in these systems is apparently accompanied by an essential change of the electron structure of the Pt atoms.

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Magnetic Disorder as a First Order Phase Transition

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It is shown that if the exchange interaction (or Curie temperature) of a ferromagnetic depends sufficiently strongly on interatomic distance and the lattice is sufficiently compressible then the ferromagnetic to paramagnetic transition may be of first order, with an associated latent heat and discontinuous density change, rather than of the usual second-order type. This treatment can account for the magnetic transition in MnAs, and is believed to be applicable to other systems.

To view the physics of our treatment, let us consider the usual method of treating magnetic disorder, in which there is assumed to be a ferromagnetic interaction between the magnetic moments localized on each atom site, and in which it is further assumed, usually implicitly, that this interaction is not a function of lattice spacing. At low temperatures there exists substantially complete magnetization or perfect long range order. As the temperature is raised, the thermal randomization tends to destroy this order and the magnetization falls. The course of the magnetization is described more or less by application of the molecualr field concept to the Brillouin function, and at the Curie temperature, T_c, the spontaneous magnetization becomes zero without discontinuity. This transformation is of second order, and the cooperative nature of the system is reflected by a discontinuity in the specific heat at T_c. There is not, however, the latent heat or discontinuous density change that characterize a first-order transition.

Now let us consider what results if we assume that the exchange energy (or Curie temperature) is a strong function of interatomic spacing. We show such a dependence in Fig. 1(a). At absolute zero, the system's free energy may be lowered by distortion of the lattice in the direction of increasing the Curie temperature. This distortion will introduce into the free energy a term in strain energy which will increase the free energy, and thus, a compromise between distortion and exchange may be found that minimizes the free energy. This volume is indicated in Fig. 1(a) as v'. If we compare the course of the magnetization with temperature of such a system that is free to distort itself (free) with that of a system whose volume is fixed (clamped), we find the behavior sketched in Fig. 1(b). At low temperatures the free system will lose less of its magnetization than the clamped system because its effective Curie temperature (close to T') is greater than that of the clamped system. If this change in effective Curie temperature is large enough, then as the temperature is raised it is possible for the free system to have net magnetization at temperatures greater than T_0, the Curie temperature of the clamped system. Since the driving force for lattice expansion is the ordering of magnetic spins, the loss in magnetic moment or order at higher temperatures causes a diminution of the lattice strain as indicated in Fig. 1(c) which omits the usual thermal expansion in order to focus upon magnetic effects. As the temperature is further increased, the magnetization can find no way to decrease smoothly to zero since it is stable at these temperatures only because the magnetization exists. At a critical temperature, T_{crit}, the magnetization and lattice distortion go to zero discontinuously.

We have calculated, in the molecular field approximation, the properties of a system in which the exchange energy dependence is given by $T_c = T_0[1+\beta(v-v_0)/v_0]$. T_c is the Curie temperature appropriate to a lattice volume v while v_0 is the equilibrium volume in the absence of magnetic interactions. The course of the magnetization with temperature of such a system depends upon the steepness β of the exchange interaction dependence on interatomic distance, the compressibility K, and upon T_0. The behavior may be the usual second-order transition to paramagnetism, but it can in fact become a first-order transition with the properties usually associated therewith, *e.g.*, latent heat and discontinuous density change. In the absence of an externally applied pressure, the transition will be of first order if

$$\eta \equiv 40\, NkKT_0\beta^2\, [j(j+1)]^2/[(2j+1)^4-1] > 1.$$

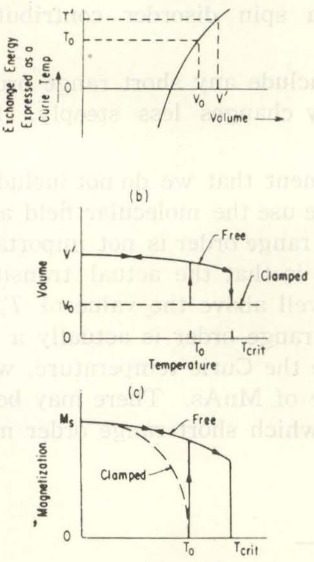

Fig. 1.

