Magnetic Ordering in Solid Helium-3

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Using a model for the magnetic properties of solid He^3 which includes both Heisenberg exchange and the motion of ground-state vacancies (concentration $\sim 10^{-4}$), we predict via mean-field theory a first-order paramagnetic- to ferromagnetic-phase transition.

The experimentally observed properties of solid He^3 cannot be described by a simple Heisenberg model[1] which previously appeared to be adequate.[2] Recently, the authors have pointed out that the presence of a small concentration of ground-state vacancies ($x \sim 10^{-4}$ vacancies/site) gives results in qualitative agreement with known thermal experimental data near melting for T above the spin-ordering temperature T_c.[3] Similarly, Greywall[4] has discussed specific-heat anomalies in solid He^3 and finds $\sim 10^{-4}$ Landau-Fermi "quasiparticles" per site which we interpret as vacancies.

The hypothesis of ground-state vacancies requires a new interpretation of well-established experimental data in the high-temperature ($T \gg T_c$) regime. In particular, we briefly consider the nuclear-magnetic-resonance (NMR) properties of solid He^3. Motionally narrowed relaxation times (T_1 and T_2) and spin diffusion (D) are empirically determined by a single correlation time τ_c which is (roughly) the time required for a spin to leave a site.[2] In the model here considered this can happen (i) if the spin moves onto a vacant neighboring site (matrix element t), or (ii) if the spin exchanges sites with a neighboring opposite spin (matrix element J). It is evident that if vacancy hopping controls the NMR properties, then

$$\tau_c^{-1} \simeq \text{const}(tx/\hbar) \quad \text{(vacancy dominated)}. \qquad (1)$$

On the other hand, if exchange dominates the NMR properties, then

$$\tau_c^{-1} \simeq \text{const}(J/\hbar) \quad \text{(exchange dominated)}. \qquad (2)$$

The conventional wisdom is the following: (i) For sufficiently high temperatures there are a large number of thermally activated vacancies [$x \simeq \exp(-\varphi/k_B T)$] so that Eq. (1) is valid. In this regime φ can be accurately determined, and t can be estimated. (ii) For lower temperatures x is neglected, Eq. (2) is considered valid, and J can be estimated.

Let us consider another interpretation. Suppose (for the moment) that J were zero. Then Eq. (1) always holds true. The fact that $\tau_c^{-1} \propto \exp(-\varphi/k_B T)$ for high T and $\tau_c^{-1} \simeq$ const for small T has the obvious interpretation that x is finite for small T! The fact that $\tau_c^{-1} \propto \exp(-\varphi/k_B T)$ through many orders of magnitude for small molar volumes[2] (where both the exchange and the ground-state-vacancy concentration can evidently be neglected) in no way implies that the ground-state-vacancy concentration near melting can be neglected.

When J, t, and the ground-state x are all important, the NMR analysis is quite complicated. We estimate $J/k_B \sim 10^{-3}$ °K, $t/k_B \sim 1$ °K, and $x \sim 10^{-4}$. If the smaller value of t usually quoted in the literature were used, a slightly larger value of x would be required in our analysis but this does not qualitatively change our conclusions.

The difficulty in providing a quantitative analysis of a model which includes ground-state vacancies is that unlike a simple Heisenberg model where $J/k_B T$ is, for physical values of T, often small, $t/k_B T$ is never small and must be treated to all orders when making detailed experimental comparisons. Even an order-of-magnitude prediction for the spin-ordering temperature is a difficult task when vacancies are taken into account. In the limit $x \to 0$ only very rough bounds on T_c have previously been computed.[5] The purpose of this Letter is to provide a mean-field theory of the phase transition to an ordered magnetic state. Our prediction is that the transition is first order if the parameters are such that the ordered state is ferromagnetic.

