PHYSICAL REVIEW VOLUME 157, NUMBER 2 10 MAY 1967

Effective-Field Theory for the Spin Ordering in Dilute Magnetic Alloys*

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(Received 23 September 1966)

A simple and mostly heuristic theory is proposed for the spin ordering in dilute magnetic alloys. It explores the idea of Marshall on the effective-field distribution and makes a self-consistent postulate in analogy with the Weiss molecular-field theory. The theory is applied to calculate the specific heat with or without external field and the susceptibility of the alloys.

I. INTRODUCTION

THE effective-field theory has been of great value in the study of magnetic ordering problems.[1] The simple version of the theory, the Weiss molecular-field theory, predicts most of the gross features of the order-disorder transition in materials where an ordered magnetic state exists at low enough temperatures. With proper modification, for example, the Bethe-Peierls-Weiss (BPW) approximation,[2] the theory also explains the short-range order above the ordering temperature. The Weiss theory postulates the existence of an effective field acting on all the spins. This field originates from the mutual interaction of all the spins and its value is assumed to be proportional to the spontaneous magnetization. In the BPW approximation, the fluctuation of the effective field on a spin due to the various possible alignments of the neighboring spins is taken into consideration. As a result, there exist a number of values for the effective field, each weighted by a temperature-dependent probability. As the temperature increases, the most probable value of the effective field shifts to lower values in direct proportion with the spontaneous magnetization.

In a dilute alloy where the distribution of spins on the lattice is at random, the effective field has another source of fluctuation, that due to all possible distances between pairs of interacting spins. Marshall[3] showed qualitatively that, if the spins interact via the long-range oscillatory Ruderman-Kittel interaction, the effective field has a continuous probability distribution. The value of the field can be either positive or negative, and at low temperatures the distribution curve is peaked at nonzero values of the field. This type of effective-field distribution leads to no phase transition, only a gentle maximum of the specific-heat curve. Klein and Brout[4] subsequently published a detailed statistical analysis of the very dilute alloys and confirmed the idea of Marshall. Klein[5] made a number of machine calculations of the effective-field distribution and evaluated the low-temperature specific heat of very dilute CuMn, CuFe, and CuCo alloys. The results are in excellent agreement with the measured values. The weakness of this theory lies in the cutting off of the cluster expansion of the partition function at the two-spin correlation term. This procedure seems to be valid only for very low concentrations, perhaps much less than 1 at.%. It is also very difficult to carry out the analysis at finite temperatures and external magnetic fields.

In view of the fact that a number of interesting properties have been observed in alloys containing 0.1–10 at.% magnetic impurity, it appears worthwhile to extend the effective-field theory to more concentrated alloys. For this purpose, it is necessary to abandon detailed analysis and resort to intuitive arguments. This paper suggests that Marshall's idea can be pushed quite far in providing a useful model for the more concentrated alloys (say, 1 at.% or more). The model contains a small number of parameters and is relatively easy to analyze at finite temperatures and fields. By a judicious choice of the parameters, one can obtain semiquantitative understanding of many properties of the alloys.

The only new postulate of this theory is that the most probable value of the effective field is temperature-dependent. It decreases with increasing temperature in proportion with a quantity analogous to the spontaneous magnetization in ordered systems. Thus, the effective-field distribution satisfies a self-consistent condition, which makes it suitable to describe the collective effect of the spins. It should be noted that this is the main point of disagreement between this work and the theory of Klein and Brout. In their analysis, they concluded that the most probable field shifts to higher values as the temperature is raised. Although the early Mössbauer measurement[6] seemed to support this idea, later and more careful experiments[7] showed the con-

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* Work performed in the Ames Laboratory of the U.S. Atomic Energy Commission. Contribution No. 1958.

[1] An excellent treatment of effective-field theories can be found in J. S. Smart, *Effective Field Theories of Magnetism* (W. B. Saunders Company, Philadelphia, Pennsylvania 1966), pp. 23–31, 53–56.

[2] P. R. Weiss, Phys. Rev. **74**, 1493 (1948).

[3] W. Marshall, Phys. Rev. **118**, 1519 (1960).

[4] M. W. Klein and R. Brout, Phys. Rev. **132**, 2412 (1963).

[5] M. W. Klein, Phys. Rev. Letters **11**, 408 (1963); Phys. Rev. **136**, A1156 (1964).

[6] W. Marshall, T. E. Cranshaw, C. E. Johnson, and M. S. Ridout, Rev. Mod. Phys. **36**, 399 (1964).

