deg C/atm, which contradicts the unambiguous positive sign predicted by (15). The observed negative sign is in accord with the Le Chatelier principle. The correction of our difficulties lies in a consideration of the possible antiferromagnetic spin configurations on a simple hexagonal layer lattice.

We recognize that, according to C. P. Bean, there may be no AF state in MnAs. The situation is not yet clear. Our discussion must be viewed essentially as an illustration of the special kind of behavior which may occur in NiAs-type structures and with noncompact spin lattices.

The value of the c lattice parameter of MnAs varies smoothly[13] near T_0, but the a parameter changes discontinuously. This implies that the sublattices are composed of lines of magnetic atoms, the lines running parallel to the c axis. We assume that the spins on an individual line all point the same way. At the F/AF transition the lines alter their spin direction. We have assumed in Eq. (1) that, referred to $\mathbf{M}_A\perp\mathbf{M}_B$, the

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[12] D. S. Rodbell (private communication).

[13] B. T. M. Willis and H. P. Rooksby, Proc. Phys. Soc. (London) **B67**, 290 (1954).

A–B exchange energy in the antiferromagnetic configuration is equal but opposite to that in the ferromagnetic configuration. An antiferromagnetic structure for which this is true we call *compact;* the layer arrangement in Cr-modified Mn_2Sb is compact. However, with lines of spins it is not possible to get as good an antiferromagnetic energy as this, for the simple hexagonal structure. Such a structure is noncompact. Wannier[14] has considered the problem on the Ising model using nearest-neighbor interactions. He finds the best antiferromagnetic array has an energy equal to $-1/3$ of the ferromagnetic array. Loudon[15] has obtained the more appropriate result $-1/2$ using the classical isotropic exchange interaction; the stable configuration under antiferromagnetic nearest-neighbor interactions is triangular. He has extended the calculation to second nearest-neighbor interactions, but we shall restrict ourselves to nearest neighbors. It is evident then that for MnAs we could patch up (1) as

$$F=\tfrac{1}{2}RV(a-a_T)^2-\rho(a-a_c)V[\mathbf{M}_A\cdot\mathbf{M}_B+\tfrac{1}{3}M^2], \tag{21}$$

as this gives (at constant a) the ratio $-1/2$ for the energies in the antiferromagnetic and ferromagnetic orientations. It is more satisfying, as Marshall Sparks has emphasized in a discussion, to go over (for MnAs with nearest-neighbor interactions between lines) to the appropriate three-sublattice model.

For three sublattices, with $M=|\mathbf{M}_A|=|\mathbf{M}_B|=|\mathbf{M}_C|$,

$$\begin{aligned}F/V=&\tfrac{1}{2}R(a-a_T)^2\\&-\rho(a-a_c)M^2[\cos\varphi+\cos\theta+\cos(\varphi-\theta)],\end{aligned} \tag{22}$$

which has extrema at θ, $\varphi=0$, $-2\pi/3$, corresponding to the values $\mathfrak{D}=3$ and $-3/2$ for the quantity in the square brackets. Thus the stable spin array is either ferromagnetic or an equilateral triangle Δ. Minimizing F/V with respect to a, we obtain

$$a=a_T+(\rho M^2/R)\mathfrak{D}, \tag{23}$$

or

$$a_F=a_T+3\rho M^2/R;\quad a_\Delta=a_T-3\rho M^2/2R,$$

and

$$\Delta a=9\rho M^2/2R, \tag{24}$$

bearing in mind that M here is 1/3 of the ferromagnetic saturation magnetization, in terms of which (24) would be $\rho M_s^2/2R$. We write

$$\delta=\mathfrak{D}-\tfrac{3}{4},$$

so that $\delta=9/4$ for F and $-9/4$ for Δ. The parts of F/V linear in δ are

$$F/V=-\rho[a_T+(3\rho M^2/4R)-a_c]M^2\delta, \tag{25}$$

and the criterion for the F/Δ transition temperature is that

$$a_c=a_T+(3\rho M^2/4R), \tag{26}$$

so that a magnetic term (a contraction) now helps determine the transition, along with the usual phonon expansion contained in a_T. In MnAs the magnetic term is almost certainly dominant near the transition.

