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Lattice Dynamics of Alkali Metals in the Self-Consistent Screening Theory*

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The self-consistent treatment of correlations in the electron liquid recently given by Singwi *et al.* is applied to calculations of the lattice dynamics of alkali metals. With the Ashcroft form for the pseudopotential, in which the only parameter is the core radius, good agreement with the measured dispersion curves is obtained for the four metals for which such data exist. For Na and K the fitted values of this parameter are close to those derived from Fermi-surface and liquid-resistivity data; for Li and Rb the fitted values lie between those obtained from the other physical properties. Phonon lifetimes due to the electron-phonon interaction are calculated for K. Finally, the cohesive energy, lattice parameter, and compressibility are derived; agreement with the measured values of all three quantities is obtained with a not unreasonable adjustment of the Hartree energy. The relation between the compressibility sum rule and the long-wavelength limit of terms containing third and fourth powers of the electron-phonon matrix element is evaluated for the case of Na within the same framework.

I. INTRODUCTION

Since the pioneering work of Toya,[1] there have been many attempts to calculate phonon dispersion relations in the alkali metals starting from first principles. Such work has been stimulated by the experimental data from inelastic neutron scattering[2–5] and also by the development of pseudopotential theory[6] which has largely justified, at least for the alkali metals, Toya's use of plane-wave states to derive the electron-phonon matrix elements. The essential ingredients of these calculations are the form of the pseudopotential and the treatment of the screening. The calculations published hitherto[7–16] have used a variety of forms for the pseudopotential, including Bardeen's,[1,8,9,15] different types of self-consistent orthogonalized-plane-wave (OPW) calculation,[7,8,15,16] the Heine-Abarenkov model potential fitted to atomic spectroscopic data,[10] and parametrized forms such as those suggested by Schneider and Stoll,[11] by Ashcroft,[12] by Brovman *et al.*,[13] and by Harrison.[14] Different forms of screening have been used also, ranging from simple Hartree screening random-phase approximation (RPA)[8,10,15] to more complicated forms incorporating exchange and correlation effects, such as Slater's,[1,15] Hubbard's modified form[7,8,10,15] and those of Bailyn,[9] Kohn and Sham,[15] Robinson *et al.*,[15] Geldart and Vosko,[8,11–15] and Geldart and Taylor.[16] Most authors assume a local pseudopotential, although several attempts have been made to include nonlocal corrections.[7,8,10] Most of the calculations are taken to second order in the electron-ion matrix element; while two groups have discussed the formalism for carrying the calculations to higher order,[17,18] no results are available at the time of writing.

The frequencies are generally within 10 to 20% of the observed ones for the first-principles calculations, somewhat closer for those containing adjustable parameters. The physical information derived from these calculations is limited by the fact that the discrepancies can be due to inadequacy on any one or more of the following five points: (i) pseudopotential, (ii) screening, (iii) local nature of the pseudopotential, (iv) restriction to second-order perturbation theory, and (v) use of the harmonic approximation. Similar difficulties apply to the interpretation of effective interionic potentials derived from inversion of the neutron data.[19]

Singwi *et al.*[20] have recently given a refinement of their earlier[21] self-consistent treatment of correlations in the electron liquid which is more satisfactory than previous treatments through the entire range of wave vector and electron density. We now have, therefore, a reasonably reliable form for the screening that should remove most of the discrepancy (ii) in the list above; discrepancies resulting from calculations with this form can therefore be largely attributed to one or more of the other four items. To investigate the effect of the self-consistent treatment, we have calculated phonon dispersion relations in the alkali metals with this and three of the earlier forms of screening. The object has been to isolate this one effect rather than to attempt a comprehensive treatment. We have therefore adopted the simplest possible course with respect to items (i), (iii), (iv), and (v) using a one-parameter local form for the pseudopotential suggested by Ashcroft,[22] the usual second-order perturbation theory, and the harmonic approximation. Calculations of the effective interionic potentials and elastic constants with the same parameters will be described in a separate paper.[23]

In Sec. II we give the basic formulas for the phonon dispersion relations, the pseudopotential, and the four forms of dielectric function used. Section III describes the calculation of the dispersion relations and discusses the results obtained. Section IV describes a calculation in the same framework of phonon lifetimes due to the electron-phonon interaction. In Sec. V we discuss the cohesive energy of the crystal and its first derivative with respect to volume, which should be zero in equilibrium at zero pressure. Section VI is concerned with the second derivative, which gives the comperssibility; this can be compared with the compressibility obtained from the long-wavelength limit of the phonon dispersion relation. This provides information about the magnitude of the third- and fourth-order perturbation terms in the long-wavelength limit. Section VII summarizes the conclusions.

II. DISPERSION RELATIONS: THEORY

The phonon dispersion relation between frequency ν and wave vector $\vec{q}$ for a Bravais lattice is given by the eigenvalues of the dynamical matrix $D_{\alpha\beta}(\vec{q})$,

$$\sum_\beta D_{\alpha\beta}(\vec{q})e_{j\beta}=\nu_j^2 e_{j\alpha}\ , \quad j=1,\ldots,3 \quad . \tag{1}$$

For a simple metal, D can be expressed[1] as the sum of three terms

$$D=D^C+D^E+D^R \quad . \tag{2}$$

D^C represents the direct Coulomb interaction between ions of charge $+Ze$ immersed in a uniform compensating negative charge, and can be evaluated by standard methods.[24] D^E is the ionic interaction via the conduction electrons with which this paper is concerned. D^R is a repulsive interaction due to core wave-function overlap which is insignificant for the lighter alkali metals[25]; while it might introduce small effects for Rb and Cs, we have no estimates of these and will therefore neglect this term here, since, in any case, our object is to investigate the effects of screening.

