

Entropy of vacancy formation in solid ^3He

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The free energy of formation of vacancies in solid ^3He is discussed in the thermal-activation regime, i.e., for temperatures sufficiently high for the vacancies to obey the statistics of ideal Boltzmann defects. It is argued on both experimental and theoretical grounds that the entropy of formation is negative and appreciably large in magnitude. As a consequence the energy of formation is much smaller than the free energy of formation and is in fact consistent with the notion of "ground state" vacancies.

I. INTRODUCTION

Among the most interesting yet not well-understood phenomena in solid helium are the mechanisms by which a helium atom moves off a quasi-equilibrium site. Roughly, this can happen if the atom exchanges site positions with neighboring atoms or if the atom tunnels onto a vacant site. Previously,¹ we have examined the possibility that both processes are operative and important for temperatures near the spin-ordering temperature. Here we wish to consider for solid ^3He the high-temperature regime where two experimental methods yield reliable estimates for vacancy concentrations, i.e., x-ray and specific-heat measurements. The only assumption made in analyzing the data is that the vacancies obey the statistics of ideal Boltzmann point defects.

We consider, with more care than is usually taken, the thermodynamic implications of the above assumption. Without detailed models for microscopic motions, it is shown that the free energy of vacancy formation $\varphi^*(v, T)$ can be extracted from the heat capacity by a process of integration. This idea was formulated by Hetherington² for the particular model whereby the free energy of formation was derived from a temperature-independent density of states for a "vacancy band."

We find that microscopic models which include (i) vacancy-phonon interactions, (ii) tunneling bands, and (iii) spin correlations all appear theoretically to imply an appreciable negative entropy of formation s^* for the vacancy. This implies a rather dramatic fall in the free energy of formation $\varphi^*(v, T)$ as the temperature is lowered. Equivalently, the energy of formation e^* is significantly lower (perhaps even negative!) than the free energy of formation φ^* . More important than the theoretical models, which are computed only semiquantitatively, the decrease in φ^* as the temperature is lowered appears to be an experi-

mental fact. This is evidently consistent with the notion of "ground-state" vacancies.

II. STATISTICAL THERMODYNAMICS

Consider a crystal containing n vacancies. If the vacancies obey the statistics of ideal Boltzmann defects, then the partition function of the crystal is of the form

$$Q_n = (q^n/n!)Q_0. \quad (1)$$

The physical significance of q as a mean number of vacancies is evident since

$$\bar{n} = \left(\sum_n n Q_n / \sum_n Q_n \right) Q_n = q. \quad (2)$$

Furthermore, the free energy of the crystal

$$F = -k_B T \ln \sum_n Q_n = -k_B T \ln Q_0 - k_B T \bar{n} \quad (3)$$

is the sum of the free energy of the defect-free crystal

$$F_0 = -k_B T \ln Q_0 \quad (4)$$

plus $-k_B T$ for each vacancy in the crystal. Thus the vacancy contribution to the crystal free energy per atom is

$$f_{vac} = -k_B T x, \quad (5)$$

where the concentration x can be written in terms of the free energy of formation φ^* as

$$x = \exp(-\varphi^*/k_B T). \quad (6)$$

Relations between quantities of formation include

$$d\varphi^* = -s^*dT - P^*dv, \quad (7)$$

$$\varphi^* = e^* - Ts^*, \quad (8)$$

$$c_v^* = T \left(\frac{\partial s^*}{\partial T} \right)_v = \left(\frac{\partial e^*}{\partial T} \right)_v. \quad (9)$$

Similarly, for vacancy contribution to the crystal free energy

$$df_{\text{vac}} = -s_{\text{vac}} dT - P_{\text{vac}} dv, \quad (10)$$

$$f_{\text{vac}} = e_{\text{vac}} - Ts_{\text{vac}}, \quad (11)$$

$$c_{\text{vac}} = T \left(\frac{\partial s_{\text{vac}}}{\partial T} \right)_v - \left(\frac{\partial e_{\text{vac}}}{\partial T} \right)_v. \quad (12)$$

Thermodynamic differentiations using Eqs. (5)–(12) yield the physically evident relations

$$P_{\text{vac}} = xP^*, \quad (13)$$

$$e_{\text{vac}} = xe^*, \quad (14)$$

$$s_{\text{vac}} = xs^* + k_B x \ln(e/x), \quad (15)$$

as well as the less evident relations

$$e^* = k_B T^2 \frac{\partial}{\partial T} \ln x, \quad v = \text{const} \quad (16)$$

and

$$c_{\text{vac}} = [c_v^* + k_B(e^*/k_B T)^2] e^{-\varphi^*/k_B T}. \quad (17)$$

Equations (6)–(9) and (13)–(17) determine all of the interesting thermodynamic properties when $\varphi^*(v, T)$ is known.

