

THEORY OF SOLID He³†

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We have calculated the properties of solid He³ at pressures $p \approx 30$ atmos and temperatures $T < 1^\circ\text{K}$ on the basis of: (A) a gas-phase 12-6 Lennard-Jones potential, modified at small interatomic distances; (B) a Heitler-London type variational wave function, for all the atoms in the solid, constructed from a suitably antisymmetrized product of single-particle orbitals localized on various lattice points; (C) a Dirac vector model to describe the symmetry energy, with an exchange integral deduced from (A) and (B); (D) a spin wave approximation at "low" temperatures, and a Kramers-Opechowski¹ approximation at "high" temperatures, for calculation of the "spin" partition function, and (E) a Debye-phonon model for description of the vibrationally excited states of the solid.

In connection with (A)-(E), we note the following:

(A) The interatomic potential used was

$$V(r_{ij}) = \epsilon [x_{ij}^{-12} - 2x_{ij}^{-6}] \exp(-\lambda x_{ij}^{-10}), \quad (1)$$

where $r_{ij} = r_0 x_{ij}$ is the distance between atoms i and j , $\epsilon = 10.2^\circ\text{K}^2$, $r_0 = 2.88$ A, and $\lambda = 1/15$. The interatomic potential of Eq. (1), in the limit $\lambda \rightarrow 0$, is the 12-6 Lennard-Jones potential with constants ϵ and r_0 appropriate to the He³ or He⁴ gas data. The exponential factor, which modifies the 12-6 potential only at small interatomic distances and consequently does not upset the fit to the gas data, represents, for a suitably chosen λ , a convenient way of avoiding divergences which arise when a singular potential is used in conjunction with variational wave functions lacking the proper atom-atom correlation at these small distances. The choice $\lambda = 1/15$ was found to give the best description of available data for (1) the cohesive energy and lattice constant of solid He⁴ at pressures ≈ 30 atmos and (2) the root mean square deviation (d_{rms}) of a He⁴ atom from its lattice site at these pressures.

(B) We used single-particle localized orbitals of the form

$$C \exp[-\frac{1}{2} \alpha^2 (\vec{r}_i - \vec{R}_n)^2], \quad (2)$$

where C is a normalization constant, \vec{R}_n gives

the position of a lattice point, and α is a variational parameter proportional to $(d_{\text{rms}})^{-1}$.

From (A)-(E) we may write the energy of solid He³ as

$$E(R, \alpha, H) = E_0(R, \alpha) - \frac{1}{2} J(R, \alpha) \sum_{n=1}^N \sum_m (1 + \vec{\sigma}_n \cdot \vec{\sigma}_m) - \mu H \sum_{n=1}^N \sigma_n^{(z)} + E_{\text{phonons}}, \quad (3)$$

where the second term is the symmetry energy, $J(R, \alpha)$ is the exchange integral, the $\vec{\sigma}$'s are spin operators, R is the distance between nearest neighbor lattice points, the sum over m for a given n runs over the nearest neighbors of n , μ is the magnetic moment of a He³ nucleus, and H is an external magnetic field. Equation (3) expresses the symmetry energy by means of the Dirac vector model; the validity of this vector model is only approximate in the present case since we use nonorthogonal orbitals. The spin-spin magnetic interaction energy ($\sim N\mu^2/R^3$) is negligible compared to the symmetry energy and is not included in Eq. (3).

In our variational procedure we first find the optimum value of α which minimizes the right-hand side of Eq. (3) for states with $E_{\text{phonons}} = 0$. In this minimization we also neglect the symmetry energy since it represents only a small part of the total cohesive energy (the Curie temperature of solid He³ is $\approx 0.1^\circ\text{K}$,³ while the cohesive energy per atom is $\approx 1-2^\circ\text{K}$). Furthermore, in evaluating $E_0(R, \alpha)$ numerically we assume an fcc lattice and sum over the first 42 neighbors. Following this procedure, we obtain the results (1)-(7):

(1) For an empirical nearest neighbor distance $R_0 = 3.8$ A, appropriate to solid He³ at $p \approx 30$ atmos, the optimum value of α is found to be $\alpha_0 = 2.6/r_0$; this yields $d_{\text{rms}} = 0.36R_0$, slightly larger than the corresponding (experimentally known) value for solid He⁴.

(2) The cohesive energy per He³ atom is found to be $\approx 2.5^\circ\text{K}$, which may be somewhat too large.

(3) The exchange integral (whose dominant contribution comes from the kinetic energy operator) is found to be $J(R_0, \alpha_0) \equiv J_0 \approx -\epsilon/200 = -0.05^\circ\text{K}$, so that the ground state of solid He³ at $p \approx 30$ atmos corresponds to an antiferromagnetic configuration.

