Ferromagnetism on the solid ^{3}He melting curve*

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We predict a ferromagnetic phase for solid ^{3}He in a narrow "sliver" (of about 1 atmosphere width) on the melting curve, due to ground-state vacancies which exist in this region of the phase diagram.

I. INTRODUCTION

The nature of the magnetic ordering in solid ^{3}He is not fully understood. For many years it appeared that an antiferromagnetic Heisenberg exchange mechanism could describe the ordered phase. The Heisenberg model, however (at least in its present form), is not adequate to explain magnetic ordering on the melting curve where the phase transition has been observed. Recently, the authors have suggested that ground-state vacancies are responsible for the deviations from Heisenberg-model antiferromagnetic exchange behavior.[1,2] In fact, along the melting curve the stable ordered phase might well be ferromagnetic. The objection to our proposal could be raised that NMR data taken away from the melting curve provide evidence against the existence of the required concentration of ground-state vacancies.[3,4] Although this evidence does not negate the existence of vacancies on the melting curve, where magnetic ordering has been observed, the vacancy concentration would be required to increase by several orders of magnitude over a very small pressure range, as the melting pressure is approached, for our mechanism to be tenable.[4]

The purpose of this work is (i) to evaluate the evidence that ground-state vacancies exist, and (ii) to propose a phase diagram in the $P-T$ plane for the ordered phases of solid ^{3}He. Our conclusion is that ground-state vacancies induce ferromagnetism in a very narrow "sliver" along the melting curve. This stable ferromagnetic phase dominates those experiments which use the fluid-solid entropy discontinuity for the cooling process. For pressures above the "sliver" the vacancy concentration is entirely negligible, and the Heisenberg antiferromagnetic exchange should then dominate. It will be argued that a rapid rise in the ground-state vacancy concentration as P approaches the melting pressure P_0 is not at all unreasonable, and that in fact such a picture is consistent with the measured pressure dependence of the vacancy activation enthalpy φ.

II. STATISTICAL THERMODYNAMICS

The motions of vacancies in solid ^{3}He are very strongly coupled to the magnetic ordering of the spins. In fact, it turns out that in the "sliver" of ferromagnetism along the melting curve it is the vacancies which induce the ferromagnetic ordering and the ferromagnetic ordering which allows ground-state vacancies. For pressures appreciably above the melting pressure, vacancies and ferromagnetic order vanish. In general, we must consider partition functions which depend on two order parameters, i.e., the number of vacancies N_V and a magnetization parameter M which represents either a true magnetic moment or a staggered magnetic moment depending on the nature of the ordered phase under consideration.

In a pressure ensemble $Q_N(T, P, M, N_V)$ determines the Gibbs free energy

$$g(T, P, m, x) = -\lim_{N\to\infty} (k_B T/N) \ln Q_N(T, P, Nm, Nx) \tag{1}$$

which obeys

$$dg = -s\,dT + v\,dP + h\,dm + \zeta\,dx. \tag{2}$$

Since the physical vacancy concentration is that which minimizes $g(T, P, m, x)$ it follows that

$$\zeta = 0 \text{ (physical value of the vacancy potential).} \tag{3}$$

For formal purposes $\zeta \neq 0$ values are considered. Finally, it follows from the usual fluctuation-response theorems that the fluctuations of vacancy numbers in a ζ ensemble are given by

$$\langle \Delta N_V^2 \rangle_{\zeta,m,T,P} = N k_B T \left(\frac{\partial x}{\partial \zeta}\right)_{T,P,m}. \tag{4}$$

III. VACANCY FREE ENERGIES

Here we consider the theoretical and experimental evidence that ground-state vacancies can indeed exist. Although we find that the theoretical situation is somewhat ambiguous, the experimental evidence appears to be in favor of our hypothesis.

Theoretical arguments for the existence of ground-state vacancies are fairly subtle. Chester has observed that the wave functions conventionally used to describe quantum crystals (when properly symmetrized) yield configurational probabilities in space closely analogous to those implied by the classical statistical mechanics of crystals at finite temperatures.[5] Hence finite vacancy fractions should exist! Although this observation has been made semiquantitative,[6] and the quantum-classical analogy is used extensively in calculating ground-state energies from first principles, this argument for ground-state vacancies is not altogether convincing. The question is whether or not the usual trial wave functions used in variational calculations properly simulate vacancy correlations whose energy is after all quite small. Another approach is to compare the energy of a crystal with zero vacancies to that of a crystal with one vacancy in order to see if vacancy formation is energetically favorable. Insofar as this has been carried out using "first principles" it is found that positive energies are required to create vacancies.[7] But this too is not altogether convincing evidence in that the computed activation energies overestimate those observed in experiments. In view of the above theoretical first-principles ambiguities it is perhaps best to rely on experimental data.