[7] U. Gonser, R. W. Grant, C. J. Meechan, A. H. Muir, Jr., and H. Wiedersich, J. Appl. Phys. **36**, 2124 (1965). See also the review article by T. A. Kitchen and P. P. Craig, J. Appl. Phys. **37**, 1187 (1966), and references therein.

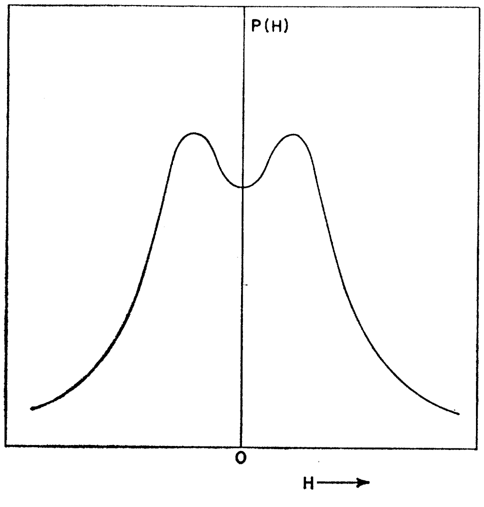

FIG. 1. The effective-field distribution curve according to Marshall's theory.

trary. The possible errors in their theory will be further discussed in the text.

II. THE EFFECTIVE-FIELD DISTRIBUTION

The Hamiltonian for the spins in an alloy may be written as

$$\mathcal{H}=-\sum_{(ij)} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j, \tag{1}$$

where J_{ij} denotes the interaction energy between the spins and the sum is carried over all pairs of spins. For the Ruderman-Kittel interaction,[8] J_{ij} is oscillatory and depends on the distance between the spins according to the inverse cube law. The effective field acting on the ith spin is defined by

$$\mathbf{H}_i=\sum_j J_{ij}\langle\mathbf{S}_j\rangle, \tag{2}$$

where $\langle\ \rangle$ denotes thermal average. Throughout this paper the effective field will be measured in energy units. In the effective-field approximation, the energy of the system is given by

$$E=-\tfrac{1}{2}\sum_i H_iSB_S(\beta H_i), \tag{3}$$

where β is the inverse temperature and $B_S(x)$ is the Brillouin function.

It is clear that the effective field is very difficult to calculate for an alloy because there are a large number of possible relative distances and orientations of pairs of interacting spins. Marshall postulated that $\mathbf{H}_i$ lies in a certain direction of space but assumes a continuous set of values, both positive and negative. The probability distribution curve of the size of $\mathbf{H}_i$ is depicted in Fig. 1. Klein and Brout showed that the minimum of the distribution curve at zero value of the field is due to the strong correlation between spins that are close together. In general, $\mathbf{H}_i$ has both an angular distribution and a size distribution. The angular distribution will be specified later, but the size distribution corresponds to the right-half of the curve in Fig. 1. For simplicity, the curve is parametrized by

$$\begin{aligned} P(H)&=a[/(H-b)^2+c^2]+a[/(H+b)^2+c^2] \\ &\qquad\qquad\text{for } H<H_c, \\ &=0 \qquad \text{for } H>H_c. \end{aligned} \tag{4}$$

The parameters b and c determine the shape of the curve and the value of a is chosen to normalize the total probability. The cutoff field H_c is necessary so that the expectation values of powers of H are finite. Usually, H_c may be chosen so large that most of the properties of the alloys are insensitive to it.

An important feature of the present theory concerns the behavior of the quantities b and c. Roughly speaking, the curve $P(H)$ is peaked at $H=b$ and has a width c under the peak. Hence, b represents the most probable value and c the fluctuation of the effective field. By comparison with the Weiss theory, it appears reasonable to assume that b depends on the temperature according to

$$b=b_0\eta, \tag{5}$$

where

$$\eta=\int_0^\infty P(H)B_S(\beta H)\,dH \tag{6}$$

is the reduced average magnetization per spin. Our knowledge about the parameter c is very limited. There are many sources of fluctuation of the effective field, and they are all very difficult to analyze. For this reason, we postulate that c is temperature-independent. This assumption is consistent with the Weiss theory, which postulates zero width for $P(H)$, and with the BPW theory, which postulates a set of δ functions for $P(H)$. It seems that the gross properties of the system over a limited range of temperature are not sensitive to variations of c.