The spin entropy of the solid was calculated, as a function of T and H , (a) in the limit of "high" temperatures ($T > 6|J_0|$) using an approximation developed by Kramers and Opechowski,¹ and (b) in the limit of "low" temperatures ($T < 6|J_0|$)

using a spin wave approximation based on a two-sublattice model⁴ of antiferromagnetism (not exactly valid for a close-packed lattice). From this calculated expression for the "high"-temperature spin entropy, we can express the magnetic susceptibility of solid He³, χ , as a power series in J_0/T which can be approximated by a Curie-Weiss law:

$$\chi = N\mu^2/(T + T_C), \quad (4)$$

where $T_C = 6|J_0| = 0.3^\circ\text{K}$. Empirically,³ χ indeed appears to be given by an expression of the form of Eq. (4), but with T_C closer to 0.1°K than to 0.3°K . Our estimate of T_C agrees with the result of Primakoff⁵ but disagrees with the estimate $T_C \approx 10^{-7}^\circ\text{K}$ suggested by Pomeranchuk⁶ in a treatment where the symmetry energy is assumed negligible compared to the spin-spin magnetic interaction energy.

From our theoretical values for the total entropy of the solid, $S = S_{\text{spin}} + S_{\text{phonon}}$, we further calculate that:

(4) $C_V \equiv T(\partial S/\partial T)_V$ exhibits an anomaly at $T \approx 0.2^\circ\text{K}$;

(5a) $(\partial S/\partial p)_T > 0$ for $T < 0.5^\circ\text{K}$,
and

(5b) $(\partial S/\partial p)_T < 0$ for $T > 0.5^\circ\text{K}$,

so that $(\partial V/\partial T)_p$ of solid He³ at $p \approx 30$ atmos should become negative below 0.5°K .

From (5a) it follows that

(6) below 0.5°K it should be possible to cool solid He³ by an adiabatic compression.

(7) Finally, we construct the "low"-temperature part of the melting curve, by means of the Clapeyron equation

$$dp/dT = (S_{\text{liq}} - S_{\text{sol}})/(V_{\text{liq}} - V_{\text{sol}})$$

and with use of (a) one experimental point: $p = 30$ atmos, $T = 0.05^\circ\text{K}$,⁷ (b) our theoretical values (suitably interpolated) for the entropy of the solid, (c) the experimental values of S_{liq} , obtained from specific heat measurements,⁸ and (d) a temperature-independent $V_{\text{liq}} - V_{\text{sol}} = 1.0$ cm³/mole.⁹

The resulting melting curve is presented in Fig. 1 (together with typical experimental points obtained by the blocked capillary method⁷) for three different values of the exchange integral J_0 and $T_{\text{Debye}} = 20^\circ\text{K}$. The results contained in Fig. 1 indicate that the melting curve should have a minimum near 0.4°K with a difference [$p(0.1^\circ\text{K}) - p(0.4^\circ\text{K})$] sufficiently large (≈ 4 atmos)

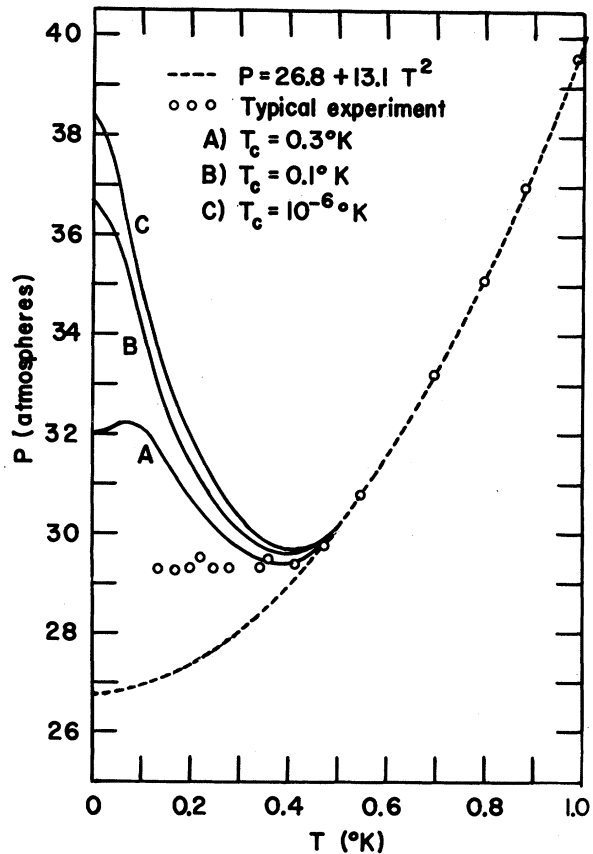


FIG. 1. Melting curve of He³: solid lines A, B, and C calculated as described in the text; the circles correspond to experimental points.⁷

for experimental observation. The failure to detect this minimum up to now may therefore be ascribed to the suggested inadequacy¹⁰ of the blocked capillary method.