Experimental observations of vacancies in one form or another are all based on observing thermal activation Boltzmann factors.[8-11] We pause to see how these might occur. Suppose that the vacancies are sufficiently dilute and that the temperatures are sufficiently high so that we can ignore both direct interactions and Fermi-statistical interactions between vacancies. Then the "ideal gas" of vacancies have positions which are statistically independent. In a well-known manner this implies that the fluctuation in vacancy number in a macroscopic volume of ^{3}He crystal obeys

$$\langle \Delta N_V^2 \rangle = \langle N_V \rangle = Nx. \tag{5}$$

Equations (4) and (5) can be made consistent only if the equation of state for the vacancies has the form

$$\zeta = k_B T \ln x + \varphi(T, P, m). \tag{6}$$

This leads [via Eq. (3)] to the equilibrium concentration

$$x = e^{-\varphi/\kappa_B T} \text{ (thermal activation)}, \tag{7}$$

where $\varphi(T, P, m)$ is the free energy of vacancy formation. This simple calculation is by no means obvious (but is nevertheless true) when one considers the mechanism for the strong coupling between the order parameters x and m. For a given spin configuration on sites, a vacancy hopping along a path through the crystal leaves a trail of "changed spins." A second vacancy "crossing" this trail "sees" statistically the spin configuration change due to first vacancy long after the first vacancy has moved away. It is not *a priori* obvious that these long-range correlations ever vanish. That they do vanish for sufficiently large temperatures [leading to Eq. (7)] will be shown in what follows.

Experimental measurements of thermally activated vacancies have been of three types: (i) nuclear-magnetic-resonance (NMR) studies,[9] (ii) heat capacity,[10] and (iii) x-ray diffraction.[11] Of these the x-ray studies are in principle the most unambiguous but in fact (owing to limitations on the range of temperatures) the least valid way of obtaining the low-temperature activation enthalpy

$$\varphi_0(P, m) = \lim_{T \to 0} \varphi(P, m, T), \tag{8}$$

which is of crucial importance in the magnetic ordering process. The great value of the x-ray data lies in the fact that when $\varphi(P, m, T)$ is measured in the most direct manner the temperature dependence is nontrivial. Let us consider this in more detail.

The x-ray data measures the total φ function, i.e., x, by literally counting sites and atoms. The NMR data and heat-capacity data measure some form of activation processes which are presumed to be due to thermally activated vacancies. All the data, however, can be brought into agreement only by assuming some rather detailed forms for the entropy of formation $(\partial s/\partial x)_{T,P,m}$, i.e., that it is roughly constant. Two questions then arise: (i) Is it reasonable to assume that these three experimental methods are all measuring activated vacancies? We assume that the answer is yes. (ii) Which experimental data should be used to estimate the enthalpy to create one vacancy at $T = 0$ in an otherwise perfect crystal, i.e., Eq. (8)? Of the experimental data available we choose the NMR studies in that they appear least sensitive to the detailed temperature dependence of φ and they can be carried out over the largest temperature range.

IV. FERMION MODEL FOR VACANCIES

Our first assumption is that the vacancies behave as an ideal Fermi gas of "holes" with a density of states dependent on pressure and the state of magnetic order in the host crystal. This implies

$$x = \int f(\epsilon) \rho(\epsilon, m, P)\, d\epsilon, \tag{9}$$

where

$$f(\epsilon) = (e^{(\epsilon-\zeta)/\kappa_B T} + 1)^{-1}. \tag{10}$$

The density of states describes the tunneling band of a single vacancy in the host crystal and is normalized to $\int \rho \, d\epsilon = 1$.