It is also important to discuss the dependence of the parameters on the magnetic impurity concentration. The analysis of Marshall suggests that the cutoff field is independent of the concentration for very dilute alloys. For a sufficiently dilute system, b_0 is proportional to the concentration. In more concentrated alloys where a linear chain of coupled spins may be established, b_0 must have a more complicated dependence.[9] The calculation of Klein shows that c increases with increasing amount of impurity when the system is very dilute. In a concentrated alloy where long-range order is approached, c must decrease with increasing concentration. There is an intermediate region where the variation of c is complicated.

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[8] M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954); T. Kasuya, Progr. Theoret. Phys. (Kyoto) **16**, 45 (1956); K. Yosida, Phys. Rev. **106**, 893 (1957).

[9] H. Sato, A. Arrott, and R. Kikuchi, J. Phys. Chem. Solids **10**, 19 (1959); P.-G. deGennes, P. Lafore, and J. P. Millot, *ibid.* **11**, 105 (1959); R. J. Elliott, *ibid.* **16**, 165 (1960); J. S. Smart, *ibid.* **16**, 169 (1960).

The model is now completely defined. The parameters b_0, c, and H_c are chosen for a certain alloy, and the probability distribution curve of the effective field of that alloy is determined by solving Eqs. (4), (5), and (6). Figure 2 shows a typical result of the solution for η as a function of the temperature. The point marked $T_{\max}(C)$ is the temperature where the specific heat reaches a maximum.[10] The minimum of the effective-field distribution curve at zero field also disappears at the neighborhood of $T_{\max}(C)$. This shows that $T_{\max}(C)$ corresponds to the temperature where the "clusters" defined by Klein and Brout are broken up by thermal excitation.

III. SPECIFIC HEAT

The internal energy of the system is given by

$$E=-\tfrac{1}{2}xNS\int_0^\infty P(H)HB_S(\beta H)dH, \tag{7}$$

where x is the concentration of magnetic impurities and N is the Avogadro's number. The internal energy does not depend on the angular distribution of the effective field. The specific heat is obtained by

$$C=\frac{dE}{dT}=\tfrac{1}{2}xRS\beta^2\frac{d}{d\beta}\int_0^\infty P(H)HB_S(\beta H)dH. \tag{8}$$

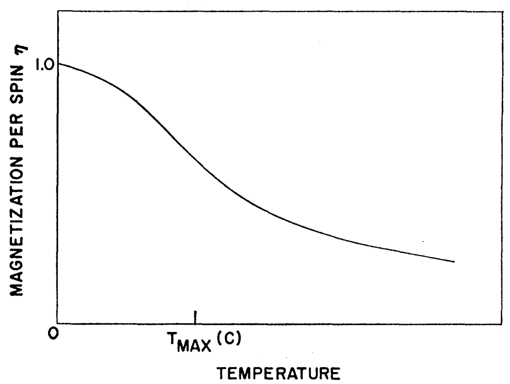

FIG. 2. The average magnetization per spin of a dilute alloy as a function of temperature.

For simplicity we shall approximate the Brillouin function by $\tanh(\frac{1}{2}\beta H)$. Then,

$$C=\tfrac{1}{2}xRS\beta^2\left[\tfrac{1}{2}\int_0^\infty P(H)H^2\operatorname{sech}^2(\tfrac{1}{2}\beta H)dH+\int_0^\infty\frac{dP(H)}{d\beta}H\tanh(\tfrac{1}{2}\beta H)dH\right], \tag{9}$$

where R is the gas constant. From Eqs. (4) and (5) we see that

$$\frac{dP(H)}{d\beta}=b_0\frac{\partial P(H)}{\partial b}\frac{d\eta}{d\beta}, \tag{10}$$

and from Eq. (6),

$$\frac{d\eta}{d\beta}=\tfrac{1}{2}\int_0^\infty P(H)H\operatorname{sech}^2(\tfrac{1}{2}\beta H)dH+b_0\frac{d\eta}{d\beta}\int_0^\infty\frac{\partial P(H)}{\partial b}\tanh(\tfrac{1}{2}\beta H)dH, \tag{11}$$

after using the result of Eq. (10). Thus, $d\eta/d\beta$ can be solved and the specific heat calculated by using Eqs. (9), (10), and (11).

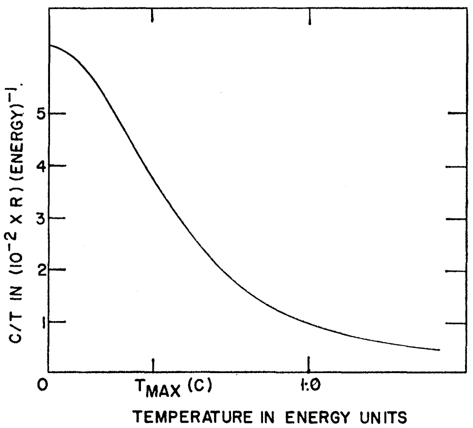

FIG. 3. The C/T curve for a dilute magnetic alloy.

