Use of Symmetry in the Determination of Magnetic Structures

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General symmetry considerations are used to determine what restrictions can be placed on the structure of the magnetic state in crystals. From the work of Landau and Lifshitz it is found that the following restrictions apply to those magnetic structures which can arise when a crystal undergoes a single second-order phase transition from the paramagnetic state to the magnetic state in question. In the immediate vicinity of the transition point the spin density of the magnetic state transforms as a basis function for a single irreducible representation of the symmetry group of the paramagnetic phase. At lower temperatures the spin density may change through the introduction of basis functions corresponding to odd order "harmonics" of the "fundamental" representation. This takes place in such a way that the symmetry of the spin density does not change. Other components may also be introduced in the spin density through other phase transitions at lower temperatures. It is further found that no such restrictions can be placed, in general, on the possible configurations of the magnetic ground state, and that definite information concerning the classical ground state cannot, therefore, be obtained by symmetry arguments alone. It is concluded that the use of symmetry in the determination of magnetic structures is restricted, in most cases, to the highest temperature magnetically ordered state exhibited by the crystal. The results are illustrated by a few examples.

INTRODUCTION

THE independent theoretical discovery of magnetic spirals in 1959 by Yoshimori,[1] Villain,[2] and Kaplan[3] has stimulated considerable interest in the general question of magnetic structure. Since the initial theoretical work, neutron diffraction investigations have disclosed a number of crystals which possess rather complicated magnetic configurations.[4] The purpose of the present work is to determine what can be said from general symmetry considerations concerning the structure of the magnetic state in crystals. It is found that some definite restrictions are placed on the magnetic structures which can arise when a crystal undergoes a single second-order phase transition from the disordered paramagnetic state to the magnetic state in question. It is further found that no such restrictions can be placed, in general, on the possible configurations of the magnetic ground state. The method is based in part on the work of Landau and Lifshitz,[5] who have employed crystal symmetry arguments in a discussion of second-order phase transitions both in magnetic and in nonmagnetic crystals. More recently, their work has been applied by Dzyaloshinsky[6,7] to phase transitions in some specific crystals for which the chemical and magnetic unit cells coincide. It is felt that the Landau-Lifshitz theory should be applicable to second-order phase transitions in general, and part of the present work consists of an application of this theory to general magnetic structures resulting from second-order phase transitions. The theory assumes that the state of the crystal can be accurately described by a single-particle density function, and hence involves a Hartree-Fock type approximation neglecting all effects due to electron correlations. It is, therefore, related to the molecular field approach, although, being based on symmetry considerations, it does not depend on any assumptions concerning the details of the specific interaction which brings about the magnetic ordering. All effects of domain formation and of crystal imperfections are neglected, and we are, therefore, concerned with the structure of a single domain of a perfect crystal. In the following section the theory[5,6,8] is developed and the general results are discussed. Also, the work of Bertaut[9] and of Alexander,[10] who have employed full crystal symmetry in the ground-state problem, is considered in light of the present work. In the final section, the results are applied to some specific structures and some general conclusions are drawn.

THEORY

As was originally pointed out by Landau,[11] a second-order phase transition is characterized by a change in crystal symmetry. At the transition point, the symmetry group[12] of the crystal changes abruptly from G_0,

[1] Akio Yoshimori, J. Phys. Soc. Japan **14**, 807 (1959).
[2] J. Villain, J. Phys. Chem. Solids **11**, 303 (1959).
[3] T. A. Kaplan, Phys. Rev. **116**, 888 (1959).
[4] The following recent articles give the structure and other properties of a large number of magnetic crystals. H. A. Alperin and S. J. Pickart, ASTIA Report AD259738, NOLTR 61-81 (1961) (unpublished); J. B. Goodenough, in *Progress in Inorganic Chemistry*, edited by F. A. Cotton [Interscience Publishers, Inc., New York (to be published)], Vol. III, Suppl. I; also, L. M. Corliss and J. M. Hastings, in *American Institute of Physics Handbook* [McGraw-Hill Book Company, Inc., New York (to be published)], 2nd ed., Table 5h-22.
[5] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley Publishing Company, Reading, Massachusetts, 1958), Chap. 14.
[6] I. Dzyaloshinsky, J. Phys. Chem. Solids **4**, 241 (1958).
[7] I. Dzyaloshinsky, Soviet Phys.—JETP **6**, 1120 (1958).
[8] An extensive treatment of the thermodynamic properties of second-order phase transitions in magnetic crystals has been given by K. P. Belov, *Magnetic Transitions* (Consultants Bureau, Enterprises, Inc., New York, 1961).
[9] E. F. Bertaut, Suppl. J. Appl. Phys. **33**, 1138 (1962) and references contained therein.
[10] S. Alexander, Phys. Rev. **127**, 420 (1962).
[11] L. D. Landau, Physik Z. Sowjetunion **11**, 545 (1937).
[12] The symmetry groups considered in this work are the Shubnikov groups (symmetrical and antisymmetrical space groups) in which the element of antisymmetry is taken to be the time reversal operator. [See N. V. Belov, N. N. Neronova, and

