

the efficiency $\eta = E_g/eU$ as postulated by Tauc, which shows that this postulate does not violate the second law of thermodynamics. We are accordingly permitted to consider a fluorescent p-n junction as a heat-pump, transferring energy from a reservoir of low temperature (lattice temperature) to the higher level of the radiation temperature.

The possibility of technical efficiencies of $\eta > 1$ must obviously be attributed to the finite flow of entropy [5] of the luminescence radiation. This flow of entropy is the greater the wider the luminescence band and the solid angle of radiation.

In the limiting condition of a disappearing emission bandwidth, as in the case of an idealised laser, the entropy flow of radiation approaches zero. As the result of this, the radiation temperature $T_f \rightarrow \infty$, so that the maximum efficiency approaches unity. So, in the laser diode, heat cannot be converted into coherent radiation. A consequence of Tauc's efficiency equation therefore is that for achieving laser action, the for-

ward bias at the p-n junction must be E_g , provided that we are concerned with a band-to-band emission. Since the transmission voltage cannot exceed the diffusion voltage, it follows that the diffusion voltage itself must exceed or be equal to the band distance E_g . Laser action is therefore only possible by means of degenerated semiconductors.

There are further experimental indications confirming the above considerations [6].

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LATTICE VIBRATIONS OF A F.C.C. CRYSTAL WITH LENNARD-JONES INTERACTION FOR VARYING LATTICE CONSTANT *

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For a monatomic f.c.c. crystal calculations are under way of various anharmonic properties, such as the thermal expansion and the shift and broadening of the one-phonon peaks in the inelastic coherent neutron scattering cross section. The atoms in the crystal are assumed to interact according to a Lennard-Jones potential of the usual form

$$\varphi(r) = 4\epsilon \left\{ \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right\}. \quad (1)$$

With the proper choice of the constants ϵ and σ

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the model is expected to give a reasonably accurate representation of the relevant properties of the noble gas solids with the exception of helium.

The free energy, including the cubic and quartic contributions, is calculated as a function of the lattice constant $2a$ ($a/\sqrt{2}$ is the nearest neighbour distance) and of the temperature T . By minimizing the free energy for given T as a function of a , the equilibrium lattice constant for that temperature is obtained. In order to carry out this minimization, we have computed the (quasi) harmonic phonon frequencies and polarization vectors for 1505 different wave vectors q in $\frac{1}{16}$ th of the Brillouin zone for each of 130 values of the dimensionless parameter σ/a . We wish to report on these latter results here [1].

The dynamical matrix attains for the potential (1) the form

$$D_{\alpha\beta}(q) = \frac{24\epsilon}{M\sigma^2} \left(\frac{\sigma}{a} \right)^8 \left[-28 \left(\frac{\sigma}{a} \right)^6 S_{16}^{\alpha\beta}(q) + 8 S_{10}^{\alpha\beta}(q) + \delta_{\alpha\beta} \left(\frac{22}{3} \left(\frac{\sigma}{a} \right)^6 S_{14}(0) - \frac{5}{3} S_8(0) + 2 \left(\frac{\sigma}{a} \right)^6 S_{14}(q) - S_8(q) \right) \right]. \quad (2)$$

The lattice sums S are defined by

$$S_n^{\alpha\beta}(q) = \sum_l \frac{\rho_{l,\alpha} \rho_{l,\beta} \exp(2\pi i q \cdot r_l)}{\rho_l^n}, \quad (3)$$

$$S_n(q) = \sum_l \frac{\exp(2\pi i q \cdot r_l)}{\rho_l^n}, \quad (4)$$

where $\rho_l = r_l/a$.

The calculations of the sums and the diagonalizations of the dynamical matrices were carried out on the Argonne CDC 3600 computer. All shells of neighbours were taken into account.

In fig. 1A we have plotted the frequency distributions obtained for $\sigma/a = 1.30$ and $\sigma/a = 1.24$. These values roughly correspond to the case of solid argon for 0°K and its melting point, 84°K, respectively. The sharp peak at the high frequency end of the spectrum is almost exclusively due to the "longitudinal" frequencies. The "longitudinal" frequency in each point of the Brillouin

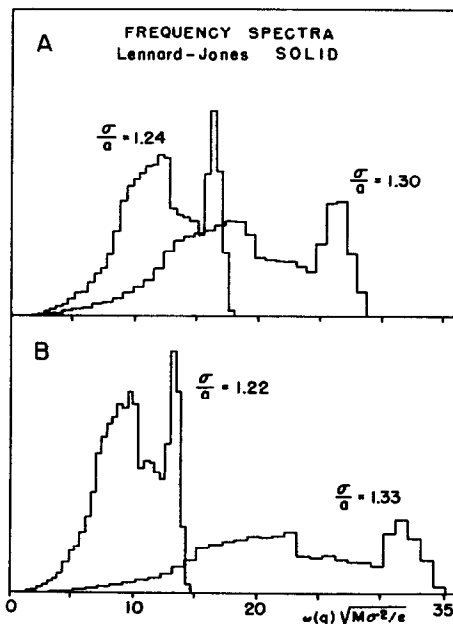


Fig. 1A. Frequency spectra for $\sigma/a = 1.30$ and $\sigma/a = 1.24$.
1B. Frequency spectra for $\sigma/a = 1.33$ and $\sigma/a = 1.22$.