We must modify the pressure coefficient $(\partial T_0/\partial p)_H$ by using in (14) for $\partial a_T/\partial T$ as written the quantity

$$(\partial a_{TM}/\partial T)=(\partial a_T/\partial T)_M+(3/4)(\rho/R)(\partial M^2/\partial T)_a, \tag{27}$$

instead of the phonon contribution alone. These considerations permit $(\partial T_0/\partial p)_H$ to be negative for MnAs, as observed, and they also remove the apparent contradiction between the nature of the low-temperature state and the sign of Δa. The result (4) goes over unchanged to the present situation, but we should take ΔV as $2V\Delta a/a$ in (13), because the cell volume is proportional to a^2c. With this adjustment in ΔV and with the value of the latent heat 1.8 cal/g measured by Bates,[1] the observed values of ΔS and ΔV satisfy the Clausius-Clapeyron relation.

NÉEL TEMPERATUE (COMPACT STRUCTURE)

We consider now the determination of the temperature T_n above which the high-temperature ordered phase becomes paramagnetic. If the high-temperature phase is antiferromagnetic, the present treatment applies only if the antiferromagnetic structure is simple or "compact." We treat MnAs, which is noncompact, later. The exchange magnetoelastic term does not enter into the determination of the Néel temperature because the paramagnetic transition is second order, so that terms in M^4 in the free energy may be neglected at the transition in comparison with terms in M^2. We therefore may assume that the Curie law is valid in the paramagnetic region, so that for $T>T_n$:

$$M_AT=c_0H_{\text{eff}}{}^A;\quad M_BT=c_0H_{\text{eff}}{}^B, \tag{28}$$

where c_0 is the specific Curie constant for each lattice, per unit volume. If the phonon thermal expansivity $\partial a_T/\partial T$ is constant, we may write

$$\rho(a_T-a_c)=(T-T_0)\nu, \tag{28}$$

where ν denotes $\rho(\partial a_T/\partial T)$.

Then

$$\begin{aligned}M_AT&=c_0[\beta M_A+(T-T_0)\nu M_B+H];\\M_BT&=c_0[(T-T_0)\nu M_A+\beta M_B+H].\end{aligned}$$

These equations have a nontrivial solution for M_A, M_B for $H=0$ when

$$\begin{vmatrix}T-c_0\beta & -(T-T_0)\nu c_0\\-(T-T_0)\nu c_0 & T-c_0\beta\end{vmatrix}=0, \tag{29}$$

so that the Néel temperature T_n is the highest solution of

$$T_n=c_0(\beta\pm T_0\nu)/(1\pm c_0\nu), \tag{30}$$

which often may be the solution for which $\pm\nu$ is

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[14] G. Wannier, Phys. Rev. **79**, 357 (1950).

[15] R. Loudon (private communication).

negative, as β is supposed to be the dominant interaction.

PARAMAGNETIC SUSCEPTIBILITY (COMPACT STRUCTURE)

The susceptibility for $T > T_n$ is found, on adding the two equations (28), to be

$$\chi = c_{\text{eff}}/(T-\theta), \tag{31}$$

where the effective Curie constant is

$$c_{\text{eff}} = 2c_0/(1-c_0\nu), \tag{32}$$

and the paramagnetic Curie temperature is

$$\theta = c_0(\beta - T_0\nu)/(1-c_0\nu). \tag{33}$$

If ν is positive, so that the upper transition is F/P, then we see that $T_n = \theta$. If ν is negative, so that the upper transition is AF/P, then $T_n = c_0(\beta + T_1\nu)/(1+c_0\nu)$ and θ will be $< T_n$. Néel noted earlier that temperature-dependent exchange interactions modify the apparent Curie constant.

FURTHER PROPERTIES

Near the F/AF transition the exchange contribution to the energy of a Bloch wall will be unusually low, provided that the directions of easy magnetization are parallel to the elements of a sublattice. The walls will also be unusually thin. It is likely that these properties of the walls will lead to very low magnetic hysteresis in the ferromagnetic state—subject to the restriction on the easy direction.

The spin-wave contribution to the low-temperature heat capacity may be abnormally large, although still of the $T^{\frac{3}{2}}$ form, as can be seen from the calculation of Herring and Kittel[16] for an orthorhombic structure. In some extreme instances it may be possible to detect experimentally the spin-wave heat capacity despite a background of a metallic type of electronic heat capacity.