the space group of the disordered phase (presumably the high-temperature phase), to a group G_1 which is a subgroup of G_0. If the transition is truly second order, it is continuous, except for the change in symmetry, and involves no latent heat and no hysteresis. The two phases are identical at the transition point. The disordered phase may be characterized by some function ρ_0 which can be thought of as a general density function, and which is, by definition, invariant under all the operations of G_0. The ordered phase may be characterized by a function ρ_1 which is invariant under all the operations of G_1 but not under those operations of G_0 which are not also contained in the group G_1. ρ_1 is a continuous function of temperature and pressure and coincides with ρ_0 at the transition point. One can write $\rho_1=\rho_0+\rho$, where ρ vanishes continuously at the transition. ρ is that portion of the general crystal density function of the ordered phase which expresses the change in symmetry which takes place at the transition point. In the present discussion, we may interpret ρ as a magnetic moment or electron spin density although it involves the lattice distortion and other effects as well. It is convenient to expand ρ in terms of the basis functions of all the irreducible representations of G_0.

$$\rho=\sum_n{}' \sum_i c_i^{(n)}\phi_i^{(n)}, \tag{1}$$

where n is the number of the irreducible representation, i designates the basis function, and the prime on the first sum indicates that we have left out the identity representation incorporating those bases in ρ_0. Notice that the expansion is unique and completely general since the basis functions ϕ form a complete set. The expansion coefficients are continuous functions of the temperature and pressure and all vanish at the transition point.

The thermodynamic potential, or free energy, of the crystal is also continuous at the transition point. Taking Φ_0 as the free energy of the disordered phase, we can write the free energy of the ordered phase as $\Phi=\Phi_0$ plus an expansion in a set of parameters which characterize the ordered phase and which vanish continuously at the transition point. Assuming that the free energy depends only on the density function, one can choose the set of coefficients $c_i^{(n)}$ for the expansion parameters. Consider the basis functions fixed such that the $c_i^{(n)}$ transform among themselves under the operations of G_0. The free energy, and thus the terms in its expansion, are invariant under G_0. There is no invariant linear in $c_i^{(n)}$ since we have omitted the identity representation. For each representation $\mathbf{D}^{(n)}$ of G_0 we can construct one quadratic invariant of the form $\sum_i(c_i^{(n)})^2$. There are no quadratic terms mixing representations since the direct product of two irreducible representations of a group contains an invariant if and only if the representations are equivalent. In general, cubic and higher order terms in the expansion will mix representations and no general form can be written for them.

Retaining only the quadratic terms, the expansion of Φ has the form

$$\Phi=\Phi_0+\sum_n{}' A^{(n)} \sum_i (c_i^{(n)})^2+\cdots. \tag{2}$$

The equilibrium state of the system corresponds to that set of values of the $c_i^{(n)}$ which minimizes Φ at a given temperature and pressure. From our definitions the disordered phase is characterized by $c_i^{(n)}=0$. In order for this to correspond to a minimum of Φ, all the $A^{(n)}$ in the disordered phase must be positive. In the ordered phase, not all the $c_i^{(n)}$ vanish such that at least one $A^{(n)}$ must be negative and, hence, we have $A^{(n)}(P_N,T_N)=0$ at the transition point. This gives a relation between P_N and T_N. If two of the A's changed sign, we would also have $A^{(m)}(P_N,T_N)=0$ and could then solve for P_N and T_N. In this case, the transition would occur at a critical point. Since magnetic transitions are generally not of this type, we can say that only one $A^{(n)}$ vanishes at the transition point. Thus, in the equilibrium state immediately below the transition, all expansion parameters vanish except those belonging to a single irreducible representation of the symmetry group of the disordered phase. Therefore, instead of Eq. (1) we can write

$$\rho=\sum_i c_i^{(n)}\phi_i^{(n)}, \tag{3}$$

and ρ must transform as a basis function of a single irreducible representation of G_0. Therefore, we have obtained the result that the spin density introduced in a second-order phase transition transforms as a basis function for a single irreducible representation of the symmetry group of the disordered phase. It will be seen later that this can also be obtained from the fact that the exchange problem is linear in the vicinity of the transition point. This result, which was originally found by Landau and Lifshitz,[5] is not valid, in general, when higher order terms are included in the expansion of Φ such that Eq. (3) is an approximation which is expected to be good only in the neighborhood of the transition point.

Before investigating this further, let us briefly consider general higher order terms in the expansion. If the disordered phase of the transition in question is the paramagnetic phase, then the space group G_0 contains the time reversal operator Θ, and since ρ represents a spin density it must change sign under Θ so that $\Theta c_i^{(n)}=-c_i^{(n)}$. However, $\Theta\Phi=\Phi$ and consequently all odd power terms in the expansion vanish. Odd power terms, specifically cubic terms, must, nevertheless, be considered in a discussion of transitions involving two magnetically ordered states. If such a transition is one

T. S. Smirnova, Soviet Phys.—Cryst. **2**, 311 (1957); and B. A. Tavger and V. M. Zaitsev, Soviet Phys.—JETP **3**, 430 (1956)]. A method for obtaining the irreducible representations of these groups has been discussed previously [J. O. Dimmock and R. G. Wheeler, Phys. Rev. **127**, 391 (1962)].