The term D^E can be related[26] to a scalar function $G(q)$ introduced by Cochran,[19] which is equal to the Fourier transform of the effective interionic potential due to the conduction electrons divided by $-4\pi Z^2e^2/\Omega q^2$. Second-order perturbation theory gives

$$D^E_{\alpha\beta}(\vec{q})=-\nu_p^2\sum_{\vec{h}}\left(\frac{(q_\alpha+h_\alpha)(q_\beta+h_\beta)}{|\vec{q}+\vec{h}|^2}G(|\vec{q}+\vec{h}|) - \frac{h_\alpha h_\beta}{h^2}G(h)\right) \ , \tag{3}$$

where $\vec{h}$ is a reciprocal-lattice vector and ν_p is the ion-plasma frequency given by

$$\nu_p^2=Z^2e^2/\pi M\Omega \quad . \tag{4}$$

Z, M, and Ω are, respectively, the number of conduction electrons, mass, and volume per ion. For a local pseudopotential, $G(q)$ is related to the bare electron-ion pseudopotential $w(q)$ and the dielectric function $\epsilon(q)$ which describes the conduction-electron screening,

$$G(q)=\left|\frac{w(q)}{-4\pi Ze^2/\Omega q^2}\right|^2\left(\frac{\epsilon(q)-1}{\epsilon(q)}\right) \quad . \tag{5}$$

As stated in the Introduction, we use a form for the pseudopotential due to Ashcroft,[22] containing only one parameter r_c, given by

$$\begin{aligned} w(r)&=-Ze^2/r\ , \qquad && r>r_c a_0 \\ &=0\ , && r<r_c a_0 \end{aligned} \tag{6}$$

where a_0 is the Bohr radius. Physically, r_c represents the radius of the ion core; Eq. (6) assumes that the effective repulsive potential arising from the orthogonalization of the conduction-electron wave function to the core wave functions exactly cancels the Coulomb potential inside the core. In this picture r_c is a property of the ion, and thus is independent of environment. Fourier transformation of Eq. (6) gives the simple result

$$\frac{w(q)}{-4\pi Ze^2/\Omega q^2}=\cos(r_c a_0 q) \quad . \tag{7}$$

Four different forms of dielectric function were used in the calculations.

A. RPA

In this approximation, the electrons respond as free particles to the influence of the Hartree potential. The dielectric function is

$$\epsilon(q)=1+Q_0(q) \quad , \tag{8}$$

where Q_0 is the Lindhard expression for the electron polarizability times $-4\pi e^2/q^2$. Explicitly,

$$Q_0(q)=(k_{\mathrm{TF}}^2/q^2)\mathfrak{F}(q/k_{\mathrm{F}}) \quad , \tag{9}$$

where

$$\mathfrak{F}(x)=\frac{1}{2}+\frac{4-x^2}{8x}\ln\left|\frac{2+x}{2-x}\right| \quad , \tag{10}$$

k_{F} is the Fermi radius $(3\pi^2 Z/\Omega)^{1/3}$, and k_{TF} is the Thomas-Fermi screening constant given by

$$k_{\mathrm{TF}}^2=(m^*/m)4k_{\mathrm{F}}/\pi a_0 \quad . \tag{11}$$

Here we have included band-structure effects by introducing an effective electron mass m^*. Only in this average sense do we include the effects of the lattice on the conduction electrons; detailed consideration of these effects requires a higher perturbation theory than we wish to use.[17,18]

B. Hubbard's Modified Expression

Hubbard has attempted to include the effects of exchange between electrons of parallel spin. His expression for the dielectric function is[27]

$$\epsilon(q)=1+Q_0(q)/[1-f(q)Q_0(q)] \quad , \tag{12}$$

where

$$f(q)=\tfrac{1}{2}q^2/[q^2+k_{\mathrm{F}}^2+k_{\mathrm{TF}}^2] \quad . \tag{13}$$

C. Geldart and Vosko

The long-wavelength limit of the dielectric function for the interacting electron gas leads to an expression for the compressibility. In a consistent theory this should agree with the value obtained by double differentiation of the cohesive energy with respect to volume. This compressibility sum rule is not obeyed by the above two dielectric functions. Geldart and Vosko[28] modified the Hubbard expression to obtain agreement by introducing a parameter ξ, replacing Eq. (13) by

$$f(q)=\tfrac{1}{2}q^2/(q^2+\xi k_{\mathrm{F}}^2) \quad . \tag{14}$$

The various theories of the electron liquid give similar values for the cohesive energy. If the interpolation scheme of Nozières and Pines[29] is used, ξ is given by

$$\xi=2/(1+0.026r_s^*) \quad , \tag{15}$$

where

$$r_s^*=(m^*/m)r_s \tag{16}$$

and r_s is the parameter defining the interelectronic distance through

$$\Omega/Z=\tfrac{4}{3}\pi r_s^3 a_0^3 \quad . \tag{17}$$

Similar considerations for the crystal as a whole are discussed in Sec. VI.

D. Self-Consistent Screening Theory

The dielectric function of Geldart and Vosko satisfies the compressibility sum rule but has the unsatisfactory behavior of the other forms for large values of q, i.e., small values of r, in that the pair correlation function goes negative, a physically impossible result. Singwi *et al.*[20] have derived a self-consistent screening theory which is satisfactory in both limits. The method consists essentially of assuming a certain pair correlation function, using this to derive the local-field corrections for Coulomb and exchange effects expressed by a function $f(q)$ in Eq. (12), and relating the dielectric function in the standard manner to the structure factor and hence back to the pair correlation function; this cycle of equations is solved iteratively on a computer until a self-consistent form is obtained. The dielectric function is obtained in tabular form; however, it is found that the expression

$$f(q)=A[1-e^{-B(q/k_{\mathrm{F}})^2}] \tag{18}$$

gives, at least for alkali metals, a rather good approximation to the self-consistent $f(q)$; it diverts from the latter only for $q>2k_{\mathrm{F}}$ where $Q_0(q)$ becomes small and hence $\epsilon(q)$ is less sensitive to the exact form of $f(q)$. The constants A and B have a weak dependence on r_s; they are tabulated for integral r_s in Ref. 20, and the values appropriate for the relevant value of r_s^* can be obtained by interpolation.