The antiferromagnetic resonance frequency should be unusually low in the AF state near the AF/F transition, and the temperature dependence of the resonance should reflect the variation of the interlattice exchange interaction.

MAGNETIC PROPERTIES IN THE ANTIFERROMAGNETIC STATE: METAMAGNETISM AND HYSTERESIS (COMPACT STRUCTURE)

The discussion of magnetic properties in the antiferromagnetic state is fairly sensitive in places to the assumption of zero anisotropy, and our results will apply only for external magnetic fields $\mathbf{H}$ large enough to cause the A and B magnetizations to arrange themselves symmetrically about the direction of $\mathbf{H}$; this is the geometry contemplated in the classical Landau[17] calculation of the perpendicular susceptibility of an antiferromagnet. We let θ be the angle between $\mathbf{M}_A$ and $\mathbf{H}$ and between $\mathbf{M}_B$ and $\mathbf{H}$. Then, from (5), with M taken to be constant,

$$F/V = -2MH\cos\theta - \alpha M^2\cos 2\theta - \eta M^4\cos^2 2\theta, \tag{34}$$

where $\alpha = \rho(a_T - a_c)$, and $\eta = (\rho^2/2R)$. The extrema are given by

$$2MH\sin\theta + 2\alpha M^2\sin 2\theta + 4\eta M^4\cos 2\theta\sin 2\theta = 0. \tag{35}$$

One root is $\sin\theta = 0$; after factoring this out the equation is

$$2MH + 4\alpha M^2\cos\theta + 8\eta M^4\cos 2\theta\cos\theta = 0. \tag{36}$$

For small deviations ϵ of θ from $\pi/2$, we have from (36):

$$\epsilon = \frac{H}{-2\alpha M + 4\eta M^3}. \tag{37}$$

The initial perpendicular susceptibility in the antiferromagnetic state is given by, for a compact structure,

$$\chi = \frac{2M\epsilon}{H} = \frac{1}{-\alpha + 2\eta M^2} = \frac{1}{-\nu(T-T_0) + 2\eta M^2}. \tag{38}$$

If ν is negative, a plot of $1/\chi$ vs T will increase linearly from $\rho\Delta a/2$ at T_0, but bending over as M^2 decreases near T_n. This behavior appears to be often observed in substances with F/AF/P transitions.[18]

At high fields there occur magnetization discontinuities and hysteresis, as usual in metamagnetic phenomena. It is convenient to rewrite (34) as

$$f = F/\rho M^4 V = -h\cos\theta + \xi\cos 2\theta - \cos^2 2\theta, \tag{39}$$

where $h = 2H/\eta M^3$ and $\xi = -\nu(T-T_0)/\eta M^2$. Letting $x = \cos\theta$, the extrema are given by

$$h = (8+4\xi)x - 16x^3, \tag{40}$$

after factoring out the solution $\sin\theta = 0$. Typical solutions are plotted in Fig. 1. The discontinuity in x, which is the relative net magnetization, for increasing h occurs at

$$x_1 = [(2+\xi)/12]^{\frac{1}{2}}; \quad h_1 = 4[(2+\xi)/3]^{\frac{3}{2}}. \tag{41}$$

On decreasing h the unstable branch of the curve sets in at

$$h_2 = 4\xi - 8. \tag{42}$$

The unstable return branch is shown only for $\xi = 5$; for $\xi = 2$, 3, and 8 it is replaced by a vertical discontinuity. There is no room on the plot to show the vertical return for $\xi = 1$, which falls at negative h. We emphasize that the hysteresis as shown is an intrinsic property of the model, but may possibly be modified by nucle-

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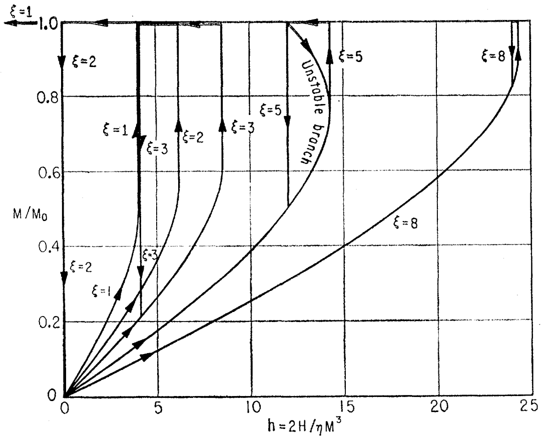

