$$\beta_3 = h(\cos\theta_1 + \cos\theta_2) + h^2\gamma^2 \cos\Theta,$$

$$\beta_4 = -h(\cos\theta_1 + \cos\theta_2) + h^2\gamma^2 \cos\Theta.$$

It is easily seen that

$$\alpha_i = \beta_i - \frac{1}{2}\beta_i^2 + \frac{1}{2}\beta_i^3 + \dots, \quad i = 1, 2, 3, 4.$$

For small h we can expand around $\alpha_i = 0$ to obtain

$$W_v = 4f(R) - 2 \frac{\partial f}{\partial R} h^2(\cos^2\theta_1 + \cos^2\theta_2 + h^2\gamma^4 \cos^2\Theta) \\ + 2 \frac{\partial^2 f}{\partial R^2} h^2(\cos^2\theta_1 + \cos^2\theta_2 + h^2\gamma^4 \cos^2\Theta) + O(h^4). \quad (A2)$$

Now we have

$$\cos^2\theta = \frac{2}{3} \left(\frac{4}{5}\pi \right)^{1/2} Y_{20}(\theta, \varphi) + \frac{1}{3},$$

$$\cos^2\Theta = \frac{1}{3} [2P_2(\Theta) + 1],$$

$$P_2(\Theta) = \frac{4}{5}\pi \sum_{\mu} Y_{2\mu}^*(\theta_1, \varphi_1) Y_{2\mu}(\theta_2, \varphi_2).$$

Therefore we have

$$W_v = \sum_{\substack{j_1 j_2 \mu \\ j_1=0,2 \\ j_2=0,2}} b_{j_1 j_2 \mu}(r_{12}) Y_{j_1 \mu}(\theta_1, \varphi_1) Y_{j_2 \mu}(\theta_2, \varphi_2) \\ + O\left(\frac{d}{r_{12}}\right)^4.$$

Referring to Eq. (1) we can show that

$$a_{j_1 j_2}(r_{12}) = \left(\frac{(2j_1+1)(2j_2+1)}{4\pi(2j+1)} \right)^{1/2} \\ \times \frac{1}{Q_{j_1 0} Q_{j_2 0}} \sum_{\mu} b_{j_1 j_2 \mu}(r_{12}) C(j_1 j_2 j; \mu, -\mu).$$

We have shown that terms with j_1 or $j_2 = 4$ are smaller than terms with $j_1 = 0$ and $j_2 = 2$ or $j_1 = 2$ and $j_2 = 0$ by a factor of the order of $(d/r_{12})^2$.

The expansion (A2) does not converge for a potential of the type $f(r) = ae^{-br}$. The same conclusions, however, are easily seen to be valid for this potential by expanding W_v in a series of Bessel functions.⁸

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Evaluation of the Third Moment of the Imaginary Part of the Dielectric Constant*

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The values of the third moment of the imaginary part of the dielectric constant are reported for a number of AB semiconductors. The frequency ω_a defined by Hopfield is obtained from these moments and is compared with the average band gap ω_g defined by the electronic part of the dielectric constant at zero frequency.

Recently, Phillips¹ and colleagues have developed an ionicity scale based on an average band gap of a solid. This average band gap ω_g is defined by the expression

$$\omega_g^2 = \frac{\omega_p^2}{\epsilon_1(0) - 1} = \omega_p^2 / \frac{2}{\pi} \int_0^\infty d\omega \frac{\epsilon_2(\omega)}{\omega}, \quad (1)$$

where ω_p is the plasma frequency. While this ionicity scale has proved useful in ordering a number of the properties of AB semiconductors and insulators, no real theoretical justification for its success has been given. On the other hand, Hopfield² has shown that the third moment of the imaginary part of the dielectric constant ϵ_2 can

FIG. 1. Values of ω_a vs ω_g .

be related to the pseudovalence charge density ρ and the bare pseudopotential V . For a cubic crystal, this relation is

$$\frac{2}{\pi} \int_0^\infty \omega^3 \epsilon_2(\omega) d\omega = \frac{\omega_p^2}{3m_e N} \int_{\text{all space}} \rho(\vec{x}) \nabla^2 V(\vec{x}) d^3x, \quad (2)$$

where m_e is the mass of the electron and N is the total number of electrons. Using Eq. (2), one can define a frequency ω_a by the expression

$$\begin{aligned} \omega_a^2 &= \frac{2}{\pi} \int_0^\infty \omega^3 \epsilon_2(\omega) d\omega / \omega_p^2 \\ &= \frac{1}{3Nm_e} \int_{\text{all space}} \rho(\vec{x}) \nabla^2 V(\vec{x}) d^3x. \end{aligned} \quad (3)$$

Hopfield² has shown that for the diamond and zinc-blende structures ω_a^2 may be split into a symmetric part ω_{aS}^2 and an antisymmetric part ω_{aA}^2 in a manner which is similar to that postulated for ω_g^2 by Phillips.¹ This fact coupled with the close connection between ω_a and the chemically significant quantities of charge density and potential have led Hopfield² to suggest that ω_a forms a basis for the chemical properties found by Phillips¹ in ω_g . However, it is obvious from comparison of relations (1) and (3) that the ω_g and ω_a involve very different moments of $\epsilon_2(\omega)$. The moment required for ω_a weights very heavily the high-frequency part of ϵ_2 while the moment required for

ω_g weights heavily the low-frequency part of ϵ_2 .