X-ray determinations of $\varphi^*(v, T)$ are via the relation³

$$\frac{\partial x(v, T)}{\partial T} = -3 \frac{\partial \ln a(v, T)}{\partial T}, \quad (18)$$

where $a(v, T)$ is the measured lattice spacing. The following considerations are important: (i) If in a given temperature regime the right-hand side of Eq. (18) vanishes, then [see Eq. (16)] either x or e^* vanishes. (ii) The energy of formation e^* is not the same as $\varphi^* = e^* - Ts^*$, and thermodynamic reasoning alone does not determine the sign of s^* . (iii) If one ignores the possibility of appreciable vacancies in the region where $a(v, T)$ is “flat” with respect to temperature changes, then Eq. (18) integrates to

$$x = -3\Delta a/a, \quad (19)$$

where $\Delta a \ll a$.

An idea due to Hetherington⁴ is that x can be obtained via the vacancy contribution to the heat capacity. The derivation which follows does not assume that q in Eq. (1) is derived from a temperature-independent density of states $g(E)$, and is thereby more general than that given by Hetherington. The procedure is as follows: (i) Integrate Eq. (12) to obtain s_{vac} from c_{vac} . (ii) Integrate Eq. (10) to obtain f_{vac} from s_{vac} . (iii) Equation (5) now implies the concentration

$$x(v, T) = \frac{1}{T} \int_0^T dT_1 \int_0^{T_1} dT_2 \frac{c_{\text{vac}}(v, T_2)}{k_B T_2}, \quad (20)$$

and $\varphi^*(v, T)$ follows from Eq. (6).

Both the x-ray data⁵ [Eq. (19)] and the heat-

TABLE I. Parameter $y = \varphi^*/k_B T$ on the solid-³He melting curve for different volumes per atom v are determined from the x-ray data of Heald and Simmons as well as from the heat-capacity data of Greywall.

y (x ray)	y (specific heat)	v (cm ³ /mole)
5.3	...	24.86
5.5	...	24.61
4.8	...	24.58
...	5.7	24.454
5.5	...	24.20
5.2	...	24.14
...	4.6	23.786
...	5.9	23.081
...	6.0	22.425
5.3	...	21.49
...	6.2	21.459
5.1	...	20.84
6.0	...	20.30

capacity data⁶ [Eq. (20)] yield x by a process of integration which neglects the possibility of residual vacancies at some low temperature. We attribute all of the heat capacity beyond the T^3 Debye term to vacancies (unlike Hetherington's procedure) and find “reasonable” agreement between x-ray and heat-capacity measurements. Values at melting are shown in Table I. The rule is that $\varphi^*/k_B T$ on the ³He melting curve is about 5 or 6.

III. MICROSCOPIC MODELS

Here we consider the microscopic motions which possibly contribute to the vacancy formation entropy

$$s^* = - \left(\frac{\partial \varphi^*}{\partial T} \right)_v. \quad (21)$$

The rigorous method of computing $\varphi^*(v, T)$ from a given model is as follows: (i) Compute the partition functions $Q_0(N, V, T)$ for an ideal crystal with no vacancies and $Q_1(N, V, T)$ for a crystal with one vacancy. (ii) Equations (1) and (2) imply that

$$q = Q_1/Q_0 \quad (22)$$

represents the mean number \bar{n} of vacancies that would be in the crystal if the crystal were in vacancy concentration thermal equilibrium. Hence

$$\varphi^* = -k_B T \ln(q/N). \quad (23)$$

That $\bar{n} = q$ is extensive assures that Eqs. (22) and (23) imply a proper thermodynamic limit for φ^* .

A contributing motion to the entropy of formation in Eq. (21) is the interaction between the vacancy and those modes of vibration (i.e., sound waves) which yield (per atom) in the pure crystal

$$S_{\text{phonon}} = k_B(4\pi^4/5)(T/\Theta)^3. \quad (24)$$

The renormalization of Eq. (24) found by the addition of one vacancy is twofold: (i) The addition of one vacancy compresses the lattice as in Eq. (18). Hence, the manner in which the Debye temperature changes with volume must be known,

$$\Gamma = -v \frac{d \ln \Theta}{dv}. \quad (25)$$

(ii) The sound waves scatter off the vacancy, yielding a phase shift which renormalizes (locally) the density of vibrational modes. If the vacancy were localized, then it could be treated as a "missing mass" scattering center in the sound wave equation. The phase shift can then be found. In total we estimate

$$S_{\text{phonon}}^* = -k_B(4\pi^4/5)(3\Gamma + \frac{3}{2})(T/\Theta)^3. \quad (26)$$

Note that this contribution is negative, and is calculated on the basis of a localized vacancy.

