matters arising

Premelting near crystal defects

BARTIS[1] has suggested that the premelting increment in heat capacity, which has been observed for some materials to be of the form

$$\Delta C = A/(T_m - T)^2 \tag{1}$$

may arise from melting below the intrinsic bulk melting point, in the vicinity of point defects. He also suggested that premature melting may occur in the vicinity of edge dislocations resulting in an incremental heat capacity of the form

$$\Delta C = B/(T_m - T)^3 \tag{2}$$

The important question arises as to whether the constants A and B are large enough to account for the observed magnitude of the premelting heat capacity. We show that B is too small for the dislocation contribution to be significant, but that for lattice vacancies A is about as large as the observed magnitude.

Gronvold[2] records that 99.99% purity bismuth is 2% molten 3 K below the atmospheric pressure melting point. By using standard expressions for the excess pressure about a dislocation[3] one finds that a dislocation density in excess of 4×10^{14} lines m^{-2} is required to admit such a degree of premelting. Such a density is three to four orders of magnitude higher than the largest density one might expect for a stable dislocation array just below the melting point. For a more likely dislocation density at the melting point of 10^{10} lines m^{-2} bismuth would be 0.1% molten 0.07 K below its normal melting temperature which may be just within the limits of observation, but this may require a prohibitively high purity sample[2].

Neither, it seems, does the dislocation core melt at all. The problem of core melting of dislocations may be treated in the same manner as core sublimation as detailed by Frank[4]. He concluded that for all dislocations with Burgers' vector <1 nm the core is not hollow. This includes all simple metals and ionic crystals. Similarly, in the case of melting below the bulk melting temperature, it can be shown[5] that the melt radius for these crystals is always less than the core radius and therefore that core melting does not occur.

These ideas are borne out by experiment. Allnatt and Sime[6] have studied the premelting rise in the electrical conductivity of NaCl after 5% compressional deformation and concluded that no contribution to the premelting arises from the dislocations, and although the premelting surface conductivity is altered by deformation,[7] this is not due to dislocation core melting. Moreover, Amelinckx and Dekeyser[8], in reviewing the relevant experimental data, conclude that intrinsic melting does not measurably occur at grain boundaries.

It seems that premature melting near dislocations either does not occur or is so small as to be immeasurable. There may, however, be a possible source of premelting behaviour as described by equation (1), in the vicinity of vacancies. A vacancy in a metal usually results in a local decrease in pressure which, in the referenced case of bismuth, increases the local melting point, and this precludes vacancy-originated premelting. However, in the case of metals with normal melting curves the local melting temperature is depressed. A calculation of the magnitude of A in equation (1) reveals that the effect is sufficiently large to explain premelting over a degree or so below the melting point. This is illustrated by considering the depression of melting point that would occur if the total free energy of a system of vacancies were distributed uniformly through the crystal lattice. For a mole fraction α of vacancies with a Gibbs' function of formation of g_ν each, in a crystal with a molar entropy of melting of ΔS_m the depression is approximately

$$\Delta T = \alpha N_A g_\nu / S_m, \tag{3}$$

where N_A is Avogadro's number. For the following typical values for metals: $g_\nu \sim 1$ eV, $\Delta S_m \sim 8.5$ J mol^{-1} K^{-1} and α $(T = T_m) \sim 10^{-4}$ we find $\Delta T \sim 1$ K. There may therefore be observable premature melting in the vicinity of lattice vacancies.

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BARTIS REPLIES – I question Tallon's assessment of the stresses around edge dislocations. If the stresses are weak, then why are nucleation and growth alongside dislocations observed so often in structural studies of polymorphic transformations? Take, for instance, the passage of manganous oxide from the paramagnetic to the antiferromagnetic state. In neutron scattering from a single crystal above the Néel point Renninger *et al.*[1] detect peaks with satellites near the superlattice positions. They ascribe these features of the diffraction pattern to small domains of the magnetically ordered form of MnO. Using an electron microscope, Barber and Evans[2] do find small antiferromagnetic regions near dislocations and inclusions of Mn_3O_4 some 25 K above T_N. In the light of these results it is especially difficult to accept Tallon's claim that premelting does not occur in the cores of crystal dislocations.

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The Golgi complex and inter-relationships of arthropods

LOCKE AND HUIE have reported[1] that the Golgi complex beads in a wide range of arthropods, but not in the Onychophora or other soft-bodied invertebrates, have a common feature—they stain with bismuth. They suggest that this favours a monophyletic rather than a polyphyletic concept of arthopod evolution. It should be remembered, however, that the taxa listed with similar Golgi staining also depend on unstriated muscle (which facilitates extensive shape changes of the body), in contrast to the sclerite-bearing arthopods. The significance of the similarity between Golgi phenomena and unstriated muscle is obscure. However, it is well known that striated muscle would not suit the requirements of the Onychophora[2–6]. Also, it is certain that striated muscle has evolved more than once in the animal kingdom. The presence or absence of striated muscle in the Onychophora and in armoured arthropods seems to be of no more than functional significance.

Locke and Huie's opening paragraph does not seem to agree with present-day views on arthropod phylogeny. To take one point: by 1972 it was time to abandon the cumbersome phrase 'Onychophora–