As discussed in Sec. II, for very dilute alloys the parameter c increases with the impurity concentration and is roughly of the same size as b_0. Figure 3 shows the C/T curve for an alloy of this kind. The general shape appears to agree with the experiment.[11] No attempt is made to fit the experimental result of any

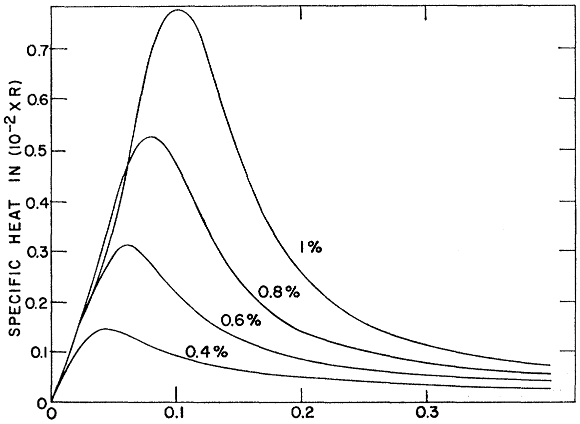

FIG. 4. The specific-heat curves of a set of hypothetical alloys with 1 at.% or less magnetic impurity.

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[10] Unless otherwise specified, all the quantities in the graphs are in reduced units, e.g., the effective-field parameters b_0 and c are in arbitrary energy units (for example, J, erg, eV, or whatever that is most convenient) the temperature in units of energy, the specific heat in units of $R\times10^{-2}$, and the susceptibility in inverse energy units per atom$\times10^{-2}$.

[11] J. E. Zimmerman and F. E. Hoare, J. Phys. Chem. Solids **17**, 52 (1960); J. P. Franck, F. D. Manchester, and D. L. Martin, Proc. Roy. Soc. (London) **A263**, 494 (1961). See also the references listed in Klein, Phys. Rev. **136**, A1156 (1964).

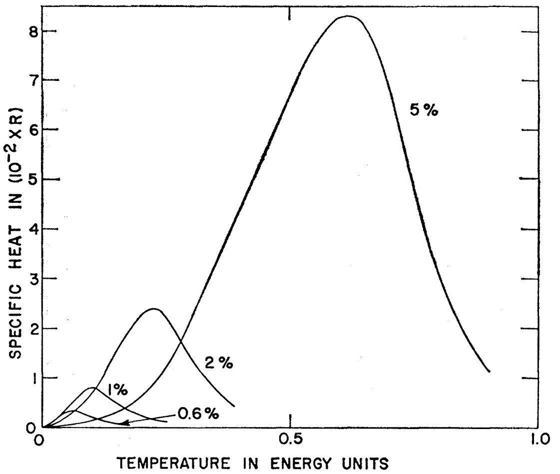

FIG. 5. The specific-heat curves of a set of hypothetical alloys with 1 at.% or more magnetic impurity.

particular alloy because the main purpose of this discussion is to describe the physical process in simple terms.

It was also argued that for more concentrated alloys the monotonous relationship between the parameter c and the concentration must break down. Figures 4 and 5 show the specific-heat curves of a set of hypothetical alloys such that c becomes independent of the concentration above 0.5 at.%. The general trend is that the initial part of the specific-heat curve becomes convex and the initial slope decreases for higher concentrations. This behavior has been observed by Veal and Rayne[12] in dilute PdFe alloys. Since the specific heat does not depend on the alignment of the spins, the curves apply both to dilute ferromagnetic and antiferromagnetic alloys.

With this simple model we may calculate the specific heat of the alloys when an external field is applied. The energy, for this case, is

$$E=-xNS\int P'(\Omega)d\Omega\left[\tfrac{1}{2}\int_0^\infty P(H)H\tanh(\tfrac{1}{2}\beta H_1)\right.$$
$$\left.\times\cos\alpha dH+\int_0^\infty P(H)H_e\tanh(\tfrac{1}{2}\beta H_1)\cos\gamma dH\right],\quad(12)$$

where H_e is the external field,

$$H_1=[H^2+H^2{}_e+2H\,H_e\cos\theta]^{1/2},\quad(13)$$

θ is the angle between $\mathbf{H}$ and $\mathbf{H}_e$, α is that between $\mathbf{H}$ and $\mathbf{H}_1$, and γ that between $\mathbf{H}_e$ and $\mathbf{H}_1$. The geometrical relationships of these quantities are shown in Fig. 6. Since the angular distribution enters the relation, we should average over the angular distribution function $P'(\Omega)$. Equation (6) should also be modified to read

$$\eta=\int P'(\Omega)d\Omega\int_0^\infty P(H)\tanh(\tfrac{1}{2}\beta H_1)dH.\quad(14)$$

The dependence of η on the external field makes $P(H)$ dependent on H_e, and in this manner the influence of the external field on the collective effect of the spins is taken into account. The calculation of the specific heat proceeds in the same way as before.