A much more dramatic contribution to s^* is present when a ^3He atom can tunnel (with matrix element t) onto a vacant site. Andreev⁷ has shown that s^* diverges negatively due to the entropy cost ($k_B \ln 2$ per spin) as $T \rightarrow 0$ in forming a "magnetic polaron,"⁸ i.e., correlating ferromagnetically the neighboring spins. One finds for the bcc lattice

$$s^* \approx -6.259 k_B (t/k_B T)^{3/5} \quad (T \ll t/k_B). \quad (27)$$

Hetherington⁴ has correctly noted that for Eq. (27) to be valid one requires that the radius of the "polaron" in units of the lattice spacing

$$R/a \approx 1.184 (t/k_B T)^{1/5} \quad (T \ll t/k_B) \quad (28)$$

must be reasonably large (say $R \gtrsim 2a$), and this condition on T most likely invalidates the application of Eq. (27) to known experimental data. Nevertheless, the physical notion that the vacancy ferromagnetically orders neighboring spins is correct and some (difficult to compute) negative spin contribution is no doubt present in s^* at temperatures of interest here.

Apart from "magnetic polaron effects" it would appear that any mobility whatsoever contributes negatively to s^* . The argument is as follows: (i) Let F_1 and F_0 represent the free energy, respectively, of a one vacancy and a vacancy-free crystal. Equations (22) and (23) (which define rigorously φ^*) imply for fixed (N, V, T)

$$\varphi^* = F_1 - F_0 + k_B T \ln N, \quad (29)$$

and hence

$$s^* = S_1 - S_0 - k_B \ln N. \quad (30)$$

In a localized model where the vacancy is fixed on a site, the last term on the right-hand side of

Eq. (30) subtracts from S_1 that degeneracy due to the number of site positions. (ii) Any mobility which splits the $k_B \ln N$ degeneracy, would (by the fundamental relation between degeneracy and entropy) lower s^* . (iii) In the temperature regime of interest, the spins have $k_B \ln 2$ per atom and this could not be made any higher. (This part of the argument is no longer valid at the much lower spin ordering temperature.) (iv) The estimate in Eq. (26) also indicates a negative contribution to s^* from phonon-vacancy interactions. The physical picture here is that when a vacancy is introduced, the "compression" over all raises the phonon-mode frequencies, with a resulting net loss of phonon entropy. [The lowest, virtually zero-frequency modes could be lowered out of the phonon band. However, this entails $3N - 3$ vibrational modes going into $3N - 3$ vibrational modes (higher in frequency), plus 3 degrees of translational freedom into a vacancy band. Note that the vacancy band transports mass opposite in direction to the vacancy motion. A mode which transports mass appreciable distances is no longer vibrational. But all of this still appears to lower the entropy for the reasons stated above.]

In brief, we conclude that if s^* is at all appreciable it should be negative. However, the above arguments do not constitute a rigorous proof.

IV. EXPERIMENTAL ENTROPIES OF FORMATION

Using Eqs. (6) and (20) we plot in Fig. 1, from Greywall's⁶ specific-heat data, φ^* as a function of T . Note the following: (i) φ^* cannot be regarded as a function of v only. (ii) The entropy of formation is appreciable and negative. (iii) If the entropy were written, in "correlated spin units", as

$$s^* = -k_B Z^* \ln 2, \quad (31)$$

then Z^* calculated from the experimental values of s^* is approximately equal to the number of nearest atoms neighboring the vacancy. [The physical motivation for the definition in Eq. (31) is crude.] (iv) The data is consistent with the notion of ground-state vacancies, i.e., the energy of formation e^* is much smaller than the free energy of formation φ^* (e^*/k_B is $\sim 1^\circ\text{K}$). (v) If s^* is attributed to a vacancy band as in Hetherington's work, then the tunneling bandwidth ($t/k_B \sim 1^\circ\text{K}$) is much larger than previously expected. This is not unreasonable. Nuclear magnetic resonance data is based on the rule

$$\frac{1}{T_2} = \left(\frac{\hbar \gamma^2}{b^3}\right)^2 \frac{t}{\hbar} e^{-\varphi^*/k_B T}, \quad (32)$$

