Chap. VIII. The point we wish to stress here is that the high-frequency limit, which has usually been discussed for complex liquids on the basis of such a model, can be calculated explicitly in a model-independent fashion. In returning to the simple model, the associated viscosity relaxation time is completely determined. The velocity v^∞ itself has more significance than the model relaxation time τ_3.

NEW MELTING LAW AT HIGH PRESSURES

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The Lindemann[1] melting formula

$$T_m = Cm\Theta_D{}^2 v_m{}^{2/3}, \qquad (1)$$

where T_m is the melting temperature, v_m the volume per atom at melting, m the molecular weight, Θ_D the Debye temperature, and C a constant, is well satisfied by the experimental melting data of simple substances. The formula (1) was applied originally to melting at atmospheric pressure because of the difficulty in obtaining experimental data on the melting volume and the Debye temperature at high pressures. Instead of (1), the Simon[2,3] fusion equation

$$P_m/a = (T_m/T_0)^c - 1 \qquad (2)$$

is usually used to correlate the melting temperature T_m and the melting pressure P_m. Equation (2) does not provide a satisfactory basis for extrapolating high-pressure laboratory melting data to the core pressure of the earth.[4]

It has been discovered by one of us (G.C.K.) that by plotting melting temperature at a given pressure against Bridgman's[5] room-temperature compression $\Delta V/V_0$ at the same pressure, a straight line of the form

$$T_m = T_m{}^0(1 + C\Delta V/V_0) \qquad (3)$$

is obtained when the pressure is allowed to vary. This result seems to apply to all substances examined which melt with an increase in volume, and to hold within the precision of the available compressibility and melting curve data.

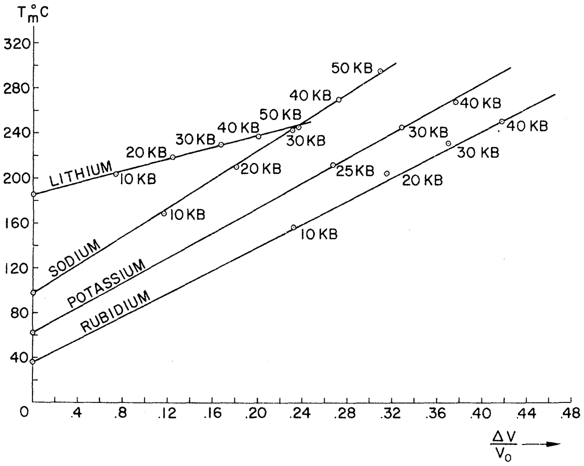

FIG. 1. Melting temperature versus isothermal compression in the alkali earths.

For example, using Bridgman's room-temperature compression data[5] with Kennedy's melting-point data[6] for the alkali metals, one finds

$$T_m(\text{Li}) = 186(1 + 1.325\Delta V/V_0)°\text{C}, \qquad (4)$$

$$T_m(\text{Na}) = 97.6(1 + 6.260\Delta V/V_0)°\text{C}, \qquad (5)$$

$$T_m(\text{K}) = 62.5(1 + 8.668\Delta V/V_0)°\text{C}, \qquad (6)$$

$$T_m(\text{Rb}) = 38.5(1 + 13.124\Delta V/V_0)°\text{C}. \qquad (7)$$

Comparison of these formulas with experiment is shown in Fig. 1.

If the energy per atom at melting is assumed to be $E_m = 3kT_m$, then (3) is equivalent to

$$(E_m - E_m{}^0)/E_m{}^0 = C\Delta V/V_0. \qquad (8)$$

Equation (8) suggests that if a solid is compressed isothermally at room temperature and then heated at constant pressure until it melts, the additional energy required to melt the solid at the higher pressure depends linearly on the amount by which the solid was compressed.