FIG. 1. Relative net magnetization in the antiferromagnetic state vs perpendicular magnetic field in normalized units, for various values of ξ, which is a direct measure of the intralattice exchange interaction or of the temperature difference $T-T_0$. Demagnetizing effects (which lead at low h to the formation of domains) have been neglected.

ation. At high fields the magnetization is shown as constant, but we should add to this the effect of the intrinsic susceptibility of each sublattice: that is, in the free energy the sublattice entropy terms and the terms in β should be retained to give the high-field intrinsic susceptibility.

NÉEL TEMPERATURE AND PARAMAGNETIC SUSCEPTIBILITY FOR NiAs STRUCTURE

We consider the molecular field

$$\mathbf{H}_A=\beta\mathbf{M}_A+\alpha(\mathbf{M}_B+\mathbf{M}_C)+\mathbf{H},\quad \text{etc.} \tag{43}$$

For β positive the Néel temperature is given by

$$T_n=c_0(\beta+|\alpha_n|), \tag{44}$$

where c_0 refers to one of the three sublattices and α_n is evaluated at T_n.

In discussing the susceptibility at $T>T_n$, it is convenient to expand α around its value at T_n:

$$\alpha=\alpha_n+\rho(da_T/dT)_{T_n}(T-T_n), \tag{45}$$

or

$$\alpha=\rho(da_T/dT)(T-T'), \tag{46}$$

where

$$T'=T_n-[\alpha_n/\rho(da_T/dT)]. \tag{47}$$

Then, if we write

$$\chi=\frac{c_{\text{eff}}}{T-\theta}, \tag{48}$$

we have

$$c_{\text{eff}}=\frac{3c_0}{1-2c_0\rho(da_T/dT)}; \tag{49}$$

$$\theta=c_0\frac{\beta-2\rho(da_T/dT)T'}{1-2c_0\rho(da_T/dT)}=T_n-c_{\text{eff}}|\alpha_n|. \tag{50}$$

A tentative numerical analysis of MnAs is given in Appendix A.

TENTATIVE ANALYSIS OF $Mn_{2-x}Cr_xSb$

According to Swoboda *et al.*[3] the transition from F to AF occurs on cooling when the c-lattice parameter decreases to 6.53 A, for compositions $Mn_{2-x}Cr_xSb$, with $x=0.04$, 0.09, and 0.12. The fact that the c axis alone suffers a discontinuity at the transition implies that the antiferromagnetic structure consists of layers (not necessarily single planes) normal to the c axis, and this is confirmed by neutron studies. The antiferromagnetic lattices are thus compact in our sense, and the theory of Eqs. (1) through (20), and (28)–(33), should apply directly. The theory shows that the criterion for the transition is that c at the mid-point of the discontinuity should determine the critical value; the experiments indicate that c just above the transition has a simpler behavior. This appears to be fortuitous within the low accuracy of reading off the published curves. The natural suggestion is that the critical parameter depends slightly upon the Cr content. The value of Δc as a function of Cr content varies approximately as M^2, in agreement with the theoretical result (4). A calculation $\Delta(\partial c/\partial T)$ using constants determined from Δc and dT_0/dp works out in fairly good agreement with the experimental value.

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APPENDIX A. TENTATIVE ANALYSIS OF THE PROPERTIES OF MnAs

In the absence of conclusive neutron diffraction structural studies on MnAs, it is premature and rash to make specific detailed applications of the above theory to this crystal, but it is of some interest to consider the orders of magnitude of relevant physical quantities, assuming that the transitions are $F/\Delta/P$.