The treatment of screening in Ref. 20 differs from that in an earlier paper by the same authors[21] in the Introduction of a screening factor in the Coulomb potential entering the local-field corrections. The earlier theory, while violating the compressibility sum rule, gave somewhat better results for small r, leading to a pair correlation function more nearly zero at $r=0$. In Ref. 20 an interpolation is attempted between the large q behavior of the earlier theory and the small q behavior of the later one; both this interpolated dielectric function and the earlier one were also tried in the dispersion-relation calculations. Prakash and Joshi[15] have recently reported phonon-frequency calculations using, among other dielectric functions, one said to be derived from Ref. 21. Unfortunately, the formula they used applies not to the self-consistent theory but to a recalculation of the original theory of Hubbard with the integrals evaluated exactly (see Sec. III of Ref. 21).

III. DISPERSION RELATIONS: CALCULATION AND RESULTS

Phonon dispersion relations were calculated for three symmetry directions and two zone boundaries for the five alkali metals, with a program written for the IBM 360 computer. The calculations followed Eqs. (1)–(7) of the text, with Eqs. (8) and (12), (13) and (12), (14) and (12), (18) used in turn for the four dielectric functions.

Due to the large discontinuity of the potential given by Eq. (6), the form factor of Eq. (7) is relatively long ranged and caused some convergence difficulties in the sums over reciprocal-lattice vectors. Rather than introduce some arbitrary cutoff or damping factor, the procedure used to handle this was to cut off the sum at successive nodes of the form factor. It was found that satisfactory convergence was obtained at the fourth node; in Na, for example, this corresponded to $(ha/2\pi)^2 = 68$. A check was provided by calculations at points which differ by a reciprocal-lattice vector where frequencies were found to agree to 1% or better. Values of the parameters used for the results shown here are given in Table I. For the four metals for which experimental data is available, the core radius r_c was adjusted to give the best fit to the experimental data for the self-consistent dielectric function. For Na and K, the optimal values were not too different from values derived by Ashcroft[12] from other physical properties, and calculations were also performed for Ashcroft's values. The values for the effective mass m^* were taken from published band-structure calculations. For Li, Rb, and Cs, there is a wide spread in the values in the literature, so m^* becomes in effect a second parameter. For Li and Rb, the calculations were repeated for a number of published values, varying r_c in each case. Since there are points such as (1, 0, 0) where the frequencies are extremely sensitive to r_c but rather insensitive to m^*, in contrast to, e.g., the long-wavelength longitudinal branches which are sensitive to both parameters, there is a definite set of values which gives the best fit. Again, the set giving the best fit for the self-consistent dielectric function was chosen. It turned out that the values of m^* giving the best agreement were the ones recently published by Shaw and Smith.[30]

Since the calculations are performed in the harmonic approximation, low-temperature values were used for the lattice constant a and so the calculated frequencies represent harmonic values for the metals. The experimental data, of course, contain anharmonic effects. Calculations of such effects in K have been performed by Buyers and Cowley,[32] who use a pseudopotential obtained by fitting to the neutron data.[3] However, in view of the other uncertainties in the theory mentioned in the Introduction, we do not make any anharmonic corrections here. Buyers and Cowley calculate anharmonic frequency shifts in K to be around 4%, usually negative, at 90 °K.

The calculated dispersion curves for Li, Na, K, and Rb are shown as solid lines in Figs. 1–8. For greater clarity, two graphs are plotted for each direction; the top graph shows the longitudinal and,

TABLE I. Values of parameters used in the calculations.[a]

	Li	Na	K	Rb	Cs
M(amu)	6.94	22.99	39.1	85.48	132.91
a(Å)	3.478	4.225	5.225	5.585	6.045
r_c	1.40	1.69 (1.66)	2.226 (2.13)	2.40	2.62[b]
m^*	1.27[c]	1.0[d]	0.93[d]	0.89[d]	0.86[b]
r_s	3.236	3.931	4.862	5.197	5.625
r_s^*	4.10	3.931	4.519	4.625	4.84
ξ	1.84	1.81	1.79	1.79	1.78
A	0.999	0.995	1.007	1.008	1.011
B	0.258	0.2625	0.249	0.247	0.242

[a] The bracketed values for r_c are those of Ashcroft (Ref. 12).

[b] Values obtained by extrapolation.

[c] See Ref. 30.

[d] See Ref. 31.