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OSCILLATORY FIELD DEPENDENCE OF THE KNIGHT SHIFT IN A MONOCRYSTAL OF TIN*

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Measurements of the Sn^{119} nuclear-magnetic-resonance (nmr) signal as a function of magnetic field in a monocrystal of white tin at 1.35°K show an oscillatory field dependence of the Knight shift. The existence of oscillations in the nmr frequency in metals superimposed on the normal linear dependence on magnetic field has been predicted by several authors.[1-4] Estimates of the amplitude of these oscillations due to oscillations in the diamagnetic shielding constant vary from $\Delta\sigma/\sigma \approx 10^{-5}$ with no dependence on applied field[2] to $\Delta\sigma/\sigma \approx 1.2\times10^{-4}$ at 10^4 G with the amplitude increasing as $H^{1/2}$.[3,4] Calculations indicate that the paramagnetic contribution to the amplitude of the oscillatory term is of order 10^{-7} to 10^{-6}.[2] A search for the oscillatory Knight shift in Sn in the field region around 10 kG was carried out by Jones and Williams[5]; no reproducible oscillatory effect was observed. In the present investigation the Knight shift was measured in the field range of 11.5 to 12.5 kG, and a definite oscillatory effect was observed. To our knowledge, this is the first direct experimental evidence that the effect is observable.

The tin monocrystal used was first cut from a zone-refined bar by spark erosion into the form of a cube approximately 1 cm on a side. This cube was then cut into 24 slices, each 0.3 mm thick, and reassembled with 0.025-mm sheets of Mylar between adjacent slices. A residual-resistance ratio measurement on a 0.6-mm thick sample cut from the same crystal gave a value of $(R_{300}/R_{4.2}) = 21\,600$. This ratio was measured in the residual field (90 G) of the magnet. Since the mean free path of the carriers is greater than 0.6 mm and magnetoresistance is appreciable at 90 G, the ratio in bulk samples at zero field would be much larger. The nmr measurements were made with a conventional Pound-Knight marginal oscillator and phase-sensitive detector. A recorder trace of the Sn^{119} resonance at 1.35°K is shown in Fig. 1. No attempt has been made to analyze the observed line shape, but it has been checked at each field and found not to change within the experimental error. The accuracy with which the absolute Knight shift could be measured is limited by the unknown position of the true resonant field on the spectrum. However, any position on the line could be determined to ±0.1 G. Since the frequency measurements were accurate to 1 part in 10^5, the total error in determining changes in the Knight shift is not greater than 3 parts in 10^5. The linewidth remains constant at 1.5 G for all fields investigated. The Sn^{119} nmr signal from a saturated solution of $SnCl_2$ in HCl with a 0.1 *M* addition of $MnCl_2$ was used as a reference to calculate the Knight shifts.

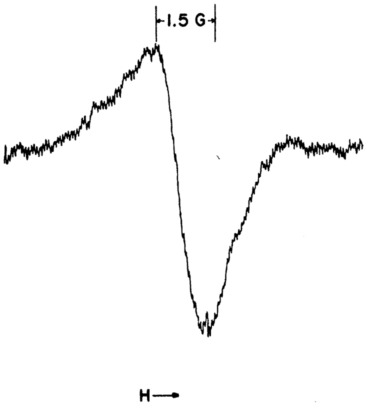

FIG. 1. A recorder trace of the derivative of the nmr signal of Sn^{119} at 1.35°K. This trace was recorded with a 0.1-G peak-to-peak, 295-Hz modulation field. A 3-sec integration time and 10-min total sweep time was used.

In Fig. 2 is shown the results of plotting the Knight shift as a function of reciprocal field for two different directions of applied field. The points of maximum Knight shift are plotted versus integers in Fig. 3. The observed periods are 4×10^{-7} G^{-1} near the (001) direction and 3.5×10^{-7} G^{-1} approximately 15° from the (001) toward the (110) direction. These periods are consistent with those found in the de Haas–van Alphen effect for oscillations due to the third-band holes in these directions.[6] It should be point-