Suppose that all of the He^3 spins were parallel. Then the vacancies would behave as a dilute Fermi gas of "spinless holes" with a bandwidth $2zt$ (where z, the number of nearest neighboring sites, is 8 for a bcc lattice).[3] If the spins are disordered, or antiferromagnetically ordered, then the bandwidth is known to decrease.[6,7] Hence, the vacancies will have the lowest energy in the ferromagnetic state.[8] For small vacancy concentrations, the above analysis is complicated by

"band tails"[7] which extend out to the full bandwidth $2zt$ although the "bulk" part of the bandwidth is narrowed. The band tails cannot hold many vacancies but they have crucial importance for $x \ll 1$.

Consider the case in which x is so small that all of the vacancies reside in the band tails. These come about because in any disordered spin system there exist fluctuations in which spins are parallel over connected regions containing fairly many lattice sites. Although these regions take up a very small fraction of sites in the crystal, each such region has a vacancy-ground-state energy which approaches the bottom of the ferromagnetic band as the fluctuation size increases.[9] Following an argument of Lifshitz,[7,10] the vacancy density of states is proportional to the probability of a completely ferromagnetic region having l sites. This is proportional to

$$\Gamma_l(m)\exp[-ls(m)/k_B], \tag{3}$$

where $s(m)$ is the entropy per site for magnetization m per site, and $\Gamma_l(m)$ is the number of orientations of the total spin of the l-site ferromagnetic region consistent with the given value of m. [If $m=0$, then $\Gamma_l(m)=2s+1=l+1$, where s is the total spin of the region.] The ground-state energy of a vacancy in such a region (relative to the bottom of the ferromagnetic band) is

$$\epsilon = bztl^{-2/3}, \tag{4}$$

where b is a positive constant which depends on the shape of the region, e.g., $b=3\pi^2/2$ for a cubic region of the bcc lattice. Assuming that each region has one vacancy, Eqs. (4) and (3) imply a density of states

$$\rho(\epsilon) \propto \exp[-(bzt/\epsilon)^{3/2}s(m)/k_B], \tag{5}$$

where we have included only the dominant energy dependence for small ϵ. If we take into account multiple-vacancy occupation of the ferromagnetic regions there is only a renormalization of b.

Integrating the density of states in Eq. (5) up to the Fermi level yields the Fermi vacancy energy

$$\epsilon_F \simeq bzt[s(m)/k_B \ln x^{-1}]^{2/3}. \tag{6}$$

The total vacancy energy per lattice site $E \simeq x\epsilon_F$ is then

$$E(m) \simeq b'ztx[s(m)/k_B \ln x^{-1}]^{2/3}, \tag{7}$$

where $b' \sim b$. To this we must add an antiferromagnetic exchange energy $\frac{1}{8}zJm^2$. Note that $E \simeq 0$ if $m=1$. This is because we have included only the dominant energy dependence for $m \neq 1$ in Eq. (5). The correction $E(m=1) \sim tx^{5/3}$ can be neglected for $x \sim 10^{-4}$. In writing Eq. (7) we have assumed that the vacancies are degenerate. This assumption will be seen later to be consistent in that $k_B T_c \ll \epsilon_F$. Finally, we choose the usual mean-field entropy,

$$S(m) = -k_B\left[\left(\frac{1+m}{2}\right)\ln\left(\frac{1+m}{2}\right) + \left(\frac{1-m}{2}\right)\ln\left(\frac{1-m}{2}\right)\right]. \tag{8}$$

To facilitate the discussion of the Helmholtz free energy $F(m)=E(m)-TS(m)$, we have sketched in Fig. 1 the general dependence of S, E, and F on the magnetization.[11] It is clear that at the temperature for which $F(m=0)=F(1)$, a first-order transition from an $m=0$ state to an $m=1$ state occurs. The spin-order temperature is given by

$$\begin{aligned} T_c &\simeq k_B^{-1}[E(0) - \tfrac{1}{8}zJ]/S(0) \\ &\simeq (z/k_B \ln 2)[b'tx(\ln 2/\ln x^{-1})^{2/3} - \tfrac{1}{8}J]. \end{aligned} \tag{9}$$

It is evident from previously quoted values of the constants in Eq. (9) that $x \sim 10^{-4}$ can easily make the first term on the right-hand side of the order of 10^{-3} °K. By differentiating the free energy twice with respect to m, the inverse susceptibility is found to be

$$\chi_T^{-1} \propto (T - T_p), \tag{10}$$

where

$$k_B T_p = \tfrac{2}{3}b'zxt(\ln 2)^{-1/3}(\ln x^{-1})^{-2/3} - \tfrac{1}{4}zJ,$$

a Curie-Weiss–law susceptibility with T_p lower than T_c (i.e., the first-order phase transition occurs before χ diverges, as expected).