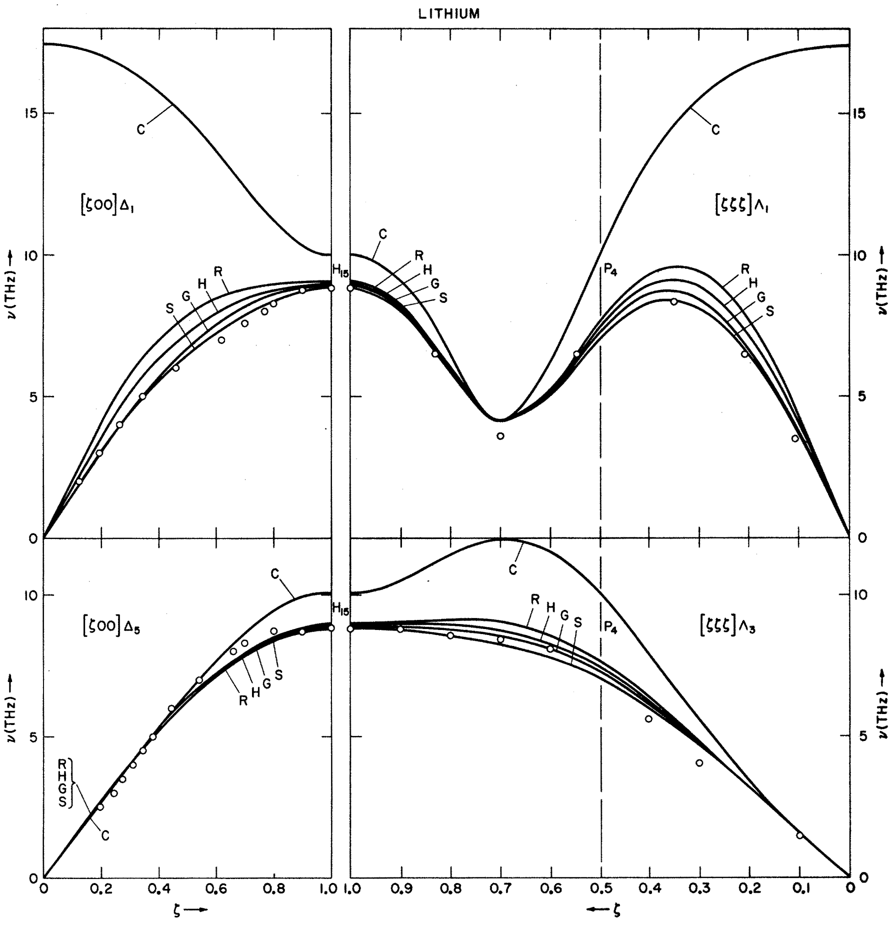

FIG. 1. Dispersion curves for Li. The notation is as follows: C, Coulomb interaction only; R, RPA dielectric function; H, Hubbard's modified dielectric function; G, Geldart and Vosko dielectric function; S, self-consistent (Singwi *et al.*) dielectric function; and open points, experimental data.

where it exists, the lower transverse branch; the bottom graph shows the higher transverse branch. The directions [ζ00] and [ζζζ] are given in the odd-numbered figures, the directions [ζζ0], [$\frac{1}{2}\frac{1}{2}$ζ], and [ζζ1] in the even-numbered ones. The four dispersion curves are labeled R, H, G, and S referring to the RPA, modified Hubbard, Geldart and Vosko, and self-consistent (Singwi *et al.*) dielectric functions, respectively. The curves labeled C refer to those calculated for a lattice of bare ions in a uniform negative charge, given by the Coulomb contribution D^C alone in Eq. (2). In Figs. 3–6 the dotted curves represent calculations with Ashcroft's values for r_c and the self-consistent dielectric function. The open circles refer to the data from neutron scattering; the experiments for Li,[4] Na,[2] K,[3] and Rb[5] were carried out at 98, 90, 9, and 120 °K, respectively.

The following conclusions can be drawn from Fig. 1–8:

(a) With certain exceptions, the dispersion curves calculated with the optimized values of r_c and the self-consistent dielectric function agree with the measurements to within 5%. Some of the exceptions represent isolated experimental points which may be in error; the Li data, in particular, were taken with a double crystal[4] and might plausibly contain some erroneous points. Other discrepancies, however, are with systematic trends in the data which must be real effects; especially noticeable are the [ζζ0]Σ_3 branch in Li, the [ζζ0]Σ_4 branch in Na and Rb, and the [$\frac{1}{2}\frac{1}{2}$ζ]D_1 branch in K and Rb. Also, all the metals show evidence of very slight discontinuities in slope in the [ζ00]Δ_1 branch which are not matched by the calculated curves. These may be caused by anharmonic effects.[33]

(b) For the values of r_c and m^* used, the self-consistent dielectric function leads to much better agreement than the other three. The question whether it is absolutely superior could only be conclusively answered by optimizing r_c (and m^* in the case of Li and Rb) separately for each dielectric function. However, in certain cases the lowering of r_c which would be necessary to bring modes for one of the other dielectric functions into agreement with experiment would obviously worsen the agreement at places such as (1, 0, 0) which are almost independent of the screening used; this is borne out by the experience with the two values of r_c used in the Na and K calculations. The experimental data for Li in the [ζ00] direction have the interesting property that the transverse branch crosses the longitudinal about half-way to the zone boundary. With the parameters used for the Li calculations, the curves calculated with the self-consistent dielectric function also show a crossover, although it is less dramatic; the calculated longitudinal frequencies are at most 1% below the transverse at corresponding values of ζ, whereas the experimental ones are as much as 10% lower; also the calculated crossover takes place at $\zeta = 0.7$ rather than 0.5. Here again anharmonic effects may be playing a significant role.[33]

The three branches for which agreement is especially poor, as noted above, are transverse branches which are rather insensitive to the screening; this is because the electronic term D^E is relatively small compared with the bare Coulomb interaction, which can be seen to yield frequencies not far from the measured points (in some cases nearer than the full calculation). The discrepancy, therefore, can be ascribed to the pseudopotential rather than to the screening. In fact, it is remarkable that a one-parameter pseudopotential should perform as well as it does.

(c) The calculations are very sensitive to the value of r_c. The dotted curves for Na, for example, are calculated with a value of r_c reduced by only 2%, yet the agreement is markedly poorer. The dotted curves for Na and K are in reasonable agreement with those calculated by Ashcroft[12] with the same values of r_c and the Geldart and Vosko dielectric function. The frequencies obtained by Ashcroft are slightly higher because the Geldart and Vosko screening reduces the negative component D^E, and because he cuts off the sum over reciprocal-lattice vectors much sooner $[(ha/2\pi)^2 \leq 22]$.