where T_2 is the relaxation time, b is a character-

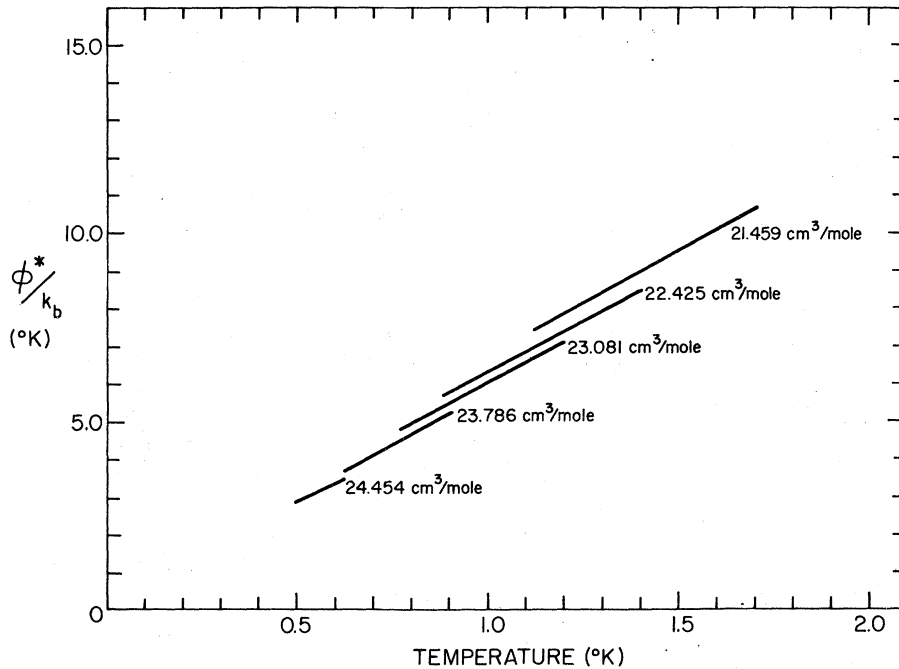


FIG. 1. Free energy of formation ϕ^* as a function of T from the specific-heat data of Greywall, for several molar volumes.

istic lattice length for the dipolar field, and t is the tunneling matrix element. (b is only known approximately.) By writing Eq. (32) in an equivalent form

$$\frac{1}{T_2} = \left(\frac{\hbar\gamma^2}{b^3}\right)^2 \left(\frac{t}{\hbar} e^{s^*/k_B T}\right) e^{-e^*/k_B T}, \quad (33)$$

it is clear that "some" of the negative s^* can easily be misinterpreted in terms of a t value that is too small or an e^* value that is too high. (vi) The x-ray data is in reasonable agreement with the heat-capacity data (see Table I), but it needs to be interpreted in terms of a $\phi^*(v, T)$ without *a priori* assumptions about temperature variations. Similarly, the NMR data also needs such interpretation. (vii) There is presently no data sensitive enough to probe $c_v^* = T(\partial s^*/\partial T)_v$.

The small value of e^* at the temperatures at which ϕ^* can be reliably computed from c_{vac} , the large bandwidths estimated by Hetherington, and the probable existence of magnetic polarons provide a reasonable argument in favor of $e^* \lesssim 0$ in the $T \rightarrow 0$ limit.

V. CONCLUSIONS

It is evidently not realistic to ignore the variation in $\phi^*(v, T)$ with temperature, and all experimental probes of vacancy concentration in the

thermally activated regime should be interpreted with this in mind. Furthermore, the idea that "ground-state vacancies" exist is both theoretically and experimentally reasonable.

If x-ray methods were used to test the hypothesis of ground-state vacancies, then the question is not whether $\phi^*(v, T)$ is "small enough" to imply zero energy of formation at $T = 0$ since this "ground state" regime is not probed. The information is in the energy of formation. With $a_0(v)$ the lattice spacing for the defect-free crystal (bcc)

$$v = (4/3\sqrt{3})a_0^3 \quad (34)$$

and

$$\Delta a(v, T) = a(v, T) - a_0(v), \quad (35)$$

then

$$\chi(v, T) = -3\Delta a(v, T)/a_0(v) \quad (36)$$

can be regarded as exact in all models and regimes of v and T . (Heat-capacity measurements require a model for the heat capacity of the defect-free crystal which we assume is the Debye model. Nuclear magnetic resonance methods require various tunneling and exchange models.) Now in the thermally activated regime Eqs. (16) and (36) imply

$$e^* = kT^2 \frac{\partial}{\partial T} \ln |\Delta a(v, T)| \quad (37)$$

for the energy of formation so that the "flat" regions [i.e., $a(v, T)$ not dependent on T] strictly mean $e^* \approx 0$! In practice $a_0(v) \neq a(v)$, some small T is assumed. In this regard, it is worthwhile to point out that $e^* < 0$ is perfectly possible and experimental indications of this need not be ignored as "error." A minimum in $a(v, T)$ even if "shallow" implies $e^* < 0$ for some regime of T and

can be regarded as very strong evidence for ground-state vacancies.

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