Thus, we have attempted to check the connection by evaluating the right-hand side of Eq. (3) for a number of AB semiconductors and comparing it with the value of ω_g given by Phillips. The Heine-Abarenkov³ pseudopotentials with the parameters given by Animalu and Heine⁴ were used as the bare pseudopotential. The charge density was obtained by computing the Thomas-Fermi charge density given by the Cohen-Bergstresser⁵ empirical pseudopotential, V_{CB} . That is,

$$\rho(\vec{x}) = \left(\frac{2m_e}{\hbar^2} [E_F - V_{CB}(\vec{x})] \right)^{3/2} / 3\pi^2. \quad (4)$$

The value of E_F was determined by the condition that the integral of $\rho(\vec{x})$ should yield the correct number of valence electrons.

The results obtained for ω_a are plotted as a function of ω_g in Fig. 1. Several points are to be noted. First, the values of ω_a are approximately twice as big as the corresponding value of ω_g suggesting that the high-frequency part of ϵ_2 is playing a more significant role in ω_a than it is in ω_g . Second, while there is some indication of correlation between ω_a and ω_g , there is no obvious simple relation connecting the two frequencies. To further check for correlations between ω_g and ω_a , we have calculated the ionicity based on ω_a using the formula

$$f_a = \omega_{aA}^2 / \omega_a^2, \quad (5)$$

which is analogous to the one used by Phillips¹ for defining the ionicity f_i . A plot of f_a vs f_i is shown in Fig. 2. From this plot one can see that there is an approximately monotonic relation between f_a and f_i . However, it is clear that the relation is

FIG. 2. Values of f_a vs f_i .

not a linear one.

In conclusion, we have evaluated the sum rule suggested by Hopfield² as a possible theoretical basis for the Phillips ionicity scale and find that ω_a exhibits trends which are similar to those shown by ω_g and, thus, could be used to order properties in the same way as Phillips has used ω_g .¹ The rather wide discrepancy in value be-

tween ω_a and ω_g may in part be due to the use of the Cohen-Bergstresser pseudopotentials which have been determined empirically by fitting a few band gaps and, thus, have not been determined in such a way that binding or the charge distribution in the crystal are closely modeled.

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Specific Heats of GaSb, GaAs, InSb, InAs, Bi, Cd, Sn, and Zn below 30 K[†]

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Previously reported heat-capacity data from 1 to 30 K for four III-V compounds and four anisotropic metals have been reanalyzed using a magnetically smoothed temperature scale (T_x). Values are given for the contributions due to free carriers in the III-V compounds and electrons in the metals, and for the lattice contributions to the specific heats at low temperatures. Excellent agreement is obtained between calorimetric and elastic-constant determinations of the limiting Debye temperature at $T=0$.

Specific-heat measurements made in this laboratory on copper¹ and on several III-V compounds¹ and anisotropic metals² were reported previously in terms of two separate temperature scales (T_{58} and T_{618}) which are not continuous near 4.2 K where the two scales overlap. A single continuous temperature scale (T_x) recently has been established in the 1-30 K region by Cetas and Swenson^{3,4} using paramagnetic-salt thermometry, and the germanium thermometer used in the previous heat-capacity work since has been calibrated directly in terms of this new scale. T_x appears to be quite smooth in the thermodynamic sense, and we have used it to reanalyze earlier heat-capacity data for copper with encouraging results.⁵ The copper analysis included an investigation of the effects of deviations in temperature scales on specific-heat results and indicated that the correction applied in our previous analyses^{1,2} for a thermometry problem below 1.5 K was incorrect. We therefore have reanalyzed the data for all samples, with the exception of the yttrium. Our yttrium sample contained magnetic impurities,² and

the uncertainties introduced by these impurities are considerably larger than those introduced by thermometry error, so nothing is to be gained by further analysis of those data.

As in the previous analyses, the power series

$$C_p = \sum_{n=0}^{10} a_{2n+1} T_x^{2n+1}$$

was fit to the reanalyzed data for each of the samples. The value of a_1 for each of the samples except bismuth was determined graphically (as in Refs. 1 and 2), after which the remaining coefficients were determined by least-squares fitting, minimizing the relative deviations in the lattice specific heats. Because of the large deviations from Debye behavior for these solids, it was not possible to obtain a fit to Eq. (1) over the entire 1-30-K range to the precision of the data. A close correspondence was found between the minimum in the equivalent Θ -vs- T curve and the highest temperature for which a valid fit could be obtained. Overlapping-fit ranges then were used to obtain smooth representations of