We have so far assumed that all vacancies reside in the band tails. Since ϵ_F given by Eq. (6) is of the order of t in the disordered state, however, the vacancies might fill the band tails and "spill" over into the bulk band. Since their concentration is very low, however, each of these excess vacancies will have an energy equal to the bulk band-edge energy which might decrease with increasing magnetization.[6] Thus, for such a case, as the magnetization decreases and hence the band tails hold fewer vacancies, we would expect the vacancy energy to follow the dashed line

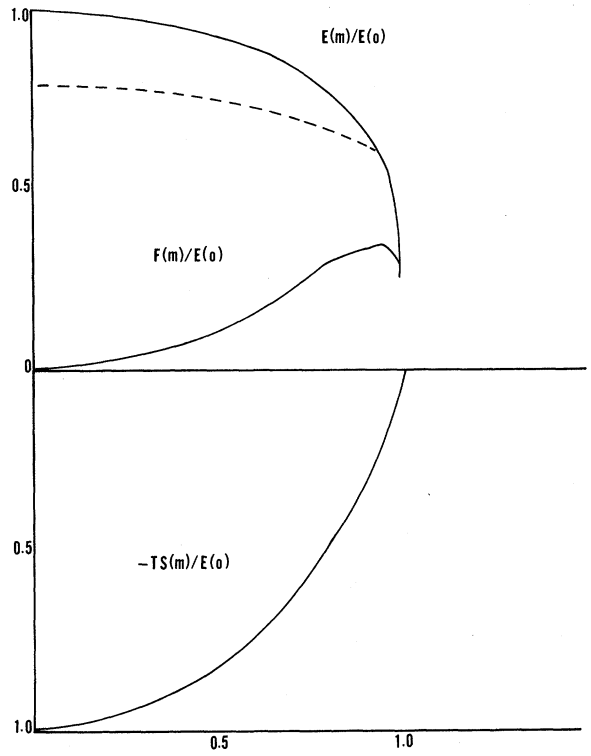

FIG. 1. We have plotted the dimensionless energy $E(m)/E(0)$ and free energy $F(m)/E(0)$ versus magnetization m above the abscissa and the entropy term $-TS(m)/E(0)$ below the abscissa. The plot has been made for $T=\frac{4}{5}T_c$. The dashed line gives $E(m)/E(0)$ qualitatively for the case in which the band tails are completely filled in the paramagnetic phase.

in Fig. 1 qualitatively. If the bulk edge varies slowly enough with m, there will still be a first-order phase transition, but with a slightly lower T_c.

Now, we are in a position to discuss the phase diagram and the interpretation of experimental data on magnetic properties of He^3 using our mean-field theory. It was suggested in Ref. 3 that for sufficiently small vacancy concentrations there could be two-phase equilibrium between ferromagnetic and antiferromagnetic phases over a wide range of vacancy concentrations. Only when $x=0$ would the system be totally antiferromagnetic. These speculations were based on arguments for the infinite-interaction Hubbard model due to Visscher,[12] which depend on the number of vacancies in the system being fixed. We might expect, however, that the number of vacancies will be in strong equilibrium with the lattice. In such a case, we have the following relationship for the chemical potential μ of the vacancies:

$$\mu=\mu_{\rm lat}+\mu_{\rm mod}=0, \tag{11}$$

where $\mu_{\rm lat}$ is the lattice contribution and $\mu_{\rm mod}$ represents the contribution due to magnetic ordering and vacancy motion. Since $\mu_{\rm lat}$ should not depend strongly on where one is in the lattice (i.e., whether one is in a ferromagnetic or antiferromagnetic phase region), $\mu_{\rm mod}$ (which is equal to the vacancy Fermi energy at $T=0$) is also uniform over the solid. Hence, the vacancy concentration in the ferromagnetic phase will be independent of how much of the solid is in this phase. Since the vacancy energies are generally higher in an antiferromagnetic phase (as they are in a disordered phase),[5,8] there are few vacancies in an antiferromagnetic phase region. Also, the antiferromagnetic phase energy per site should be reduced by the lattice energy necessary to eliminate the vacancies in the antiferromagnetic phase, which is $x|\mu_{\rm lat}|$, where x is the concentration of vacancies that would be present if the lattice were in the ferromagnetic phase and $|\mu_{\rm lat}|\sim t$. Under these assumptions there will no longer be a tendency to have phase equilibrium between ferromagnetic and antiferromagnetic phases over a wide range of values of J and xt, as in the Hubbard model. Since the ferromagnetic-state vacancy energy under the present assumptions is proportional to the number of sites in the ferromagnetic phase region, phase equilibrium only occurs when $zJ-x|\mu_{\rm lat}|$ is equal to the ferromagnetic-state energy per site which is $\sim xt$. Therefore, a second-order transition to the antiferromagnetic phase most likely occurs for $J>xt$ at some temperature and a first-order phase transition to a ferromagnetic state occurs at some temperature for $J<xt$.

We conclude with some qualitative suggestions of how to interpret the experimental data. Our mean-field theory suggests that if the magnetic phase is actually ferromagnetic rather than antiferromagnetic, the phase transition might be first order, which is consistent with experimental data.[1] Although mean-field theory is not suitable for calculating rigorously the precursory behavior for $T>T_c$, it should be noted that our inverse suceptibility above T_c will have a negative intercept but the system will still order ferromagnetically by a first-order transition if

$$E(0)\lesssim zJ<2E(0). \tag{12}$$

This illustrates that the occurrence of an inverse susceptibility with a negative intercept does not

necessarily mean that the system must order antiferromagnetically (as is the case in the Heisenberg model).

Experimental data have recently been recorded[13] which show a general increase in T_c with increasing applied magnetic intensity H. These data cannot be interpreted in terms of a transition from a paramagnetic phase to a spin-flipped antiferromagnetic phase because of the small value of the magnetic dipole anisotropy energy, nor as simply due to free spins partially ordering in the applied field because H was not large enough to produce the needed entropy changes. If the phase transition is first order, we may use the magnetic Clausius-Clapyeron equation

$$dT_c/dH = -\Delta M/\Delta S,$$

where ΔS and ΔM are respectively the discontinuities in the entropy and magnetization. Since $\Delta S = S(\text{disordered}) - S(\text{ordered}) > 0$, $\Delta M = M(\text{disordered}) - M(\text{ordered})$ must be opposite in sign to dT_c/dH. Thus, $dT_c/dH > 0$ implies ferromagnetism! If the usual second-order ferromagnetic transition occurs, there are no singularities in the thermodynamic variables, but there is still a peak in the specific heat for small H, whose temperature increases with increasing H. Of course, we cannot rule out antiferromagnetism from these data for very low fields, but the data are too uncertain at such fields for further speculation.

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Structural Manifestations in Amorphous Alloys: Resistance Minima*

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Logarithmic anomalies in the temperature-dependent resistivity of a series of amorphous alloys have been measured and shown to be nonmagnetic in origin. We associate these anomalies with the noncrystalline structure.

Much of the recent interest in amorphous solids has focused on finding properties which are a direct consequence of the noncrystalline structure. Most striking is the low-temperature linear specific heat observed in insulating glasses,[1] which has been explained[2] by the existence of a number of atomic configurations of equivalent energy separated by low energy barriers. In amorphous metals, on the other hand, no *common* property has as yet been exclusively associated with the disordered structure, despite the qualitatively similar atomic arrangements.[3]

We report here the observation of resistance anomalies in four amorphous metal alloys of quite different composition produced by three different techniques in three different laborato-