VACANCY FORMATION ENERGY IN THE QUANTAL CRYSTALS OF THE TWO HELIUM ISOTOPES

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ABSTRACT

We derive a simple expression for the vacancy formation energy in a quantal crystal near melting in terms of its Lindemann parameter and of the density response of its liquid near freezing. Numerical illustrations are given for vacancies in $^4$He and $^3$He crystals.

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Early work of Andreev and Lifshitz (1969) proposed that vacancies should behave as highly delocalized quasiparticles in quantal crystals where the amplitude of the zero-point fluctuations is large. Delocalization causes the energy of a vacancy to spread into an energy band and may lower the formation energy to the point where a finite concentration of vacancies may be present even in the ground state. Their arguments drew attention to the role of the quantal kinetic energy in allowing a relatively high concentration of vacancies in quantal crystals near melting at very low temperatures.

A great deal of experimental attention has been given in the above context to the two isotopes of He. Values of the vacancy formation energy \(E_v\) in \(^4\text{He}\) crystals near melting have been extracted from X-ray measurements of the lattice parameter (Fraass et al. 1989), sound attenuation experiments (Lengua and Goodkind 1990), self-diffusion and isotope diffusion measurements (Dyumin et al. 1994, Kisvarsanyi and Sullivan 1994) and studies of the phase diagram (Steel et al. 1994). \(E_v\) is of order \(6k_BT_m\) at melting temperature \(T_m\) near 2 K and decreases with \(T_m\) towards the minimum in the density-temperature melting curve at \(T_m \approx 0.8\) K. X-ray measurements on \(^3\text{He}\) crystals (Heald et al. 1984) have yielded a vacancy concentration of about 0.5 % in the bcc structure and 0.1 % in the hcp structure, essentially independently of \(T_m\) in the range 3.1 - 0.6 K. The relation \(E_v \approx 5k_BT_m\) holds in this temperature range. The above values for the ratio \(E_v/k_BT_m\) in the two He isotopes are appreciably smaller than those found for classical crystals: thus, \(E_v = 10k_BT_m\) in a number of metals (see e.g. Bernasconi et al. 1986) and \(E_S = 25k_BT_m\) for the Schottky defect in ionic crystals (Barr and Lidiard 1970).

In this letter we derive a simple expression for the vacancy formation energy in a quantal crystal near melting at zero temperature. It relates \(E_v\) to the linear static density response function of the liquid near freezing and to the Lindemann parameter giving the mean square fluctuations of the atoms around their lattice sites in the crystal near melting. The numerical illustrations that we present below for vacancies in the two He isotopes emphasize the role of the quantal kinetic energy in balancing the loss of potential energy associated with the extraction of an atom from a lattice site.

Our derivation is given within a density functional theory (DFT) framework as applied to the calculation of phonon dispersion relations in quantal crystals near melting (Tozzini and Tosi
1995) and to the theory of freezing of quantal fluids (Likos et al. 1997). DFT relates changes in energy to changes in density. We take the liquid as reference for the crystal near melting and write

\[ E_v = (E[n_r(r)] - E[n_r]) - (E[n_p(r)] - E[n_t]) \]  

where \( E[n(r)] \) is the energy functional, \( n_r(r) \) and \( n_p(r) \) are the density profiles of the defective and the perfect crystal and \( n_t \) is the density of the liquid. After splitting \( E[n(r)] \) into the sum of the ideal kinetic energy \( T_0[n(r)] \) and the excess energy \( E_{ex}[n(r)] \), we have

\[ E_v = \Delta T_0 + \Delta E_{ex} \]  

We separately estimate below the changes in excess energy \( \Delta E_{ex} \) and in kinetic energy \( \Delta T_0 \) associated with the creation of a vacancy.