Since for a range of temperatures large compared to the Fermi degeneracy temperature Boltzmann statistics is an adequate approximation, Eqs. (9) and (10) imply

$$x \simeq e^{(\zeta-\varphi)\kappa_B T}, \tag{11}$$

where

$$\varphi(P, m, T) = -k_B T \ln \int \rho(\epsilon, m, P) e^{-\epsilon/\kappa_B T} \, d\epsilon \tag{12}$$

is the "free energy" of vacancy activation. [Note: the condition $\zeta = 0$ and Eq. (11) imply Eq. (7).]

The Maxwell relations which follow from Eq. (2), i.e.,

$$\left(\frac{\partial \zeta}{\partial P}\right)_{T,m,x} = \left(\frac{\partial v}{\partial x}\right)_{T,m,P} \text{ and } \left(\frac{\partial \zeta}{\partial T}\right)_{P,m,x} = -\left(\frac{\partial s}{\partial x}\right)_{T,m,P}, \tag{13}$$

can be combined with Eq. (11) to establish the physical significance of

$$\Delta v = \left(\frac{\partial \varphi}{\partial P}\right)_{T,m} \tag{14a}$$

and

$$\Delta s = -\left(\frac{\partial \varphi}{\partial T}\right)_{P,m} \tag{14b}$$

as, respectively, the volume and entropy change that accompanies thermally activated vacancies.

The experimental fact is that the temperature dependence of φ (i.e., Δs) cannot be too weak if direct x-ray observations of thermally activated vacancies are to be made consistent with NMR studies.[11] Nevertheless, for our purposes we shall examine Eq. (12) in the $T \to 0$ limit and presume that $\varphi \to \varphi_0(P, m)$ can be analyzed on the basis of NMR data plus the theoretical band narrowing known to accompany magnetic disorder. For pressures substantially above the melting pressure P_0, where $\varphi_0(P, m = 0)$ is significant, this is quite accurate. As $P \to P_0$, however, $\varphi(P, m = 0, T)$ is fairly small and $x = e^{-\varphi/\kappa_B T}$ becomes difficult to obtain from experimental data without further theoretical analysis.

Our theoretical ansatz near melting (i.e., as $P \to P_0$) is

$$\varphi_0(P, m) = \varphi_0(P_0, 0) + (\Delta v/v)(P - P_0) - 8[\alpha(m) - \alpha(0)]t(P), \tag{15}$$

where (i) $\varphi_0(P_0, 0)$ is the residual activation energy for creating a vacancy in the magnetically disordered crystal on the melting curve. (ii) $\Delta v/v$ is the fractional change in volume which arises when an atom is replaced by a vacancy at a given pressure [i.e., Eq. (14a)]. Experimentally $\Delta v/v \simeq 0.4$ near melting.[8,9] (iii) $t(P)$ is the vacancy hopping matrix element to one of the eight nearest-neighboring sites in the bcc crystal, and (iv) $\alpha(m)$ is the Brinkman-Rice band-edge lowering factor associated with the ferromagnetically ordered crystal [$\alpha(m = 1) = 1$ and $\alpha(0) \simeq 0.66$].

The NMR data are consistent with the extrapolation $\varphi_0(P_0, 0) \simeq 0$! We will assume for simplicity in all that follows that this is indeed the case, i.e.,

$$\varphi_0(P, m) \simeq (\Delta v/v)(P - P_0) - 8[\alpha(m) - \alpha(0)]t(P); \tag{16}$$

however, our results can be qualitatively valid even if this assumption is relaxed. Here we also have assumed that the "band tails," which exist in the disordered state,[2,12,13] hold a negligible fraction of the vacancies.

V. MAGNETIC ORDERING

At temperatures near the critical point for magnetic ordering, the Fermi gas of vacancies becomes degenerate. In a picture where the energy of the band edge is changed upon ordering but the band shape is unchanged, Eqs. (9), (10), and (12) imply

$$\zeta = \varphi_0(P, m) + t(P)(12\pi^2 x)^{2/3} + \cdots. \tag{17}$$

In order to obtain the total magnetic enthalpy at $T = 0$ we integrate Eq. (17) from zero to x and add a mean-field approximation to the Heisenberg exchange process,

$$g_{\text{mag}}(P, m) = \varphi_0(P, m)x + \tfrac{3}{5}x(12\pi^2 x)^{2/3}t(P) + 4Jm^2 \tag{18a}$$