for which $A^{(n)}(P_N,T_N)=0$, corresponding to the representation $\mathbf{D}^{(n)}$, a cubic term $B^{(3n)}$ will exist in the expansion if the direct cube of $\mathbf{D}^{(n)}$ contains the identity representation of G_0. If such a term exists, then either $B^{(3n)}(P_N,T_N)=0$, or $B^{(3n)}(P_N,T_N)\neq 0$. In the former case, the transition takes place at a singular point. In the latter case, one can show that the transition is first order.[6,13] There always exists in the expansion a quartic term $C^{(4n)}$ corresponding to the fourth power of $\mathbf{D}^{(n)}$ and we need comment here only that, in the absence of cubic terms, if the quartic term is positive the transition is second order, whereas if it is negative the transition is first order. One might hope to apply the symmetry arguments to first- as well as second-order transitions but there is a definite objection to this. The neglect of higher order terms in the expansion of Φ, and indeed the very convergence of this expansion, depends on the $c_i^{(n)}$ taking on sufficiently small values in the vicinity of the transition. In the case of first-order transitions, the $c_i^{(n)}$ change discontinuously from zero to some finite value. Only in the case of a very small discontinuity could one expect the theory to yield meaningful results.

Let us now consider how the inclusion of higher order terms in the expansion of the free energy affects the transformation properties of the spin density. If at the transition point $A^{(n)}=0$ corresponding to the irreducible representation $\mathbf{D}^{(n)}$ of the symmetry group of the disordered phase, then, as we saw above, in the neighborhood of the transition point ρ transforms as a basis function of $\mathbf{D}^{(n)}$. If there is a fourth-order term in the expansion consisting of an invariant formed from the direct product $\mathbf{D}^{(n)}\times\mathbf{D}^{(n)}\times\mathbf{D}^{(n)}\times\mathbf{D}^{(m)}$, where $\mathbf{D}^{(m)}$ is a different irreducible representation of G_0, a spin density component which transforms as a basis function of $\mathbf{D}^{(m)}$ will contribute to ρ as one moves away from the transition point. A necessary and sufficient condition for such an invariant to exist is that $\mathbf{D}^{(m)}$ occur in the decomposition of the direct cube of $\mathbf{D}^{(n)}$. $\mathbf{D}^{(m)}$ can then be thought of as a third "harmonic" of the "fundamental" representation, $\mathbf{D}^{(n)}$. In general, harmonics of all orders can contribute to ρ but those of lower order will be more important. From the Landau-Lifshitz theory,[5] the temperature dependence of the fundamental component is $(T_N-T)^{1/2}$ near the transition point. It is easy to show, by including higher terms in the expansion, that the temperature dependence of the jth harmonic is $(T_N-T)^{j/2}$, such that the higher order harmonics do indeed enter more slowly. If the disordered phase of the transition in question is the paramagnetic state, the expansion of the free energy contains only even terms and ρ contains only odd harmonics of the fundamental.

The above discussion of the transformation properties of ρ in terms of the irreducible representations of G_0 is correct as far as it goes, but more information can be obtained by considering the basis functions themselves. However, a more complete treatment in terms of the Landau-Lifshitz theory is rather involved. Fortunately, a little insight yields the final results directly. Let us, therefore, reconsider the problem starting at the beginning and using the results obtained thus far. Recall that in the disordered phase the crystal is invariant under a symmetry group G_0 and that at the transition point the symmetry of the crystal changes. This is brought about by the introduction of a spin density ρ which, in the vicinity of the transition point, transforms as a basis function for a single irreducible representation $\mathbf{D}^{(n)}$ of G_0. The particular basis function of $\mathbf{D}^{(n)}$ contributing to ρ is selected by the anisotropy terms in the expansion of the free energy. The symmetry group, G_1, of the ordered phase is the largest subgroup of G_0 which leaves ρ invariant. G_1 is not determined by G_0 and $\mathbf{D}^{(n)}$ alone in the case where the dimension of $\mathbf{D}^{(n)}$ is greater than one, since the basis function, as selected by the anisotropy terms, which contributes to ρ may have more symmetry than a general basis function of $\mathbf{D}^{(n)}$. As the temperature is lowered further, the symmetry of the crystal remains the same unless it undergoes another transition. Assuming that this does not happen, ρ must remain invariant under G_1. We saw above that ρ changes through the introduction of components which transform according to "harmonics" of the fundamental representation. We now have the additional restriction that these components must be invariant under G_1. In the next section these results are applied to a few specific magnetic structures for illustration.