Calculations for the earlier form of self-consis-

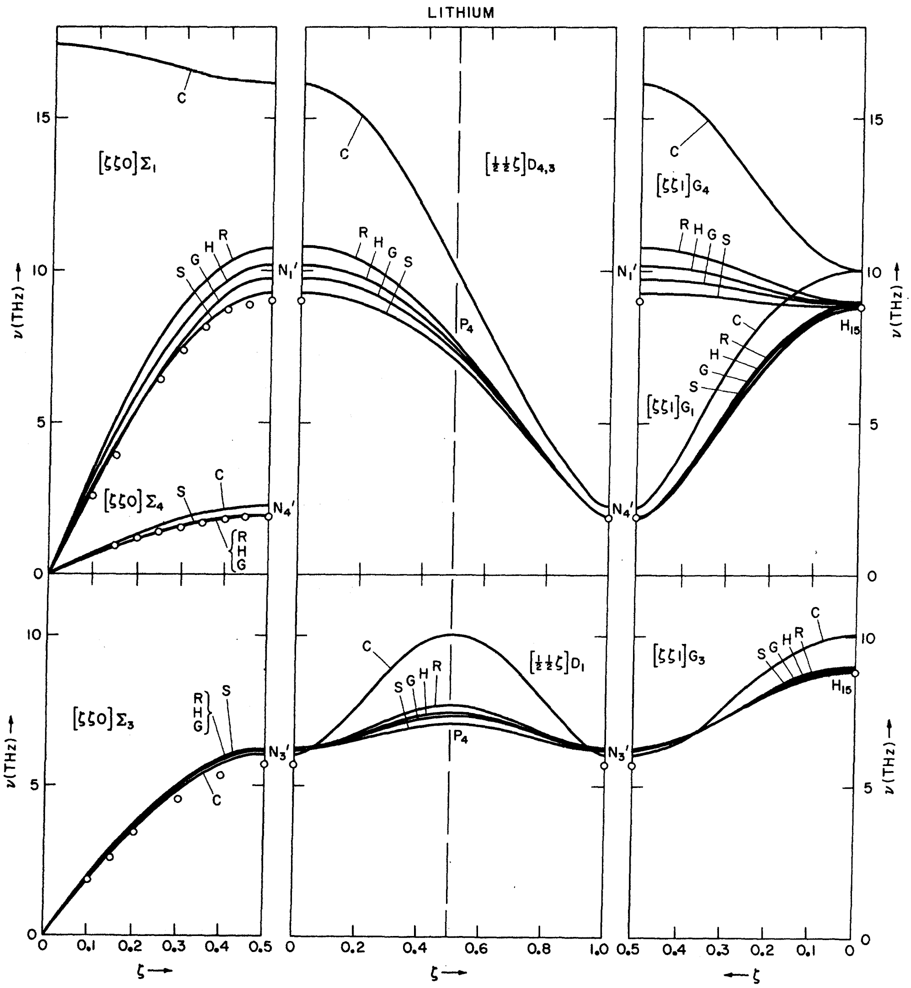

FIG. 2. Dispersion curves for Li. Notation as for Fig. 1.

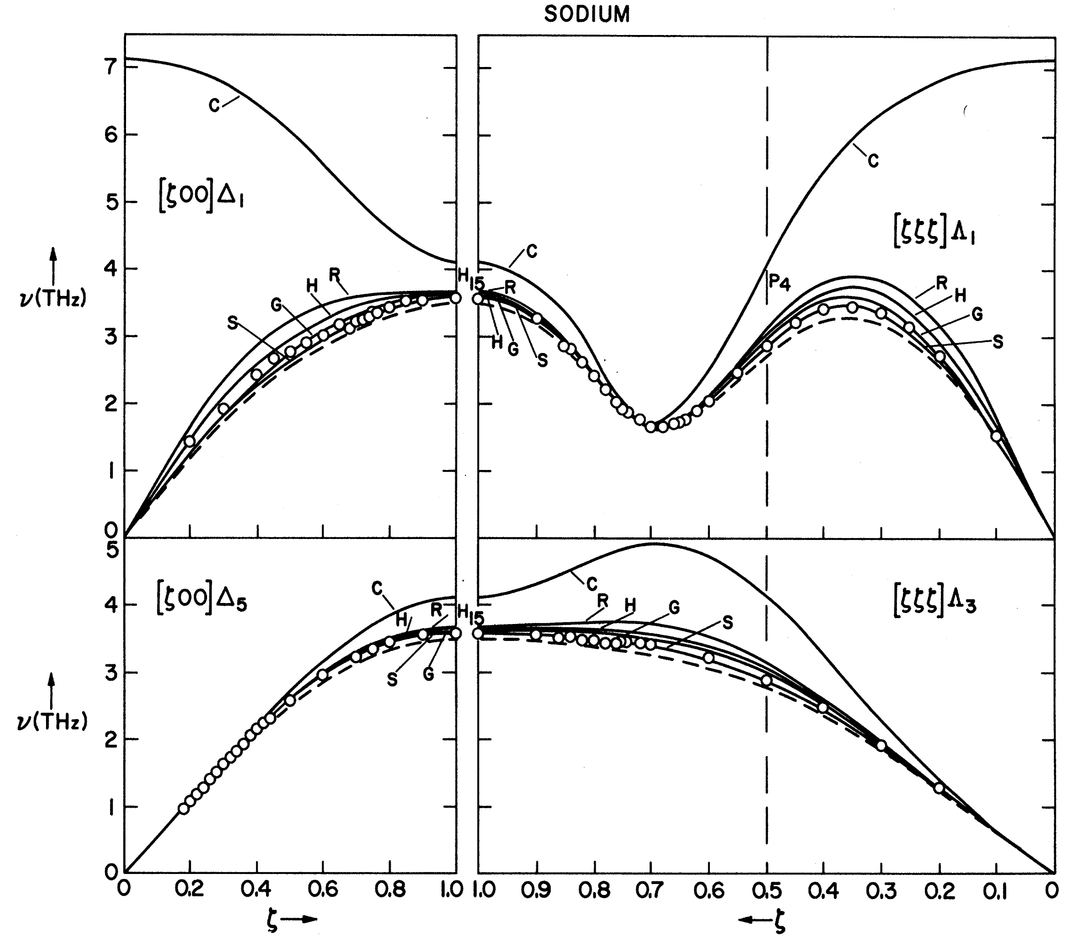

FIG. 3. Dispersion curves for Na. Notation for the solid curves as for Fig. 1. The dotted curves represent calculations with Ashcroft's value of r_c and the self-consistent dielectric function.

tent theory[21] mentioned in Sec. II gave dispersion curves for the longitudinal branches which were far too low for smaller values of q. This is consistent with the fact that the compressibility sum rule is not obeyed. The dielectric function interpolated between the two forms gave a similar but less marked behavior; the interpolation thus goes over to the old theory at too small a value of q to be satisfactory.

The optimal values of r_c for the four lightest alkali metals fall approximately on a straight line plotted against r_s (see Fig. 10). This fact was used to extrapolate a value of r_c for Cs; a value for m^* was similarly extrapolated. No experimental phonon data are available for Cs, and the dispersion curves were calculated only for the self-consistent dielectric function; these are shown in Fig. 9. The heavy lines represent initial slopes derived from the measured elastic constants of Cs at 78 °K.[34] These are in rather good agreement with the initial slopes of the calculated curves. However, not too much importance should be ascribed to this agreement in view of the neglect of certain higher-order terms which violates the compressibility sum rule, as discussed in Sec. VI. In Cs this effect is accentuated by the fact that the self-consistent dielectric function does not itself satisfy the compressibility sum rule as well as it does for smaller values of r_s^*.