$$= \tfrac{2}{5}\varphi_0(P, m)x + 4Jm^2, \tag{18b}$$

where (18b) follows from (18a) by setting $\zeta = 0$ in Eq. (17). Equations (16), (17), and (18b) imply that the vacancy contribution to the magnetic ordering free energy increases in magnitude for increasing magnetization. If the vacancies prevail, the system will be ferromagnetically ordered at $T = 0$ on the melting curve. A first-order transition from ferromagnetism to paramagnetism (like that found in Ref. 2) will occur as the temperature is increased if either $\alpha(m)$ is a very rapidly varying function of[9] m near $m = 1$ or if g_{mag} is independent of m for small m (which would occur if φ_{melt} were nonzero, i.e., if there were no vacancies present in the paramagnetic state). If the phase transition which occurs is from the totally ferromagnetic to

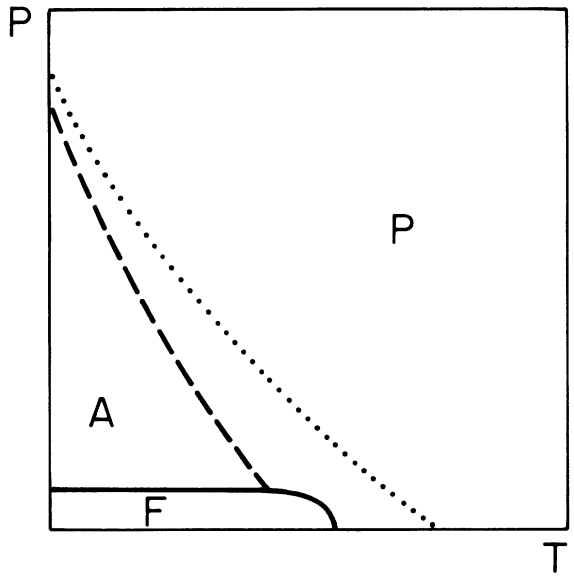

FIG. 1. Sketch of a proposed phase diagram (solid phase) in the P-T plane based on our model is given. The dotted and dashed phase boundaries give two possible positions of the antiferromagnetic to paramagnetic state phase boundaries.

the paramagnetic state (as in Ref. 2), the Curie temperature will occur at the observed 1 mK,[14] if t is chosen to be about 0.2 °K, which is consistent with NMR data on thermally activated vacancies.[3] The value of x on the melting curve (in the ferromagnetic state) is about 0.05, which is about equal to the concentration of thermally activated vacancies which generally occurs on the melting curve at higher temperatures.

Increased pressure will destroy ferromagnetism in favor of antiferromagnetism when the free energy of the ferromagnetic state is reduced below $-4J$, the free energy of the antiferromagnetic state. This is estimated from Eqs. (9), (10), (16), and (17) to occur at a critical pressure P_c which is about 1 atm above the melting pressure. Thus, the ferromagnetic state will only exist for a very small range of pressures above the melting curve. We can easily show that the vacancy concentration will also be reduced to zero at a pressure of this order of magnitude,[15] and therefore, it is not surprising that experiments appreciably above the melting curve imply entirely negligible concentrations of ground-state vacancies.

Since the antiferromagnetic exchange is not expected to vary too much over a pressure range of the order of 1 atm in the vicinity of the melting curve, we expect solid ^{3}He to behave as a normal Heisenberg-model antiferromagnet at pressures above P_c, with the ferromagnetically ordered state occurring only for a small range of pressures near the melting curve. Depending on the value of J there are two possible positions of the antiferromagnetic to paramagnetic state phase boundary. These are illustrated in the proposed phase diagram in Fig. 1. The dotted line position of the ferromagnetic-paramagnetic state phase boundary would imply that on the melting curve a transition to an antiferromagnetic state would occur before the first-order transition to the ferromagnetic state as we go down in temperature. The small peak in the specific heat versus temperature curve observed by Richardson *et al.*[14] could actually be this phase transition.

VI. CONCLUSION

In conclusion, we propose that evidence against the existence of ground-state vacancies in solid ^{3}He off the melting curve does not preclude the possibility of such vacancies producing ferromagnetic ordering for a very small range of pressures in the vicinity of the melting pressure. We have shown that such an effect is not only consistent with existing NMR data, but these data can be interpreted as evidence of the existence of such a mechanism. Above the critical pressure which will destroy the ferromagnetic ordering, we expect Heisenberg-model antiferromagnetic ordering to occur.

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