(a) Excess energy change. The crystalline density profile is taken as a superposition of Gaussian clouds centred on lattice sites and the excess energy change is treated by a second-order functional expansion of the crystal around the liquid. The expansion introduces an effective interparticle potential \( v_{eff}(r) \) given in Fourier transform by

\[ v_{eff}(k) = f^2(k)K(k) \]  

(Tozzini and Tosi 1995). Here, \( K(k) \) is a generalized force constant given in terms of the static linear density response functions of the liquid \( \chi(k) \) and of the ideal (Bose or Fermi) gas \( \chi_0(k) \),

\[ K(k) = -\chi^{-1}(k) + \chi_0^{-1}(k) \]  

and \( f(k) \) is the Fourier transform of a Gaussian cloud,

\[ f(k) = \exp(-\frac{1}{6} k^2 <u^2>) \]  

The mean square atomic displacement \( <u^2> \) in Eq. (5) is given at melting by

\[ <u^2> = L^2 d^2 \]  

where \( L \) is the Lindemann parameter and \( d \) is the first-neighbour distance in the crystal.

If we now assume that the vacancy is created by extracting an atom from a site in the bulk and reinserting it at a suitable surface site where it experiences one-half of the effective interactions with its neighbours, we obtain for a vacancy in a Bravais lattice structure

\[ \Delta E_{ex} = -\frac{1}{2} \sum_{G \neq 0} n_s f^2(G)K(G) \]  

where \( n_s \) is the mean density of the crystal and \( G \) denotes a reciprocal lattice vector of the lattice. Equation (7) should be an overestimate of the excess energy loss on vacancy creation, since no
account has been taken of the energy gain associated with the relaxation of the crystal around the vacancy.

In the classical limit one has $K(k) \rightarrow -k_BTc(k)/\eta$, where $c(k)$ is the Ornstein-Zernike direct correlation function. Equation (7) can then be compared with the expression for the potential energy change associated with vacancy creation in a classical crystal,

$$\Delta E_{pc} = -\frac{1}{2}\eta\int d\tau g(r)\phi(r)$$  \hspace{1cm} (8)$$

where $g(r)$ is the pair distribution function of the liquid and $\phi(r)$ is the pair potential (Bhatia and March 1984). Evidently, in the classical limit Eq. (7) replaces the liquid by the crystalline structure factor and the pair potential by an effective potential given by the direct correlation function.

(b) Kinetic energy change. The evaluation of the change in ideal kinetic energy would involve solving a one-body Schrödinger equation in the self-consistent Kohn-Sham effective potential. We use again the Gaussian Ansatz and neglect relaxation and overlap of the Gaussian clouds to relate $\Delta T_o$ to the average ideal kinetic energy of a particle before its extraction from a lattice site, with the result

$$\Delta T_o = -\frac{\hbar^2}{2M} \frac{9}{4 \langle u^2 \rangle}$$  \hspace{1cm} (9)$$

(see Likos et al. 1997).

Equation (9) may be expected to overestimate the magnitude of the kinetic energy change, since the extracted atom has been taken to be completely delocalized after re-insertion on the surface. Some cancellation of errors will therefore occur when Eq. (7) and Eq. (9) are combined to yield an estimate of the vacancy formation energy in Eq. (2).

(c) Numerical estimates for $^4$He. The input needed to evaluate the expressions (7) and (9) in the crystal at melting are the density response function $\chi(k)$ of the fluid phase in Eq. (4) and the Lindemann parameter $L$ in Eq. (6). Quantum Monte Carlo (QMC) work on fcc $^4$He near melting at $T = 0$ and $n_s = 0.028$ Å$^{-3}$ has shown that the Debye-Waller factor closely obeys Gaussian behaviour with $L = 0.267$ (Whitlock et al. 1979). A slightly larger value ($L = 0.30$) has been proposed from the measured phonon dispersion relations of hcp $^4$He at $T = 1.03$ K and $n_s = 0.029$ Å$^{-3}$ (Minkiewicz et al. 1968) and of bcc $^4$He at $T = 1.628$ K and $n_s = 0.0287$ Å$^{-3}$ (Osgood et al. 1971). The density response function is also known for liquid $^4$He near freezing at $T = 0$ and $n_I = 0.0262$ Å$^{-3}$ from QMC work (Moroni et al. 1992).