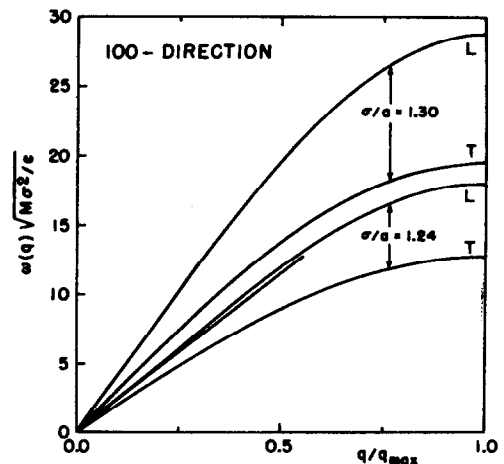


Fig. 2. Dispersion curves in the 100-direction for $\sigma/a = 1.30$ and $\sigma/a = 1.24$. L and T indicate the longitudinal and transverse branches.

zone is defined as the frequency of the mode of which the polarization vector has the largest projection along the wave vector q . The broad peak more to the left in the spectrum is due to the "transverse" modes. The large change in the frequencies over a range of linear expansion of less than 5% is quite striking. Fig. 1B shows the frequency distributions for $\sigma/a = 1.33$ and $\sigma/a = 1.22$, respectively. These values roughly correspond to xenon at 0°K and neon near its melting point, 24.4°K, respectively. In fig. 2 we have plotted the dispersion curves $\omega(q)$ in the 100-direction for the same (σ/a) -values (1.30 and 1.24) for which the spectra were given in fig. 1A. Notice that for $\sigma/a = 1.24$ the slope of the $\omega(q)$ -curve for the longitudinal branch increases slightly with increasing q for small values of q .

The spectrum and the dispersion curves for the case $\sigma/a = 1.297$ have been published recently by Grindlay and Howard [2]. This value of σ/a corresponds to the density of the noble gas solids at absolute zero if the zero-point energy is neglected (in which case the law of corresponding states would hold). These authors evaluate the specific heat as a function of temperature from the spectrum at absolute zero. However, we wish to stress that, in view of the strong density dependence of the spectrum, a reliable calculation of the thermodynamic properties of the noble gas solids in a given temperature range (with or without inclusion of the anharmonic contributions) necessitates the calculation of the spectrum for all densities corresponding to that temperature range.

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OBSERVATIONS OF THE MÖSSBAUER EFFECT IN A MONOLAYER OF ^{119}Sn ON PLATINUM

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Monolayers of certain metals have been formed on a platinum substrate by maintaining a platinum electrode in an acid solution of the metal cation at a potential more anodic than that required to produce a multilayer deposit [1]. By careful control of the potential, or of the total amount of adsorbing cation present, fractional monolayers may also be obtained. Tin was among the metals shown to exhibit this phenomenon and we report here the use of the Mössbauer effect of ^{119}Sn to study the environment of such monolayers. In particular, the Mössbauer effect distinguishes unambiguously between the hypotheses of monolayer formation by adsorption in the electrical double layer and actual plating of a monolayer on to the platinum substrate. Only the latter mechanism would be expected to produce an appreciable fraction of Mössbauer γ -rays.

In the experiment, ^{119}Sn of high specific activity was obtained by irradiating mass-separated ^{118}Sn in a flux of about 5×10^{13} neutrons/cm²sec for about a year. This was adsorbed from a solution in 0.1 M HCl on to a platinum black electrode whose potential was maintained at 0.1 V (normal hydrogen electrode) anodic with respect to the solution in its immediate vicinity by means of a potentiostat. The surface area of the platinum black was about 4000 cm² as determined by the hydrogen adsorption region of the charging curve though its physical dimensions were only 1" x 1 1/4".

The resonance absorber was 28 mg/cm² of SnO₂ incorporated as filler in a rigid thermosetting plastic and this was vibrated by a moving coil drive, as part of a standard Mössbauer spectrometer [2]. A critical absorber of 3.0 mg/cm² of palladium metal was used to reduce the contribution from the tin X-ray, and the de-

tector was a half-inch NaI(Tl) scintillator.

A Mössbauer resonance absorption line was observed and this is shown in fig. 1 together with results obtained from bulk metallic tin, and data derived from the spectra by a fitting programme are given in table 1. These spectra show that the monolayer of tin was not held in the double layer but that it was in fact remarkably similar to metallic tin. Such differences as were evident support the concept of a monolayer of tin metal on the platinum.

In the first place the chemical shift is about half-way between that for tin metal and that reported for the alloy Pt-Sn [3]. This is reasonable since the demand of the platinum for the tin s-electrons in a monolayer should only be about half that of the alloy where the tin is surrounded by platinum atoms.

Secondly the area under the spectrum for absorbed tin is larger than that for tin metal. The increased recoilless fraction implies that the tin is bound more firmly to the platinum than it is in tin metal. This is to be expected since difference of potential between bonding tin to platinum and tin to tin can be related to the free energy differences of the two processes. The monolayer forming process occurs at more anodic potentials, and this implies a stronger bond for tin bound to platinum.

Thirdly there is evidence of quadrupole splitting amounting to some 10^{-7} eV. This is not surprising since an atom at such an interface would be expected to have a considerable field-gradient at the nucleus due to the highly asymmetrical binding. Examination of these two split lines show no evidence for the effect postulated by Goldanskii [4] of different line intensities due