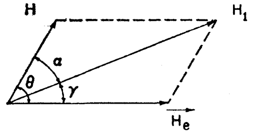

FIG. 6. The geometrical relationship between the vectors $\mathbf{H}$, $\mathbf{H}_e$, and $\mathbf{H}_1$.

At this point, we must face the problem of angular distribution of $\mathbf{H}$. However, we can learn a great deal by assuming a simple distribution $P'(\Omega)$ for the following reason. It is easy to see that the spins sitting at points of low effective field give rise to most of the specific heat at low temperatures. These spins are more or less aligned with the external field when it is turned on. Hence, the specific heat should not be very sensitive to the angular distribution, and we may take $P'(\Omega)$ for ferromagnetic alignment for this calculation. The result of $C(H_e)$ for a 1 at.% LaGd alloy is plotted in Fig. 7. In this calculation the parameters b_0 and c are chosen to fit the position and width of the zero-field-specific-heat peak, and the highest field is 20 kG. The experimental verification is under way and the initial data seem to agree with the predicted behavior.[13]

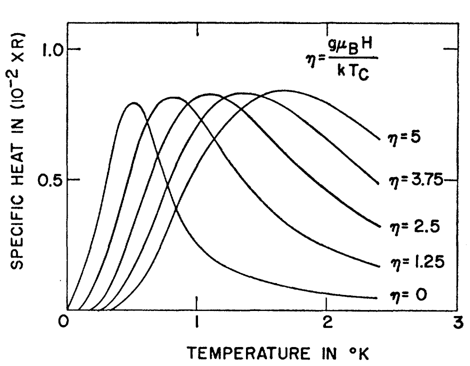

FIG. 7. The predicted specific heat of 1 at.% LaGd alloy under strong magnetic fields. The important parameters are chosen by fitting the zero-field data.

IV. SUSCEPTIBILITY

The susceptibility of the alloy is given by

$$\chi=\partial\sigma/\partial H_e\,|_{H_e\to 0},\quad(15)$$

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[12] B. W. Veal and J. A. Rayne, Phys. Rev. 135, A442 (1964).

[13] D. K. Finnemore (private communication).

where σ is the net magnetization in the direction of $\mathbf{H}_e$:

$$\sigma = xNS\int P'(\Omega)\,d\Omega\int_0^\infty P(H)\ \tanh(\tfrac{1}{2}\beta H_1)\ \cos\gamma\, dH. \tag{16}$$

The result of the differentiation is easily found to be

$$\chi = xNS\left\{\int_0^\infty P(H)\left[\tfrac{1}{2}\beta\,\mathrm{sech}^2(\tfrac{1}{2}\beta H)\,\langle\cos^2\theta\rangle + \tfrac{1}{2}H^{-1}\tanh(\tfrac{1}{2}\beta H)\,(1-\langle\cos^2\theta\rangle)\right]dH + \langle\cos\theta\rangle\int_0^\infty \frac{\partial P(H)}{\partial H_e}\tanh(\tfrac{1}{2}\beta H)\,dH\right\}, \tag{17}$$

where

$$\langle\cos^n\theta\rangle = \int P'(\Omega)\ \cos^n\theta\, d\Omega. \tag{18}$$

It is implicitly assumed here that the field dependence of $P'(\Omega)$ is negligible. This is done in order to avoid complications because we do not have sufficient knowledge about the field dependence of $P'(\Omega)$. Again using Eqs. (5) and (14), we find

$$\partial P(H)/\partial H_e = b_0(\partial\eta/\partial H_e)[\partial P(H)/\partial b], \tag{19}$$

and

$$\frac{\partial\eta}{\partial H_e} = b_0\frac{\partial\eta}{\partial H_e}\int_0^\infty \frac{\partial P(H)}{\partial b}\tanh(\tfrac{1}{2}\beta H)\,dH + \tfrac{1}{2}\beta\langle\cos\theta\rangle\int_0^\infty P(H)\ \mathrm{sech}^2(\tfrac{1}{2}\beta H)\,dH.$$