In Fig. 10 the optimal values of r_c are plotted against r_s as open circles. The straight line is an approximate fit to the points given by

$$r_c \approx 0.53 r_s - 0.35 \quad . \tag{19a}$$

A linear relation between r_c and r_s seems plausible for the following reason: In the expression for the energy of the crystal derived in Sec. V, the terms which depend most strongly on r_s are found to be the electrostatic term E_{es} and the Hartree term E_H (see Fig. 12). The energy can therefore be expressed by

$$E = -1.792 Z^{5/3}/r_s + 3Z r_c^2/r_s^3$$
$$+ (\text{terms weakly dependent on } r_s) \;.$$

The equilibrium condition at zero pressure then gives

$$\frac{\partial E}{\partial r_s} \approx \frac{1.792 Z^{5/3}}{r_s^2} - \frac{9 Z r_c^2}{r_s^4}$$
$$= 0, \quad r_c \approx 0.45 r_s \;. \tag{19b}$$

The difference between (19a) and (19b) can be ascribed to the terms neglected above and the modification to the Hartree term discussed in Sec. V.

The crosses in Fig. 10 represent values which Ashcroft has found to fit other physical properties.[12,35,36] The two values given for Li are alternative fits to liquid-resistivity data; the values for Na and K are in good agreement with both Fermi-surface and liquid-resistivity data. Of the pairs of values given for Rb and Cs, the lower fits the liquid-resistivity and the upper the Fermi-surface measurements. In the latter case, however, nonlocal terms in the potential may be influencing the Fermi surface.[12] The spread in the values of r_c fitted to different properties of the same metal is an indication of lack of validity in the Ashcroft potential, and perhaps, also in the local pseudopotential concept; if it is not really valid, the value of r_c represents an average property of the potential which will be different for different types of measurement. Thus, the Ashcroft pseudopotential appears to be rather a good concept for Na and K but less so for Li, Rb, and Cs. In this respect, the phonon calculations are consistent with the conclusions derived from the other physical properties.

A different approach to the problem of correlations in the electron liquid has recently been given by Geldart and Taylor,[37] who attempt to calculate the lower-order Hartree-Fock terms exactly and approximate the higher-order terms with an interpolation scheme. The resulting dielectric function is used in a subsequent paper[16] to calculate the phonon-dispersion relations in Na with a single

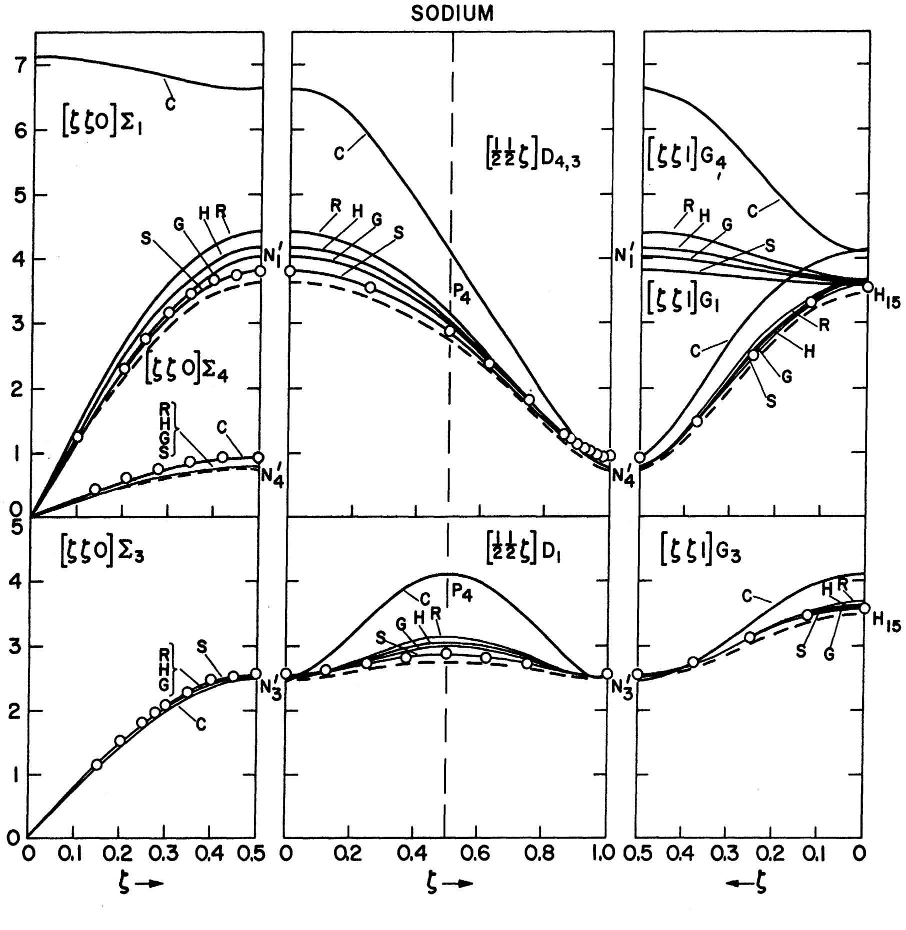

FIG. 4. Dispersion curves for Na. Notation as for Figs. 1 and 3.