In the original development of the theory,[5] a restriction was placed on the representation $\mathbf{D}^{(n)}$ for which nonzero $c_i^{(n)}$ could occur. (All $\mathbf{D}^{(n)}$ were eliminated whose antisymmetric direct product contains in its decomposition the vector representation of G_0.) The restriction eliminates all structures for which ρ varies continuously throughout the crystal, among which are spiral and sinusoidally modulated magnetic structures. In view of the fact that spiral structures are not only stable states at high temperatures[2] but may exist as ground-state configurations,[3] it appears desirable to re-examine this restriction. In the above development the $c_i^{(n)}$ are considered to be constant throughout the crystal. However, Landau and Lifshitz have argued[5] that the free energy must be a minimum with respect to a spatial variation of the $c_i^{(n)}$ within the crystal. Their results show that this criterion is not satisfied by those $c_i^{(n)}$ which give a continuously varying ρ. However, the following argument against this criterion can be offered. For a given complete orthonormal set of basis functions ρ is completely specified by a set of spatially constant coefficients. Therefore, if the free energy of the magnetic state depends only on ρ, which is a basic assumption of the Landau-Lifshitz theory as well as of the molecular field theory, then the free energy can be expressed in terms of these coefficients alone. The set of coefficients is unique for a given ρ and consequently so is the free energy. Therefore, the

[13] D. S. Rodbell and C. P. Bean, Suppl. J. Appl. Phys. **33**, 1037 (1962); Phys. Rev. **126**, 104 (1962).

theory is self-consistent if the $c_i^{(n)}$ are spatially constant coefficients. However, if we allow the $c_i^{(n)}$ to be functions of position for a given set of basis functions the expansion of ρ is not unique. If now the free energy is expressed in terms of a volume integral of some function of these spatially dependent $c_i^{(n)}$ and their derivatives, the free energy will depend not only on ρ but, in general, on the specific way in which the expansion is performed, and will not be unique for a given ρ. This result is a contradiction since the particular expansion does not represent a physical property of the system. We are, therefore, inclined to drop the additional criterion concerning the spatial variation of the $c_i^{(n)}$. If this is done, the Landau-Lifshitz theory is applicable to second-order phase transitions involving general magnetic configurations, and consequently so are the results obtained above.

This essentially completes our discussion of the use of symmetry in the determination of magnetic structure in terms of the Landau-Lifshitz theory of second-order phase transitions. It is now of interest to consider what results are obtained in the ground-state problem through the use of symmetry. For convenience, and in order to compare with the results obtained by Bertaut[9] and by Alexander,[10] assume that the classical exchange energy is a bilinear function of the spins at the various ion sites, given by

$$E=-\sum_{\mathbf{R},\mathbf{R}'}\mathbf{S}_{\mathbf{R}}\cdot\mathbf{J}_{\mathbf{R}\mathbf{R}'}\cdot\mathbf{S}_{\mathbf{R}'}, \tag{4}$$

where $\mathbf{S}_{\mathbf{R}}$ is the spin vector on the magnetic ion at $\mathbf{R}$. In the ground-state problem, the spin vectors are assumed to be subject to a set of nonlinear constraints

$$\mathbf{S}_{\mathbf{R}}\cdot\mathbf{S}_{\mathbf{R}}=S_{\mathbf{R}}^2, \tag{5}$$

where $S_{\mathbf{R}}^2$ is a fixed quantity dependent only on the type of ion at $\mathbf{R}$. The constraints serve to fix the magnitude of each spin vector allowing only the direction to vary. Using the method of Lagrange multipliers, one finds that the stationary or equilibrium solutions of Eq. (4) subject to these constraints satisfy

$$\lambda_{\mathbf{R}}\mathbf{S}_{\mathbf{R}}=\sum_{\mathbf{R}'}\mathbf{J}_{\mathbf{R}\mathbf{R}'}\cdot\mathbf{S}_{\mathbf{R}'}, \tag{6}$$

with energy

$$E=-\sum_{\mathbf{R}}\lambda_{\mathbf{R}}S_{\mathbf{R}}^2. \tag{7}$$

The exchange tensor $\mathbf{J}_{\mathbf{R}\mathbf{R}'}$ will be invariant under the symmetry operations of some group G_0. This is the nonmagnetic space group of Alexander and need not be the symmetry group of the disordered phase. It, however, plays the same roll in the ground-state problem as the latter did in the Landau-Lifshitz theory. Equation (6) has a complete set of solutions each of which transforms as a basis function for some irreducible representation of G_0 and for which $\lambda_{\mathbf{R}}$ is invariant under the operations of G_0. However, many of these solutions will not satisfy the constraints, Eq. (5), and must be rejected.[10] In addition, Eq. (6) possesses many solutions for which $\lambda_{\mathbf{R}}$ is not invariant under G_0, but which satisfy the constraints. These latter solutions need not transform according to single irreducible representations of G_0.

Bertaut[9] has assumed that $\lambda_{\mathbf{R}}$ is invariant under G_0 and, therefore, has obtained the result that the ground-state spin density transforms as a single irreducible representation of G_0. Alexander,[10] on the other hand, has used instead of Eq. (5) the weak constraint condition which yields Eq. (6) with $\lambda_{\mathbf{R}}$ invariant under G_0, and obtained this result subject to the qualification that other solutions exist as well. The fact that solutions to Eq. (6) subject to the constraints of Eq. (5), which do not transform according to any single irreducible representation of G_0, can indeed exist in real crystals has been demonstrated by Kaplan *et al.*,[14] in the case of the spinel structure. Their calculations yield a ground-state configuration which consists of a ferrimagnetic spiral. This structure has since been found to be a good approximation to the ground state in $MnCr_2O_4$ by Hastings and Corliss[15] and in $CoCr_2O_4$ by Menyuk and Dwight.[16] It, however, does not transform according to any single irreducible representation of the symmetry group of the disordered phase of these spinels, which is the group under which the exchange parameter used is invariant. Consequently, it appears that group theory has limited usefulness in the ground-state problem principally because of the nonlinear constraint condition, and there is no *a priori* reason to expect the paramagnetic symmetry of the crystal lattice to be strongly reflected in the ground-state spin configuration.[14]