Hence,

$$\frac{\partial\eta}{\partial H_e} = \tfrac{1}{2}\beta\langle\cos\theta\rangle\int_0^\infty P(H)\ \mathrm{sech}^2(\tfrac{1}{2}\beta H)\,dH \bigg/ \left[1 - b_0\int_0^\infty \frac{\partial P(H)}{\partial b}\tanh(\tfrac{1}{2}\beta H)\,dH\right]^{-1}, \tag{20}$$

and the final formula for χ follows by substituting Eqs. (19) and (20) into Eq. (17).

The above expression for χ is certainly very complicated. However, if we assume the angular distribution of **H** to be antiferromagnetic, we obtain

$$\langle\cos\theta\rangle = 0,$$

and

$$\chi = xNS\int_0^\infty P(H)\left[\tfrac{1}{2}\beta\ \mathrm{sech}^2(\tfrac{1}{2}\beta H)\,\langle\cos^2\theta\rangle + \tfrac{1}{2}H^{-1}\tanh(\tfrac{1}{2}\beta H)\,(1-\langle\cos^2\theta\rangle)\right]dH. \tag{21}$$

Furthermore, in very dilute alloys it is reasonable to expect a random distribution, so we may put $\langle\cos^2\theta\rangle = \frac{1}{3}$ in Eq. (21). Figure 8 shows the calculated χ for the hypothetical alloys of Sec. IV. In the very dilute cases where b_0 and c are roughly the same size, the susceptibility is a monotonically decreasing function of the temperature. A peak in χ only appears for those alloys for which c is relatively small compared with b_0 ($b_0/c \cong 6$ for the 2% alloy). The size of the peak is insensitive to the concentration, and the position is proportional to the concentration. Except for very dilute alloys these results agree with the predictions of Klein.[14]

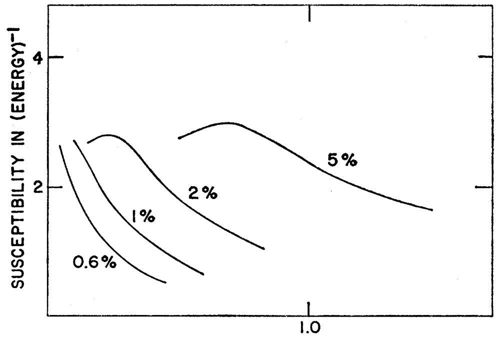

FIG. 8. Magnetic susceptibility of a set of hypothetical alloys with random distribution of effective-field direction.

Recent measurements of the susceptibility indicate that the size of the peak is quite sensitive to the concentration.[15] It seems that the only way to resolve this difficulty is to modify the assumption about the random direction of **H**. Indeed, neutron-diffraction experiments[16] show the surprising fact that a helical spin structure exists in alloys with as low as 5% of heavy rare earths in yttrium. The helical axis is along the c axis of the

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[14] M. W. Klein, Phys. Rev. **141**, 489 (1966).

[15] O. S. Lutes and J. S. Schmit, Phys. Rev. **134**, A676 (1964); D. K. Finnemore, D. C. Hopkins, and P. E. Palmer, Phys. Rev. Letters **15**, 891 (1965). R. P. Guertin, J. E. Crow, and R. D. Parks, *ibid.* **16**, 24 (1966). See also the references listed in M. W. Klein, Phys. Rev. **136**, A1156 (1964).

[16] H. R. Child, W. C. Koehler, E. O. Wollan, and J. W. Cable, Phys. Rev. **138**, A1655 (1965).

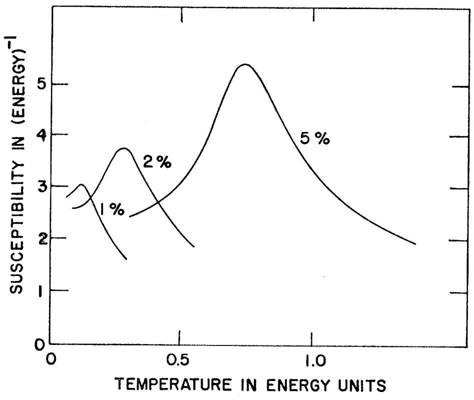

FIG. 9. Magnetic susceptibility of a set of hypothetical alloys with helical spin structure. $\langle\cos\theta\rangle=0.6$, $\langle\cos^2\theta\rangle=0.3$.