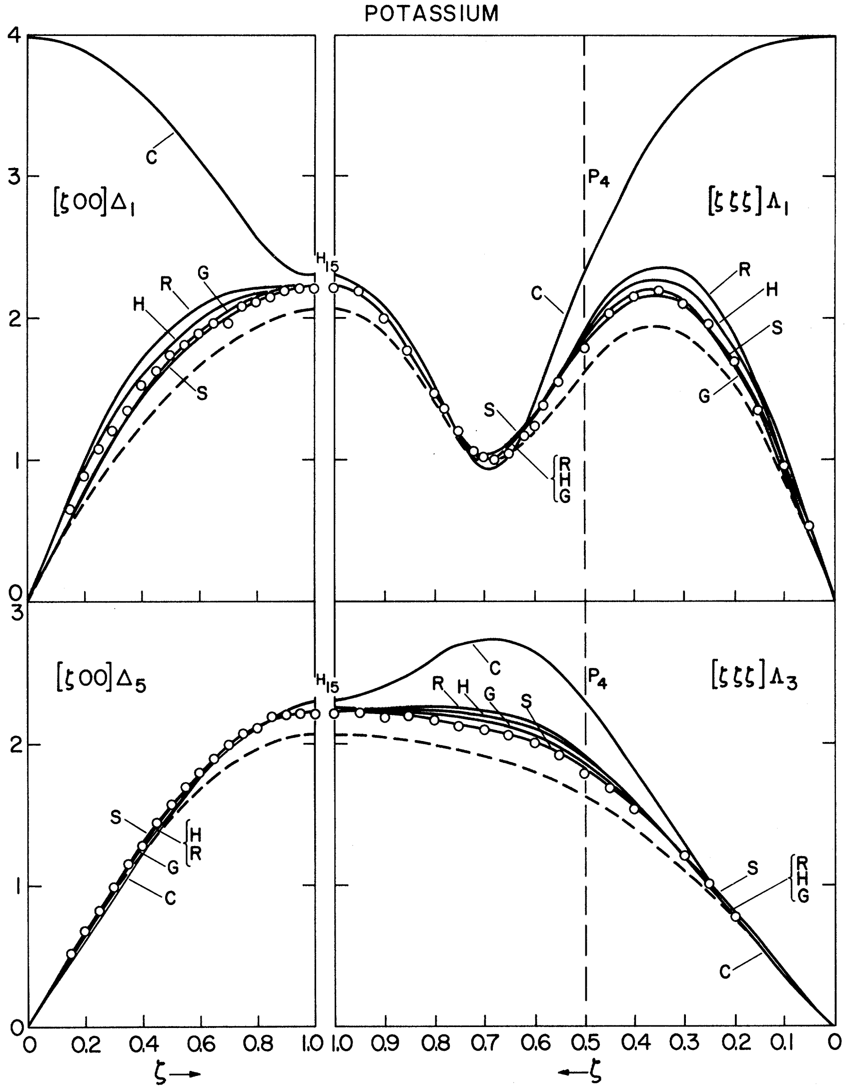

Fig. 5. Dispersion curves for K. Notation as for Figs. 1 and 3.

OPW pseudopotential, leading to rather good agreement with the experimental frequencies. Since the dielectric function is, at least for Na, considerably higher then the self-consistent one, one would need a larger value of r_c with the Ashcroft potential as used here. There does not, however, appear to be any criterion based on the lattice dynamics for preferring either this approach or the self-consistent treatment.

IV. PHONON LIFETIMES DUE TO ELECTRON PHONON INTERACTION

There are three processes limiting the lifetime of the phonon in a metal: scattering by defects, by other phonons, and by the conduction electrons. The first two are beyond the scope of this article; the last, however, is related to the imaginary part of the dielectric function, the real part of which was described in Sec. II. With the notation used there, the electron-phonon contribution to the phonon width 2Γ (full width at half-maximum) is given by[38]

$$2\Gamma_j(\vec{q}) = \frac{m^*(\pi\nu_p)^2}{\hbar k_F^2} \sum_{\vec{h}} \left(\frac{|\vec{e}_j\cdot(\vec{q}+\vec{h})|^2}{|\vec{q}+\vec{h}|^2} I(|\vec{q}+\vec{h}|) - \frac{|\vec{e}_j\cdot\vec{h}|^2 I(h)}{h^2} \right) , \qquad (20)$$

where

$$I(q) = \frac{k_F}{q} \frac{G(q)}{\mathfrak{F}(q/k_F)\epsilon'(q)} . \qquad (21a)$$

G and $\mathfrak{F}$ are defined in Eqs. (5) and (10), and ϵ' is defined as

$$\epsilon'(q)=1+[1-f(q)]Q_0(q) \quad . \tag{21b}$$

Calculations of 2Γ for the $[\zeta 00]$ direction in K were performed with the parameters used in the dispersion-relation calculation. The results are shown in Fig. 11, where it is seen that the use of different dielectric functions leads to differences of the order of 10% in 2Γ in the range of ζ where it is largest. However, at the zone boundary the values differ by nearly a factor of 2 for the extreme cases. Unfortunately, it is at present impossible to measure such quantities with neutron scattering, since they are masked by anharmonic effects. Even at 0 °K, the anharmonic widths due to zero-point motions are of the same order of magnitude.[32] Further, it is very difficult to measure absolute widths since this requires accurate knowledge of the instrumental resolution, and the usual procedure is to measure changes with temperature. The change of the electron-phonon widths with temperature is, according to Buyers and Cowley, extremely small.[32]

V. COHESIVE ENERGY AND EQUILIBRIUM

On the basis of the theory described in Sec. II, the total energy of the crystal can be written[35,39]

$$E=E_g+E_{es}+E_H+E_{bs} \quad , \tag{22}$$

where the energies are measure in Ry per ion. The terms on the right-hand side signify the energy of the interacting electron gas, the electrostatic energy of the lattice of positive ions in a uniform compensating negative charge, the Hartree energy representing the interaction of the conduction electrons with the nonelectrostatic part of the bare potential, and the band-structure energy representing