The constraints are not important, however, in the high-temperature problem. In the vicinity of the transition point the molecular field approximation yields the following equation[2,17,18]:

$$\mathbf{S}_{\mathbf{R}}=\frac{2S_{\mathbf{R}}(S_{\mathbf{R}}+1)}{3kT}\sum_{\mathbf{R}'}\mathbf{J}_{\mathbf{R}\mathbf{R}'}\cdot\mathbf{S}_{\mathbf{R}'}. \tag{8}$$

This bears a strong resemblance to Eq. (6) which was obtained in the ground-state problem but differs from it in two essential ways. First, the coefficient $2S_{\mathbf{R}}(S_{\mathbf{R}}+1)/3kT$ is invariant, with $\mathbf{J}_{\mathbf{R}\mathbf{R}'}$, under the symmetry group of the disordered phase G_0. Second, the spin vectors are not subject to any additional constraints. The solutions of Eq. (8), therefore, do indeed transform according to single irreducible representations of G_0 in agreement with the Landau-Lifshitz theory. Consequently, the results obtained above are not affected by the nonlinear constraints in the case of the transition between the paramagnetic state and the highest temperature magnetically ordered state. On the other hand, one should be cautious in

[14] D. H. Lyons, T. A. Kaplan, K. Dwight, and N. Menyuk, Phys. Rev. **126**, 540 (1962).
[15] J. M. Hastings and L. M. Corliss, Phys. Rev. **126**, 556 (1962).
[16] N. Menyuk and K. Dwight (to be published).
[17] M. J. Freiser, Phys. Rev. **123**, 2003 (1961).
[18] T. A. Kaplan, Phys. Rev. **124**, 329 (1961).

applying the Landau-Lifshitz theory to a low-temperature transition in which the spin values of both states are nearly saturated. In this case the constraints must be considered. It appears that many of these low-temperature transitions are first order[13] which may be due to this, or to the presence of cubic terms in the expansion of the free energy.

A few more remarks regarding the application of group theory to the ground-state problem should be made at this time. Although one might generally assume that the group G_0, under which $\mathbf{J}_{RR'}$ is invariant, corresponds to the symmetry group of the paramagnetic state, Alexander[10] has pointed out that a more careful definition is necessary. Therefore, he defines G_0 to be "the space group determined by x rays when the crystal is in the magnetic state," taking into account the fact that at low temperatures the symmetry of $\mathbf{J}_{RR'}$ is reduced due to magnetically induced crystal distortions (magnetostriction). G_0 is determined, in this case, in part by the spin configuration. It is, in fact, given by G_1, the symmetry group of the magnetic state, supplemented by the time reversal operator. Since G_1, in turn, is determined by the spin configuration, any argument which attempts to determine the spin configuration from G_0 defined in this way is clearly circular. This difficulty is related to the presence of higher order terms in the expansion of the free energy which, in the Landau-Lifshitz theory, led to the introduction of spin density components which transform according to various representations of the symmetry group of the disordered phase. If, as determined by x rays, the crystal in the magnetic state is only slightly distorted, then, neglecting the difficulties introduced by the nonlinear constraints, one might expect the spin density to be rather well approximated by a basis function for a single irreducible representation of the paramagnetic space group. Inasmuch as the crystal deviates from this symmetry, one might expect to find other components in the spin density. This is exactly what happens in the Landau-Lifshitz theory due to the higher order terms in the free-energy expansion. Furthermore, it is just these terms which account for the magnetostriction. However, in comparing the results of the work on the ground-state problem with those of the Landau-Lifshitz theory, one must recall that the latter is a high-temperature approximation dependent on a power series expansion of free energy about the transition point and that the convergence of the expansion and general applicability of the theory at lower temperatures must be seriously questioned.

Before applying the results obtained in this section to some specific magnetic structures, it is useful to briefly summarize these results. Consider a paramagnetic single crystal with a symmetry group G_0 whose temperature is being slowly lowered. If, at some temperature, the crystal undergoes a second-order phase transition to a magnetically ordered state, the spin density of the magnetic state transforms, in the immediate vicinity of the transition point, as a basis function for a single irreducible representation of G_0. At lower temperatures, basis functions of odd order "harmonics" of the "fundamental" representation may be introduced. These harmonics are those representations of G_0 which are contained in the decomposition of the odd powers of the fundamental representation. The symmetry group, G_1, of the ordered phase is determined by G_0 and the spin density introduced at the transition point. Since the spin density remains invariant under G_1 until the crystal undergoes another phase transition, the additional components introduced from the harmonic representations must also be invariant under G_1. In other words, the spin density may change as the temperature is lowered away from the transition point such that it need no longer transform according to a single irreducible representation of G_0 provided it remains invariant under G_1. In many cases G_1 has enough symmetry to restrict sufficiently the spin density such that it must transform according to a single irreducible representation of G_0 at all temperatures, or at least down to a second transition. This is always the case if the fundamental representation is unidimensional. It is found that many ground-state configurations belong to single irreducible representations of the symmetry group of the paramagnetic phase of the crystal. In the framework of the Landau-Lifshitz theory this occurs when the crystal has only one phase transition, which is of second order, and G_1 imposes a sufficient restriction on the spin density. If the crystal undergoes a second transition, the above discussion again applies with G_1 replacing G_0 and a new symmetry group G_2 replacing G_1, except that in this case one must be concerned with cubic terms in the expansion of the free energy. Furthermore, if the magnetic moments are nearly saturated in the vicinity of this second transition, the constraints on the magnitude of individual spin vectors are important and the problem is nonlinear. If this is true, the theory does not apply. The ground-state problem is inherently nonlinear such that definite information cannot be obtained by symmetry arguments in this case. It is concluded, therefore, that the use of symmetry in the determination of magnetic structures is restricted, in most cases, to the highest temperature magnetically ordered state exhibited by the crystal. The applications discussed in the following section are all so restricted.