hexagonal crystal and the turn angle of adjacent layer is about 50°. In the following we give a rough estimate of how this would affect the susceptibility. Around the susceptibility maximum the spins are already very loosely coupled together. It is not difficult for the measuring field to align a sizable number of the spins. If the external field lies in the basal plane, the effective field acting on a spin due to other spins in the same basal plane is mainly in the direction of the external field, while the effect fields due to spins in the neighboring planes make angles of approximately 50° with the direction of the field. This shows that the quantity $\langle\cos\theta\rangle$ may have a value of 0.5 or higher. Figures 9 and 10 show the susceptibility of some hypothetical alloys with helical spin structure. For the curves in Fig. 9 we assume $\langle\cos\theta\rangle=0.6$ and $\langle\cos^2\theta\rangle=0.3$, and for those in Fig. 10, $\langle\cos\theta\rangle=0.7$ and $\langle\cos^2\theta\rangle=0.5$. Again the shapes of the curves and the trend of the concentration dependence are in qualitative agreement with the experiment. There is large uncertainty in these calculations because of the many crude approximations.

Figure 11 shows the $T_{\max}$ of the susceptibility and the $T_{\max}$ of the specific heat for the hypothetical alloys plotted as functions of the concentration. A straight line is drawn through the $T_{\max}(C)$ of the dilute alloys for comparison purposes. For all the alloys the parameter b_0 is assumed to be proportional to the concentration and c is taken as a constant. The value of $T_{\max}(\chi)$ is insensitive to the assumed spin alignment. At the low concentration end $T_{\max}(\chi)$ vanishes at a nonzero value of the concentration. But for more concentrated alloys $T_{\max}(\chi)$ is generally larger than $T_{\max}(C)$. That both $T_{\max}(\chi)$ and $T_{\max}(C)$ vary faster than linearly with the concentration may not have physical significance because of the uncertainty in the assumed concentration dependence of b_0 and c.

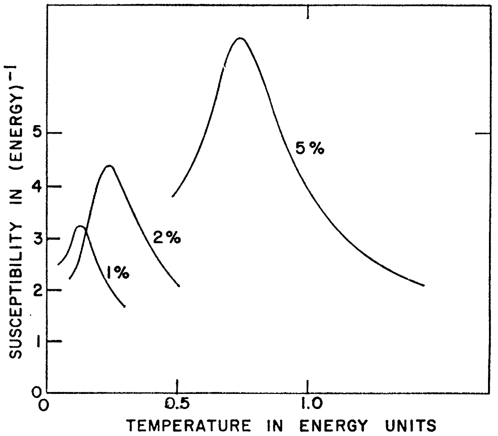

FIG. 10. Magnetic susceptibility of a set of hypothetical alloys with helical spin structure. $\langle\cos\theta\rangle=0.7$, $\langle\cos^2\theta\rangle=0.5$.

V. DISCUSSION

The present theory makes no pretense that everything is understood, because the most important parameters in the basic hypothesis must be either determined from measurements or calculated by some microscopic analysis such as the theory of Klein and Brout. Therefore, it is never intended as a substitute for a microscopic theory. Instead, it may serve as a supplement when the latter becomes too complicated to manipulate. Take, for example, the temperature dependence of the effective-field distribution curve. The present theory draws its conclusion by analogy with the Weiss theory. The fact that the most probable field becomes lower at higher temperatures is in accordance with our general understanding of all magnetic ordering problems. However, through some approximate analysis, Klein and Brout obtained just the opposite behavior, i.e., the effective field moves to higher values at elevated temperatures. We shall attempt to show where their analysis may go wrong.

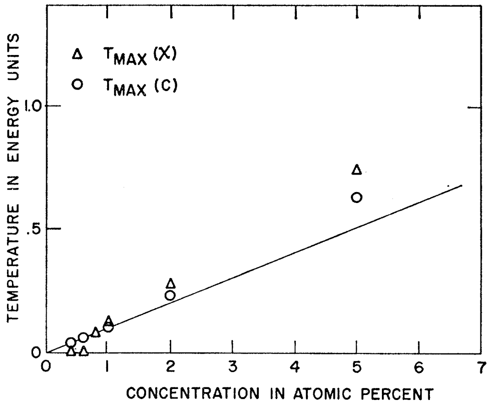

FIG. 11. The concentration dependence of $T_{\max}(C)$ and $T_{\max}(\chi)$ for the hypothetical alloys studied in the text.