The pressure coefficient $(\partial T_0/\partial p)_H$ has the value -1.2×10^{-8} deg/dyne cm^{-2}, according to Rodbell. From the expansion data of Willis and Rooksby we estimate for the orientation-independent part of the expansivity $\partial a_{TM}/\partial T\approx1.5\times10^{-12}$ cm/deg near T_0, by taking the average on either side of the transition. From (14), as modified by the discussion following (27), we estimate the elastic modulus for the special strain involved:

$$a^2R = 2a/(\partial a_{TM}/\partial T)(\partial T/\partial p)_H \approx 4.2\times 10^{12}\ \text{erg/cm}^3. \quad \text{(A.1)}$$

It would be good if this were known directly. From $a_{\mathrm{F}} - a_{\mathrm{AF}} = 3.4\times 10^{-10}$ cm, we estimate

$$\rho = 2(a_{\mathrm{F}} - a_{\mathrm{AF}})R/9M^2 \approx 5.4\times 10^{12}\ \text{cm}^{-1}. \quad \text{(A.2)}$$

Note that ρ is positive. In terms of the strain dependence of the exchange integral, this value of ρ corresponds roughly to $\partial J/\partial e \approx 2\times 10^{-13}$ ergs, which is quite plausible. We can check these estimates independently by looking at the difference in $\partial a/\partial T$ above and below the transition, which is given by

$$(\partial a_{\mathrm{F}}/\partial T) - (\partial a_{\mathrm{AF}}/\partial T) = (\Delta a/M^2)(dM^2/dT) \approx -3.4\times 10^{-12}\ \text{cm/deg}. \quad \text{(A.3)}$$

The observed value of the left-hand side of (48) is -7×10^{-12} cm/deg, which is a partial check. It is not clear how all the discrepancy arises, although dM^2/dT is not too well known.

The paramagnetic data may be analyzed using the machinery we have developed, but the comparison of the theoretical and experimental results are highly sensitive to the values chosen for $\partial a_{TM}/\partial T$ as defined by (27). It is not possible to get from available measurements a single value of the contribution of $\partial a_T/\partial T$ valid over the entire range of interest—such as at T_0, T_n, and up into the paramagnetic region. We suspect that the difficulty occurs either because the phase we have called AF or Δ may not be substantially ordered, or else because of magnetic effects on $\partial a_T/\partial T$—such effects could come quite naturally from interlattice interactions, and from short-range order in the paramagnetic region.

We note that the effect of substitutions in MnAs can be nontrivial. We know[19] that small amounts of Sb, an ion larger than As, depress the F/AF transition temperature, although the steric effect of the larger ion should be to raise T_0, because dT_0/dp is negative. It is perhaps not entirely surprising that the delicate balance of the interlattice interactions should be modified by changing anions, as these are the carriers of the superexchange part of the interaction.

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Kinetics of Magnetic Annealing in Cobalt-Substituted Magnetite*

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The time dependence of the magnetic annealing effect in single crystals of magnetite containing various amounts of substituted cobalt has been investigated by a technique which permits observation of the effect at the annealing temperature. The annealing kinetics in a particular crystallographic direction are determined by measuring the decay of the torque in the (001) plane following a preparatory anneal in a direction 45° removed. The directions chosen for study are the [100] and [110] directions, which are nodes of the cubic torque curve. The absence of a cubic torque in the directions of measurement allows precise observation of the anneal-induced uniaxial torque. The annealing kinetics observed in the two directions are different, and the nature of the torque decay in both directions depends upon the cobalt concentration of the sample. The torque decay in the [100] direction is attributed to the redistribution of single cobalt ions and certain pairs of adjacent cobalt ions over the octahedral cation sites, whereas the decay in the [110] direction is attributed to the redistribution of cobalt ion pairs only. The results of a theoretical analysis of the annealing kinetics that would result from such ionic redistribution are in good agreement with the experimental observations. Comparison of the annealing behavior of samples in different states of oxidation indicates that ionic redistribution occurs by a vacancy diffusion mechanism, and the activation energy observed for this process is 1.05±0.03 ev. In addition to the measurements performed at the annealing temperature, the torque in the [110] direction was determined as a function of temperature in a sample which had been quenched at the end of its preparatory anneal. These two measurements are used to show that there exists a repulsive interaction energy of 0.093±0.04 ev between two adjacent cobalt ions.

I. INTRODUCTION

The uniaxial anisotropy produced in ferrites containing cobalt by magnetic annealing has been the object of a number of investigations in recent years.[1–8] Penoyer and Bickford[4] have studied this effect in single-crystal samples of cobalt-substituted magnetite as a function of both cobalt content and annealing direction. They have found that the noncubic aniso-

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