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²We choose our units so that the Boltzmann constant is a pure number equal to unity; hence energy will be expressed in degrees Kelvin.

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CYCLOTRON RESONANCE EFFECTS IN ZINC

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We have observed cyclotron resonance effects in single-crystal samples of zinc at about 1.3°K and at both 24 000 Mc/sec and 72 000 Mc/sec. We have done the experiment both with the magnetic field along a twofold and along a sixfold axis.

The experiments were done by using the same technique used previously in experiments on bismuth^{1,2} and graphite.³ The crystallographically oriented plane surface of a disk sample was made to form part of the wall of a microwave cavity in an area where circularly polarized radiation was incident upon it. In the experiments on zinc, the sensitivity of the experiment was increased by making the sample form a larger part of the cavity end-wall than in the earlier work. As a result, the two circular polarizations in the radiation incident on the sample have a ratio as low as 7.5 in some cases, but this does not seem to have led to vital difficulties.

Single-crystal boules of zinc were grown in a stream of hydrogen at atmospheric pressure by pulling a seed from a melt formed from New Jersey Zinc Company's "super-purity" zinc. Disks with at least one plane, carefully oriented surface were cut from these, some with the plane surface normal to a twofold axis, $\langle 10\cdot0 \rangle$, so that a sixfold axis was in the surface, and some with the plane surface normal to a sixfold axis in which case twofold axes were in the plane. The data in the figures are from two samples, both cut from a crystal in which the dc resistance ratio $R(300^\circ\text{K})/R(4.2^\circ\text{K})$ was about 9000.

For each sample type, experiments were done both with the field in the plane of the sample and

normal to it. When the field was in the plane of the sample, the behavior observed was like that predicted by Azbel' and Kaner⁴ and observed by others in tin, lead and copper.⁵ Data taken under these conditions at 24 000 Mc/sec showed the appropriate frequency dependence and generally confirmed those taken at 72 000 Mc/sec but were not as good, and only the latter are presented.

Figure 1 shows data taken with the field in the sample plane and along a sixfold axis. The data

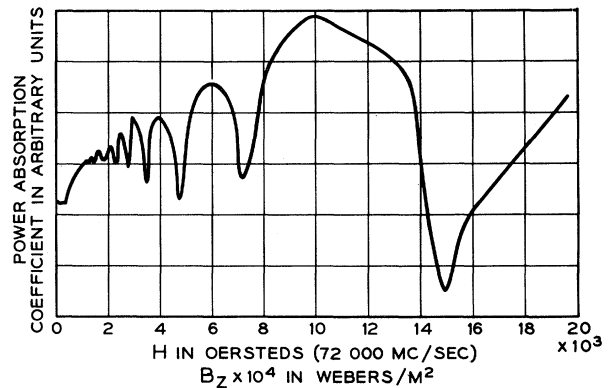


FIG. 1. Cyclotron resonance data at 72 000 Mc/sec and 1.3°K for zinc with magnetic field in sample plane and along a sixfold axis.

below one kilogauss do not constitute a well-resolved signal, but they do indicate the presence of a carrier of cyclotron mass less than $0.015m_0$. This part of the data agrees qualitatively with de Haas-van Alphen data,⁶ which give a cyclotron mass of $0.005m_0$ for carrier motions about this axis. The high-field region in Fig. 1 shows a well-resolved signal of the type predicted by Azbel' and Kaner which is from another carrier. These data fit reasonably well the behavior of $R(H)/R(0)$ derived from the formula given by Azbel' and Kaner⁴ for $Z(H)/Z(0)$ using a mass of $0.55m_0 \pm 5\%$, an $\omega\tau$ of about 20, and a phase of $e^{-i\pi/3}$ in $Z(0)$. This signal also has the characteristic predicted by Azbel' and Kaner that it disappears unless the field is within about one degree of the sample surface. The fit to the theory is not perfect, but the misfit probably arises primarily from imperfect tracking of the cavity and signal oscillator frequencies, so that the signal partly reflects the surface reactance as well as the surface resistance.

Figure 2 shows data taken with the field in the sample plane and along a twofold axis. Here we