APPLICATIONS

Much effort has been directed toward the understanding of the magnetic structures exhibited by the heavy rare earth metals.[17–28] It is, therefore, of interest

[19] R. J. Elliott, Phys. Rev. **124**, 346 (1961).
[20] H. Miwa and K. Yoshida, Progr. Theoret. Phys. (Kyoto) **26**, 693 (1961); Suppl. J. Appl. Phys. **32**, 8S (1961).
[21] Takeo Nagamiya, Suppl. J. Appl. Phys. **33**, 1029 (1962).
[22] K. Yoshida and A. Watabe, Progr. Theoret. Phys. (Kyoto) **28**, 361 (1962).
[23] W. C. Koehler, E. O. Wollan, M. K. Wilkinson, and J. Cable,

to apply the Landau-Lifshitz theory to these structures. The first magnetically ordered state to appear as the temperature is lowered is either a spiral, as in the case of holmium,[23] terbium,[23,24] and dysprosium,[25] or a sinusoidally modulated structure, as in the case of erbium[26] and thulium.[28] In both instances the spin density has a temperature dependence near T_N given approximately by $(T_N-T)^{1/2}$ as expected, and has a propagation vector $\mathbf{k}_0$. In view of the Landau-Lifshitz theory as well as the work of Kaplan,[18] the spin density should develop a component with propagation vector $3\mathbf{k}_0$ and with a temperature dependence of $(T_N-T)^{3/2}$. However, there is no evidence at present, to the author's knowledge, of such a component in the high-temperature magnetic phase of rare earth metals. One is, therefore, forced to conclude that the coefficient of this term in the spin density is quite small. From molecular field theory calculations this indeed appears to be the case.[29] In some of the rare earths (holmium,[23] dysprosium,[25] and erbium[26]) the propagation vector $\mathbf{k}_0$ is found to vary continuously with temperature. This has been discussed in terms of the molecular field theory,[17,19,20] and it is necessary to only comment here that this variation is not in contradiction with the Landau-Lifshitz theory if one is willing to assume the existence of a large number of very closely spaced second-order phase transitions.

An immediate result of the theory is that an antiphase type structure, as that originally proposed for chromium by Corliss, Hastings, and Weiss,[30] cannot exist in the immediate vicinity of the transition point. Such structures contain a number of higher harmonics and thus may exist only well below the transition. In view of this fact, it is interesting to examine the magnetic structure of $MnSe_2$.[31] The structure proposed by Hastings, Elliott, and Corliss, Fig. 1(a), is an antiphase type and cannot be represented by basis functions of a single irreducible representation of the symmetry group of the paramagnetic phase, G_0. This group is[12] $Pa3\,1'$ but the following discussion is not altered if the structure is assumed to be face-centered cubic in which case G_0 is $Fm3m1'$. The symmetry group of the magnetic state G_1 is $Pb'c'a$ or with this simplification C_Ammm. The magnetic structure which is used to describe the neutron diffraction

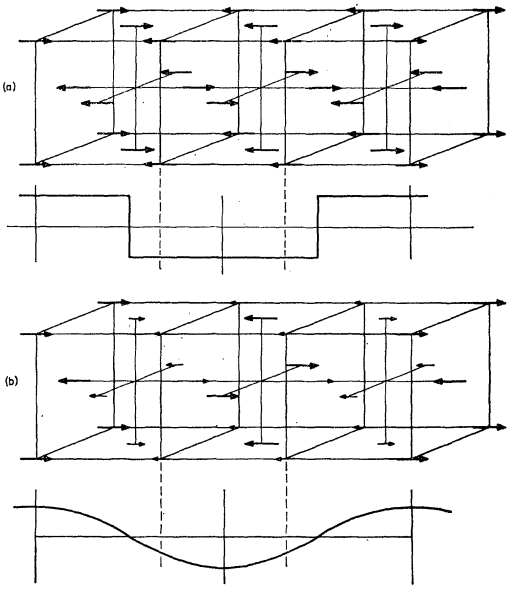

FIG. 1. Magnetic structures of $MnSe_2$. (a) shows the magnetic structure proposed for $MnSe_2$ at 4.2°K by Hastings, Elliott and Corliss (see reference 31). Only the Mn ions are shown. The square wave beneath the drawing refers to the front face of the figure and indicates the antiphase nature of the structure. (b) shows the magnetic structure proposed in the present work for $MnSe_2$ in the vicinity of the transition point. Again, only the Mn ions are shown and the *relative* lengths of the arrows indicate the *relative* magnitudes of the thermal averages of the spin vectors at the various ion sites. The shorter arrows indicate magnetic moments whose magnitude is half of that indicated by the longer arrows. The absolute magnitudes of these vectors are, of course, much less than in (a). The sine wave beneath the drawing refers to the front face of the figure as above and indicates the sinusoidal nature of the structure. It is expected that as the temperature is lowered, the structure of $MnSe_2$ will make a continuous transition from that of (b) to that of (a).