In order to illustrate the connection of this theory with a real system, we compare it to the compound MnAs in Fig. 2. There are no adjustable parameters. The data are from several different samples and some independent measurements. T_0 is taken from Serres[1)] as the intercept of $1/\chi$ *vs.* T while the slope of that curve indicates $j=3/2$ to be the most likely spin state. η is determined to be 2 from the observed[2)] 1.8% volume change at the transition. Space limitations do not permit further comparisons of theory to this or other systems, but we believe the applicability of our treatment to be justfied by more than one physical system.

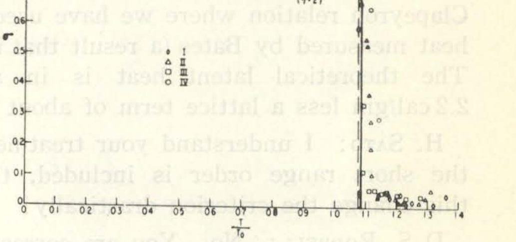

Fig. 2.

A more complete treatment of this subject will appear in the March 15th issue of the *Physical Review*[3)].

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DISCUSSION

L. F. BATES: How did you prepare your specimens? When I prepared MnAs many years ago, I had to make my own manganese and purify arsenic myself.

D. S. RODBELL: We make our MnAs samples much in the way that you described in your early work. Since that time good purity materials have become readily available, and with additions of a small excess of As, we can compensate for the condensation of some As on the walls of the quartz tubes in which we synthesize our samples (a few hours at 750°C of mixed powders of Mn and As in an inert atomosphere).

J. B. GOODENOUGH: One would anticipate that in the ideal NiAs structure the Mn-Mn interactions along the *c*-axis would be particularly sensitive to the lattice parameter. Can you explain why the volume change only, independent of the *c*/*a* ratio, enters your analysis?

D. S. RODBELL: You have put your finger on a very important point and a shortcoming of the theory that we use. In MnAs (NiAs structure) the nearest neighbor distance is *c*/2 where *c* is the unique axis of the unit cell. If the dominant exchange is between nearest neighbors, we would expect that the *c*-axis is the most important in the crystal as far as exchange is concerned. It is therefore surprising that the *a*-axis is the one that does indeed change discontinuously at the transition. It is clear that more than simple nearest neighbor exchange is involved in this as well as most other materials. A more refined picture with other neighbor interactions might clarify the situation but we have not yet proceeded in that direction.

B. T. MATTHIAS: What is the pressure dependence of the Curie point?

D. S. RODBELL: The pressure dependence of the Curie point is $dT_c/dp = -0.12$°C/bar, a value that we have determined experimentally and also theoretically from the Clausius-Clapeyron relation where we have used the measured volume changes and the latent heat measured by Bates (a result that incidentally was originally determined in 1928). The theoretical latent heat is in accord with a spin disorder contribution of 2.2 cal/gm less a lattice term of about 0.5 cal/gm.

H. SATO: I understand your treatment does not include any short range order. If the short range order is included, the free energy changes less steeply. Doesn't this change the criterion drastically?

D. S. RODBELL: No. You are correct in the statement that we do not include short range order. That is a consequence of the fact that we use the molecular field approximation. In the case of MnAs the exclusion of short range order is not important and does not modify our treatment. The reason for this is that the actual transition of MnAs takes places as we have seen near 40°C, well above the value of T_0 (11°C) appropriate to the collapsed lattice. Since the short range order is actually a rapidly disappearing quantity as temperature increases above the Curie temperature, we need not be concerned about short range order in the case of MnAs. There may be cases, subject to the same theory that we use here, for which short range order must be accounted.