The most important concept in the treatment of Klein and Brout is the correlation length. They show that, because of the oscillatory nature of the Ruderman–Kittel interaction, the direct correlation of two spins is disrupted if they are far enough apart to allow a third spin to be near either one of them. In this sense, the correlation of the two is screened by the third spin, and the correlation length is a measure of the average nearest-neighbor distance. They also observed that the correlation between spins becomes weaker at a higher temperature, and this weakened correlation may be converted into a shorter correlation length. It then follows from analysis that a reduced correlation length leads to a shift of the effective field to higher values. A possible loophole in this series of arguments may be the following. One can see from the analysis of two spin correlation that the screening effect is only complete at 0°K, and it becomes progressively less effective as the temperature is raised. As a result, the spins outside the correlation distance from the central spin become partially correlated to it when the temperature is finite. It is possible that the breaking down of the screening effect actually causes a net increase in correlation length at finite temperatures, and this in turn reduces the effective field. It seems necessary to study more carefully the two competing effects: the reduced correlation between nearby spins and the increased correlation between more distant spins at finite temperatures.

We can also understand from the present description of the effective-field distribution why there is not always a paramagnetic line in the Mössbauer spectrum of dilute alloys at low temperatures.[7] The paramagnetic line is caused by the spins that are at points of low effective fields. The number of such spins is measured by the value of $P(0)$. When the cutoff field H_c is sufficiently large, the parameter a is approximately c/π. So, at low temperatures the value of $P(0)$ may be sizable if $b_0 \cong c$ but is very small if $b_0 \gg c$. For the latter group of alloys the paramagnetic line will be missing. The ratio of b_0 and c also determines the shapes of the specific-heat and the magnetic-susceptibility curves. Simultaneous measurements of the three properties will give a direct test of the effective-field theory.

ACKNOWLEDGMENTS

The author would like to thank Dr. D. K. Finnemore and Dr. R. G. Barnes for helpful discussions.

PHYSICAL REVIEW VOLUME 157, NUMBER 2 10 MAY 1967

Magnetic Resonance Studies of Ferroelectric Methylammonium Alum*

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(Received 28 November 1966)

The electron paramagnetic resonance of $CH_3NH_3Al(SO_4)_2\cdot 12H_2O$ (MASD) doped with Cr^{3+} was studied from 90 to 300°K. At the first-order ferroelectric Curie point (177°K), an abrupt change in the fine-structure splitting as well as the resonance linewidths was observed. Continuous-wave and pulsed proton-resonance experiments were performed on ordinary and partially deuterated MASD. The relaxation time in the rotating coordinate system ($T_{1\rho}$) exhibited a discontinuity at the transition temperature T_c. The $T_{1\rho}$ data are interpreted as due to a 180° flip motion of the $CH_3NH_3^+$ ion which changes abruptly at T_c. The T_1 data show a single minimum characteristic of rotation of the CH_3 group about the triad axis. It is suggested that the ferroelectric transition in MASD results from a one-dimensional reorientation of the $CH_3NH_3^+$ ions. Possible reasons for the first-order nature of the transition are given.

I. INTRODUCTION

A CONSIDERABLE number of alums

$$M^+M'^{3+}(RO_4)_2\cdot 12\,H_2O$$

exhibit ferroelectricity[1] particularly with $M^+=NH_4^+$ or $CH_3NH_3^+$. The ferroelectric properties of methylammonium aluminum sulfate (MASD) were investigated by Pepinsky and co-workers.[1] MASD undergoes a first-order phase transition at 177°K with a spontaneous polarization of $0.9\,\mu C\,cm^{-2}$. The crystal structure has been determined[2] to be cubic space group $Pa3$ in the paraelectric phase and monoclinic space group $Pca2_1$ in the ferroelectric phase. The detailed structure for the ferroelectric crystal was determined by Fletcher and Steeple,[2c] including positions of hydrogen atoms of the water molecules and methylammonium ion. A mechanism for the appearance of ferroelectricity in MASD, however, has not been put forth.

In the present investigation, essentially two types of experiments were performed: (1) electron paramagnetic resonance (EPR) spectroscopy of MASD doped with

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* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

[1] (a) R. Pepinsky, F. Jona, and G. Shirane, Phys. Rev. **102**, 1181 (1956); (b) F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon Press, Inc., New York, 1962), Chap. VIII.

[2] (a) H. Lipson, Phil. Mag. **19**, 887 (1935); (b) Y. Okaya, M. S. Ahmed, R. Pepinsky, and V. Vand, Z. Krist. **109**, 367 (1957); (c) R. O. W. Fletcher and H. Steeple, Acta Cryst. **17**, 290 (1964).