pattern at 4.2°K can be represented as a magnetic moment density of the form

$$\rho=\mu_x \cos\frac{2\pi}{a}z\left(\frac{4}{3}\cos\frac{2\pi}{3a}x-\frac{1}{3}\cos\frac{2\pi}{a}x\right). \tag{9}$$

μ_x indicates a magnetic moment directed along the x axis. The dimension of the cubic chemical unit cell is a, and the magnetic cell is three times the length of the chemical cell in the x direction. [See Fig. 1(a).] Let

$$\rho=\alpha\rho_1-\beta\rho_2, \tag{10}$$

where

$$\rho_1=\mu_x \cos\frac{2\pi}{a}z\cos\frac{2\pi}{3a}x,$$
$$\rho_2=\mu_x \cos\frac{2\pi}{a}z\cos\frac{2\pi}{a}x, \tag{11}$$

and at 4.2°K, $\beta/\alpha=1/4$. ρ_1 transforms as a basis function for a single irreducible representation of G_0 as does ρ_2. Both ρ_1 and ρ_2 are invariant under the group G_1, and the ρ_2 representation is contained in the decomposition

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of the direct cube of the ρ_1 representation. According to the Landau-Lifshitz theory, the structure found by Hastings, Elliott, and Corliss cannot exist at temperatures close to the transition point. In order to account for this structure at 4.2°K, assuming only one phase transition and that this is of second order, we propose that for T close to T_N the spin density is approximated by ρ_1 which is a sinusoidally modulated function. This structure is shown in Fig. 1(b). If this is the case, the magnetic structure at high temperatures is represented by the spin density ρ, [Eqs. (10) and (11)], with $\alpha \approx (T_N - T)^{1/2}$ and $\beta \approx (T_N - T)^{3/2}$, and with decreasing temperature goes continuously from that of Fig. 1(b) to that of Fig. 1(a). Note that this occurs without any change in crystal symmetry.

Consider next the group of magnetic crystals with the NaCl-type structure.[32–35] The symmetry group of the disordered phase of these crystals is $Fm3m1'$. Most of the materials of this type investigated thus far exhibit magnetic ordering of the second kind.[34] This structure, shown in Fig. 2, consists of ferromagnetic ordering within (111) planes and antiferromagnetic ordering between the planes. Without specifying the spin direction the magnetic moment density which reproduces this structure is

$$\rho = \cos[\pi(x+y+z)/a]. \tag{12}$$

The direction of the spin vector in the vicinity of the transition point is restricted by the fact that, in this region, ρ must transform as a basis function of a single irreducible representation of the symmetry group $Fm3m1'$. One can show that the spin vector must lie either in the [111] direction or in the (111) plane. In the former case, the symmetry group of the ordered phase is $R_I\bar{3}c$, and since the spins lie along a threefold axis, their direction is fixed and may not vary as the temperature is lowered without changing the crystal symmetry. FeO appears to be an example of a structure of this type.[33,35] In the latter case, due to crystalline anisotropy, the spins lie in the $[1\bar{1}0]$, $[\bar{1}\bar{1}2]$, or equivalent directions in the (111) plane. If the spins lie along $[1\bar{1}0]$ the symmetry group of the ordered phase is C_c2/m. The spins lie along the twofold axis and again their direction may not change without changing the crystal symmetry. MnO may be an example of a structure of this type.[35] Finally, if the spins lie along $[\bar{1}\bar{1}2]$ the symmetry group of the ordered phase is C_c2/c. The spins lie in the reflection plane $(1\bar{1}0)$ and the spin direction is free to rotate in this plane without changing the crystal symmetry. CoO may be an example of a structure of this type.[35] At the transition point, the spins lie along $[\bar{1}\bar{1}2]$ in the (111) plane and rotate from the plane as the temperature is lowered.

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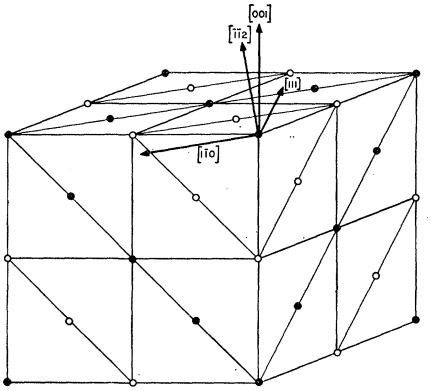

FIG. 2. Magnetic ordering of the second kind. This figure represents the ordering found in many magnetic crystals with the NaCl face-centered cubic type structure. Only the magnetic ions are shown. The spins of all the ions represented by solid circles are parallel to one another and are antiparallel to the spins of all the ions represented by open circles.

