

not only is the intensity of the atomic lines increased but the molecular spectrum of helium is fully brought out. The spectra from the wider portions of the tube for lower values of the field at the capillary, showed only the atomic lines. It is to be inferred that the excitation of the helium molecule bands is a sudden process occurring within a narrow range of field strength near about the "throbbing" field. Most of the He₂ bands are identified with the triplet electronic states, and they involve only the two lowest states $2p\pi^3\Pi_g$ and $2s\sigma^3\Sigma_u^+$.

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ELASTIC BEHAVIOUR OF METALS NEAR THE MELTING POINT

THE velocity of sound in metals in the solid state, just below the melting-point, is about twice as great as that of the liquid metal, just above the melting-point. Certain abnormal metals, however, such as bismuth, show an increase in velocity in the liquid state. The mathematical relation between the velocity of sound and elastic modulus for a solid and the coefficient of compressibility for a liquid are well known. They involve only the properties stated and the density. The abrupt change in the velocity of sound and the elastic properties, is explained on the basis of the harmonic model developed by Fowler and Guggenheim.¹

It is well known that the frequency of vibration of atoms in the solid is dependent on the elastic constants. Considering an isotropic solid and assuming that the atoms are vibrating about mean fixed positions with a single frequency ν_k , it may be easily shown that the atomic frequency is proportional to $\frac{\nu_k}{\sigma_k}$ where ν_k is the velocity of sound for longitudinal vibrations and σ_k is the mean molecular distance in the solid given by $\left(\frac{V_k}{N}\right)^{\frac{1}{3}}$, V_k being the molecular volume and N the Avogadro number.

Considering the liquid near the melting-point as an assemblage of a large number of linear harmonic oscillators, each vibrating with a frequency ν_L about a slowly displaced equilibrium position it is easy to show that the frequency ν_L is related to the velocity of sound by the relation

$$\nu_L = \nu_L \left(\frac{3N}{4\pi V_L} \right)^{\frac{1}{3}}$$

The above model, although crude, has been applied to explain the viscosity of molten metals by Andrade² and surface tension by Sibaiya and Rama Rao³ and thermal conductivity by Rama Rao.⁴

On the assumption that the densities of the molten and solid metal are the same at temperatures just above and below the melting-point, it follows that

$$\frac{\nu_k}{\nu_L} = \frac{v_k}{v_L} 0.75 \quad (1)$$

On the basis of the harmonic oscillator model for the liquid and the solid, the partial potential of liquid at ordinary pressure is given by

$$x_0^L = -x_0^L - 3kT \log \frac{kT}{h\nu_L} - kT + kT \log J^L(T)$$

where the superscript L refers to the liquid. For the solid the partial potential is given by

$$F^k = -x_0^k - 3kT \log \frac{kT}{h\nu^k} - kT \log J^k(T)$$

where the superscript k refers to the solid. Assuming that there is no discontinuity between the internal degrees of freedom in the solid and the liquid, the melting temperature T_m is given by

$$\frac{x_0^k - x_0^L}{kT_m} = 3 \log \frac{\nu_k}{\nu_L} + 1$$

Denoting λ_m as the molecular heat of melting we obtain

$$\frac{\lambda_m}{T_m} = 3k \log \frac{\nu_k}{\nu_L} \quad (2)$$

Hence combining 1 and 2 we have

$$\frac{\nu_k}{\nu_L} = \frac{\lambda_m}{3kT_m} e^{\frac{\lambda_m}{3kT_m}} \quad (3)$$

Table I gives the values of T_m , ν_k and ν_L as measured by Stierstadt⁵ and the values compared with calculated results.

TABLE I

Metal	Velocity solid (Metres per sec.)	Velocity liquid (Metres per sec.)	T_m in °A	Ratio ν_k/ν_L	Ratio (Calc.) ν_k/ν_L
Cadmium	2665	1313	594	2.03	2.16
Mercury	2673	1290	234	2.07	2.10
Lead	1350	699	590	1.93	1.89
Tin	2643	1295	505	2.04	2.08

The agreement obtained between theory and experiment for normal metals is satisfactory. It shows that the lower velocity in the liquid is due to greater amplitude of the atomic oscillations and not to any extent to the irregularity of the arrangement of the atoms, as contrasted with their regular arrangement in the crystalline solid. On the basis of the above theory the decrease in the thermal conductivity of metals at the melting-point has been explained.⁶ The formula also offers a method of calculating the compressibility of the molten metals from a knowledge of the elastic constants of the solid.

The elastic behaviour of solids at the melting-point and their relation to the crystal structure will be discussed in a separate note.

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1. Fowler and Guggenheim, *Statistica Thermodynamica*, 1939. 2. Andrade, *Phil. Mag.*, 1934, 17, 698. 3. Sibaiya and Rama Rao, *Ind. Jour. Phy.*, 1939, 13, 293. 4. Rama Rao, *Phy. Rev*, 1941, 59, 212. 5. Stierstadt *Metallwirt. Schafft*, 8th and 15th Feb. 1932. 6. Rama Rao, *Ind. Jour. Phy.*, 1942, 16, 155.