ON VACANCIES AND MELTING

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(Received 19 March, 1976)
(Revised 20 May, 1976)

Tiwari and Patil (1) have recently illustrated via melting considerations that there exists a correlation between vacancy formation energy $E_v$ and cohesive energy $U_c$. On the basis of this correlation it was concluded that the structural instability of the lattice at melting results from thermal expansion and vacancy formation. The purpose of this note is to comment on the recurring idea of a connection between vacancies and melting.

As a preliminary comment we note that vacancies are in stable thermodynamic equilibrium, thus it is rather difficult to conceive of them drastically affecting the melting process which involves a breakdown of the lattice stability. Further, the involvement of vacancies in melting would seem to be inconsistent with investigations of premelting phenomena. Wenzl and Mair (2) have searched for premelting phenomena in Ga crystals with anomalous x-ray transmission, detecting no such phenomena within $10^{-4}$ °C of the melting temperature. If the generation of vacancies were indeed involved in or responsible for the melting process one would assume that such an effect would have been observed in the temperature dependence of the integrated intensity under the Bragg peak unless vacancies play an indirect role in melting. Such an indirect role would be that vacancies do not initiate melting directly and thus are not themselves directly involved in the melting process but rather initiate the melting mechanism in some unknown way. This possibility would not, however, seem to provide evidence for or against the correlation of $E_v$ with $U_c$. An examination of Goralcki's (3) useful table shows that the ratio $E_v/U_c$ in fact varies by more than a factor of two for metals. Such a poor correlation hardly seems to us an adequate basis for the connection of vacancies with melting.

Further, the oft-mentioned correlation of the vacancy formation energy and absolute melting temperature $T_m$ is also rather poor. The ratio of these parameters varies for metals by more than a factor of two (3). These correlations, while useful for estimating vacancy formation energies, do not seem on the whole particularly supportive of the hypothesis that vacancies are involved in melting any more than the approximate correlation between Young's modulus and melting temperature indicates that melting is a phenomena caused by or directly related to Young's modulus.

The most natural explanation of the correlation of $E_v$ with $U_c$ and $T_m$ would seem to us to be reasonably straightforward. The energy to form a vacancy must be related to the cohesive energy of the atoms as it is this energy which must be overcome before an atom can be removed from a lattice site. The energy regained by placing the atom on the surface, and the relaxation subsequent to bond-breaking partly compensates the cohesive energy. Only in a rigid lattice would one expect a well-behaved correlation between $E_v$ and $U_c$. The absolute melting temperature is itself an approximate measure of the cohesive energy of the lattice. This is necessarily so because if the cohesive energy at any temperature $T<T_m$ was less than the thermal energy of the atoms or molecules (itself directly proportional to the absolute temperature in the harmonic approximation...
at high temperature), the lattice would spontaneously disorder at $T$ rather than $T_m$ (4). Thus the thermal energy of the atoms in the lattice at the melting temperature provides an absolute lower limit on the lattice cohesive energy at this temperature. Couchman and Reynolds (5) have also illustrated that the correlation (3) of $E_v$ with the latent heat of fusion is a consequence of the correlation between $E_v$ and $T_m$ and the similarity of the entropy of fusion (Richard’s rule) for metals.

Gorécki (3) has defended the idea that vacancies are crucial to melting even more vigorously than have Tiwari and Patil (1), implying that the volume change in metals on melting is caused by a vacancy concentration change at melting with the liquid structure being interpreted in terms of Frenkel’s (6) hole theory. This interpretation then is that at the melting temperature additional vacancies are formed at the cost of the heat of fusion. However, Gorécki’s argument is based in part on a useful but dubious model of the liquid state. For example, the marked difference between the pair correlation function in the liquid and solid states cannot be explained in terms of small concentrations of vacancies (7). Further, while his reasoning contains elements of plausibility for metals which expand on melting, it would seem entirely inappropriate for those metals which contract on melting. This would then apparently require, if we directly extend Gorécki’s arguments, a negative heat of fusion.

In conclusion, it is our opinion that vacancies cannot be directly responsible for melting.

References

4. This observation is germane to the thesis of the Lindemann theory of melting (F. A. Lindemann, Physik. Z. 11, 609 (1910)) which takes as its central assumption the equality of the lattice cohesive energy and the thermal energy at the melting temperature.