Finally, let us briefly consider the magnetic structure of the NiAs type compound CrSe.[36] One can show from the Landau-Lifshitz theory that the "umbrella" model for the spin configuration proposed by Corliss *et al.*, cannot arise from the disordered phase by a single second-order phase transition unless the moments parallel to the hexagonal axis are identically zero. It is possible for these moments to order antiferromagnetically as proposed only at a second phase transition. On the other hand, they may order ferromagnetically as the temperature is lowered without changing the crystal symmetry. This would make CrSe weakly ferromagnetic with the moment confined to the hexagonal axis. It is necessary to mention[36] that these are not the only possible magnetic structures for CrSe. In addition to the "umbrella" structure of CrSe, the ferrimagnetic spiral[14,15] and the conical spiral[23,26] cannot arise from the disordered state by a single second-order phase transition. In the cases where these structures have been found[15,23,26] they are not the highest temperature magnetically ordered phase but arise only at lower temperatures after additional phase transitions, in agreement with the Landau-Lifshitz theory.

In concluding this section, let us summarize the types of information which can be obtained by applying the Landau-Lifshitz theory to specific magnetic structures, assuming that these structures arise from the disordered phase through a single second-order phase transition. First, it is possible to show that some magnetic structures, as that proposed for $MnSe_2$, cannot exist in the immediate vicinity of the transition point but can only occur at lower temperatures. Second, it is sometimes possible to restrict the spin direction in a crystal whose general magnetic structure is known. Third, it is possible to show that some magnetic configurations cannot arise

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from the disordered phase of the crystal by a single second-order phase transition. Fourth, in those cases where the spin direction or magnitude in a proposed structure is not fixed by the crystal symmetry in the ordered phase it can be expected, in general, to be temperature dependent. Therefore, although the Landau-Lifshitz theory is based on rather general considerations, it makes some definite predictions concerning the symmetry of magnetic structures, and should be useful both in connection with the determination of new structures and in considerations of already proposed configurations in magnetic crystals.

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Infrared Cyclotron Resonance in *n*-Type InAs

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Cyclotron resonance absorption of conduction electrons in InAs has been measured in the infrared spectral region 23–34 μ using magnetic fields as high as 150 kG. The absorption was resolved into three lines, this structure being interpreted on the basis of the changing effective g factor of the conduction electrons.

1. INTRODUCTION

INFRARED cyclotron resonance in *n*-type InAs has been observed by Keyes *et al.*,[1] and Palik and Wallis.[2] The effective mass ratio at the bottom of the band has been found to be about 0.023 at room and liquid-nitrogen temperatures.[2] Also, the mass variation with magnetic field, due to the nonparabolic character of the conduction band, has been measured.

In cyclotron resonance measurements on *n*-type InSb by Palik *et al.*,[3] additional structure was observed in the form of lower frequency satellite lines. These were interpreted as transitions between various Landau levels with unequal spin splittings due to the changing effective g factor. Similar structure should be present in the cyclotron absorption of conduction electrons in InAs but was not observed, probably due to insufficient spectral resolution or lack of sufficiently high magnetic fields.[1,2] The present paper reports the observation of this structure.

2. EXPERIMENTAL RESULTS AND DISCUSSION

Recently, the NRL magnet group has built an air core, solenoidal magnet with a 1.25-in. cylindrical aperture which has produced steady fields in excess of 150 kG. We have used this magnet to study cyclotron resonance in *n*-type InAs and InSb at room temperature and near liquid-nitrogen temperature. The InAs sample, the same one used by Palik and Wallis,[2] was about 20 μ thick mounted on a silicon backing with a thermoplastic cement. It contained $\sim 7\times 10^{15}$ carriers/cm^3 and had a mobility of 70 100 cm^2/V sec at liquid-nitrogen temperature and 23 700 cm^2/V sec at room temperature. The sample transmission was measured at fixed wavelengths in the spectral region 23–34 μ as a function of slowly increasing magnetic field. The transverse sample orientation with direction of propagation perpendicular to magnetic field was used. Some results are shown in Fig. 1. The magnetic field H was varied from 0 to 150 kG. At room temperature two absorption lines are resolved, a strong one at lower field and a weaker satellite at higher field as shown in Fig. 1(a). When the sample was cooled, the strong line sharpened somewhat and split into two lines at high fields, while the satellite essentially disappeared as shown in Fig. 1(b). The positions of the room-temperature and low-temperature lines were about the same.

This structure, similar to structure observed in InSb by Palik *et al.*,[3] has been interpreted as shown in Fig. 2. The Landau levels each have two spin states, the g factor decreasing with increasing energy into the band. The levels are designated $E(l,k_z,\pm)$, l being the Landau quantum number, k_z the propagation constant along the magnetic field, and $\pm$ the spin direction with respect to the magnetic field. Consequently, the transitions $E(0,0,+)\rightarrow E(1,0,+)$ and $E(0,0,-)\rightarrow E(1,0,-)$ will not coincide. Higher transitions will not coincide, either. For a fixed photon energy of 0.0451 eV as the magnetic field is increased, the positions of the low-temperature lines are shown on the energy level dia-

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