The above mentioned QMC data as well as some minor adjustments suggested by our earlier calculations of the phonon dispersion curves of hcp $^4$He in comparison with experiment
(Tozzini and Tosi 1995) have been used to obtain the numerical estimates shown in the top part of Table 1 for the vacancy formation energy in $^4$He in the fcc and bcc structures at $T = 0$ and $n_s = 0.0287 \text{Å}^{-3}$. The corresponding effective potential as defined in Eq. (3) is shown in Figure 1.

The main point to be noticed from the results for $^4$He in Table 1 is that there is a very substantial cancellation between the estimated gain in kinetic energy and the estimated loss in excess energy on vacancy formation in the quantal crystal. The estimated value of $E_V$ at $T_m = 0$ is essentially zero, which is consistent with the available experimental evidence cited at the beginning of this letter. Of course, for a quantitative theoretical assessment of $E_V$ a refined study of the defective quantal crystal would be necessary, as was recently initiated in the work of Pederiva et al. (1997 and to be published).

(d) Numerical estimates for $^3$He. A theoretical study of phonons in bcc $^3$He yields $L = 0.37$ near melting at $T < 1 \text{K}$ (Glyde and Hernady 1981). The density response function for a model of liquid $^3$He at $T = 0$ has been calculated by Ng and Singwi (1987) in the so-called STLS approximation. We have used these available inputs to estimate the vacancy formation energy in bcc $^3$He at $T = 0$ and $n_s = 0.0246 \text{Å}^{-3}$. The choice $L = 0.30$ has also been tested for the sake of a comparison between the two isotopes. The results are shown in Figure 1 and in the bottom part of Table 1.

Compensation between the excess energy loss and the kinetic energy gain on vacancy formation is evident also for crystalline $^3$He. In fact, our estimates suggest that vacancies may be a ground state property for the lighter isotope. Unfortunately, the input used for the density response function in our calculation is not as reliable as the outcome of QMC work, so that the above suggestion must be regarded as merely tentative. For what concerns the role of the Lindemann parameter, we may remark that (i) the effective potentials in Figure 1 are very similar for the two isotopes when the same value is assumed for $L$, and (ii) an increase in $L$ affects proportionately more the excess energy change than the kinetic energy change.

(e) Conclusions. In conclusion, we have demonstrated by simple numerical estimates that quantal fluctuations in crystals of the two isotopes of He at zero temperature favour lattice vacancies via a substantial cancellation of the excess energy loss by the quantal kinetic energy gain on vacancy formation.
REFERENCES

Table 1. Energies of lattice vacancy formation in the two isotopes of He near melting at T = 0.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta E_{\text{ct}}$ (K)</th>
<th>$\Delta T_0$ (K)</th>
<th>$E_v$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4\text{He}$ ($n_s = 0.0287\text{Å}^{-3}$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fcc ($\chi(k)$ from QMC; L = 0.27)</td>
<td>16</td>
<td>- 14</td>
<td>2</td>
</tr>
<tr>
<td>fcc ($\chi(k)$ from phonons; L = 0.27)</td>
<td>18</td>
<td>- 14</td>
<td>4</td>
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<tr>
<td>bcc ($\chi(k)$ from QMC; L = 0.30)</td>
<td>12</td>
<td>- 12</td>
<td>0</td>
</tr>
<tr>
<td>bcc ($\chi(k)$ from phonons; L = 0.30)</td>
<td>13</td>
<td>- 12</td>
<td>1</td>
</tr>
<tr>
<td>$^3\text{He}$ ($n_s = 0.0246\text{Å}^{-3}$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bcc ($\chi(k)$ from STLS; L = 0.30)</td>
<td>12</td>
<td>- 14</td>
<td>- 2</td>
</tr>
<tr>
<td>bcc ($\chi(k)$ from STLS; L = 0.37)</td>
<td>5</td>
<td>- 9</td>
<td>- 5</td>
</tr>
</tbody>
</table>
Fig. 1. Effective pair potential \( v_{\text{eff}}(k) \) as defined in Eq. (3) (left) and its Fourier transform \( v_{\text{eff}}(r) \) (right). The cases shown are for \(^4\text{He}\) with \( L = 0.30 \) (full curves) and for \(^3\text{He}\) with \( L = 0.30 \) (dashed curves) and \( L = 0.37 \) (dotted curves).