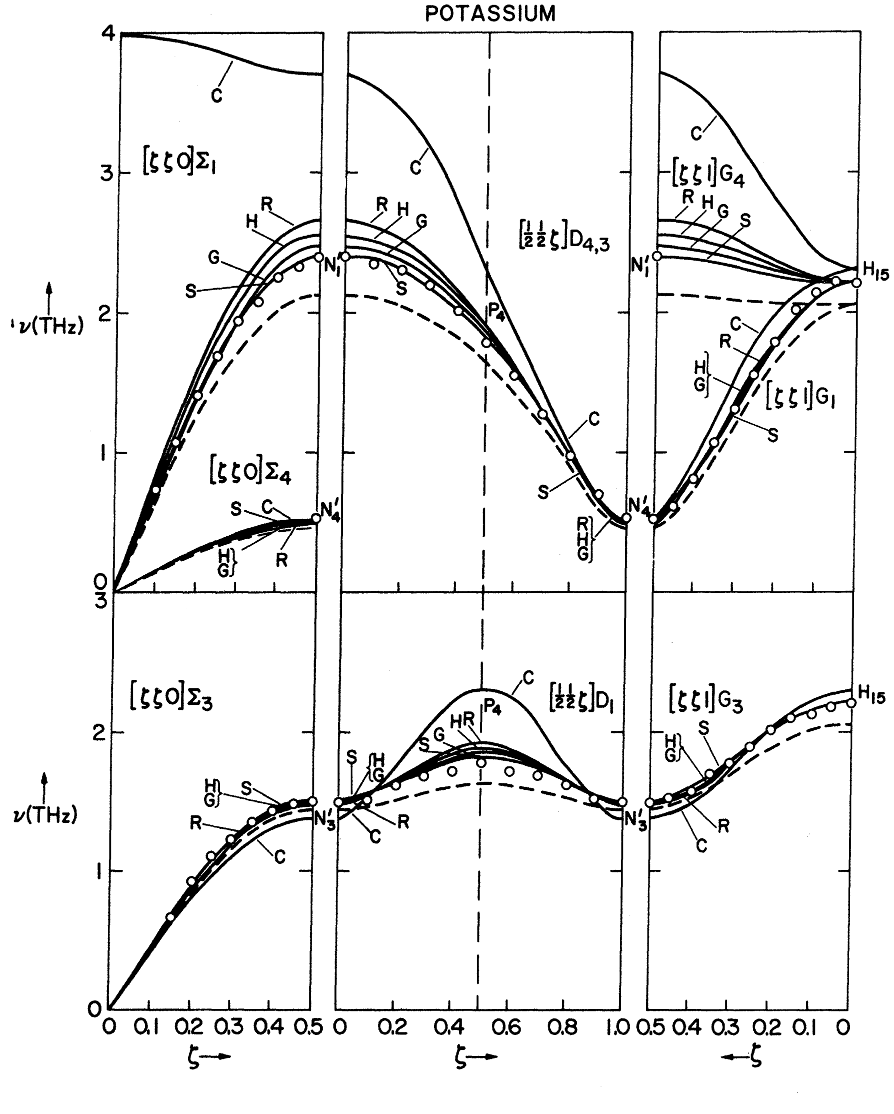

FIG. 6. Dispersion curves for K. Notation as for Figs. 1 and 3.

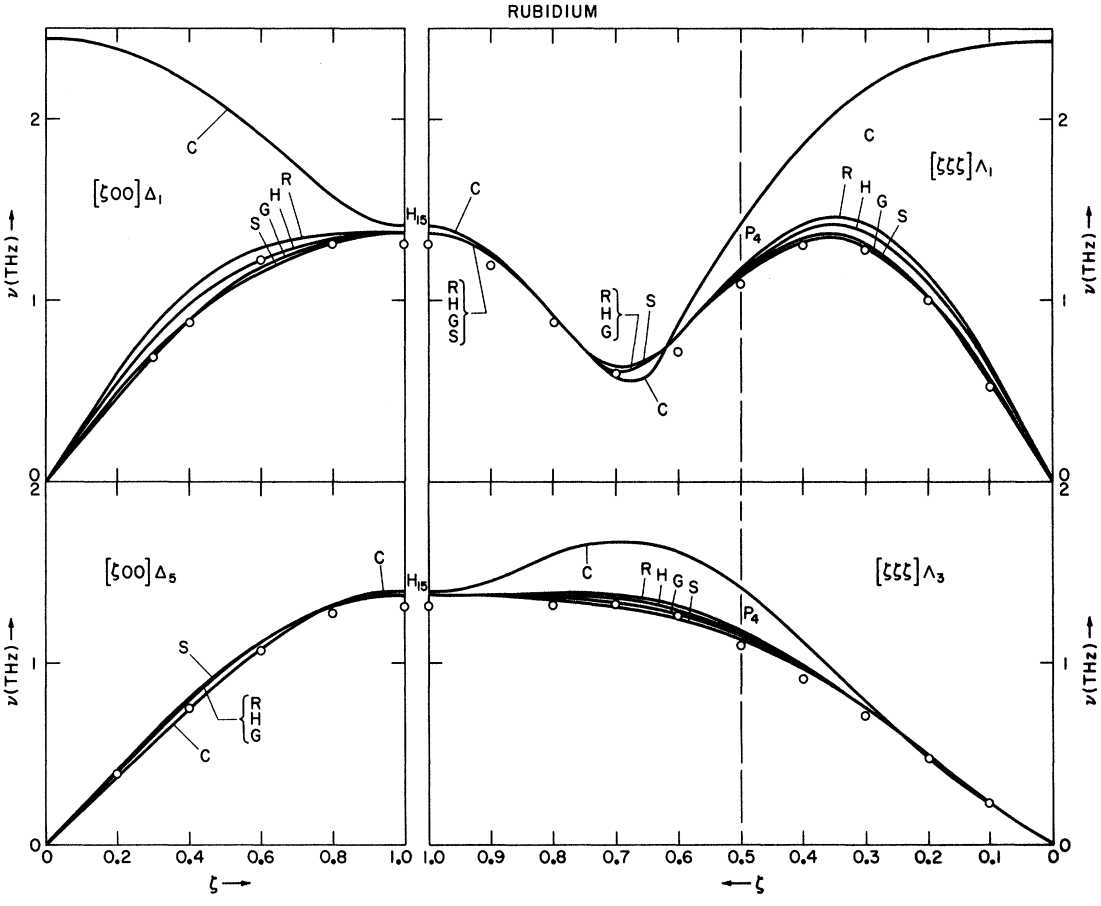

FIG. 7. Dispersion curves for Rb. Notation as for Fig. 1.

the ionic interaction via the conduction electrons. As discussed earlier, the different theories of the electron liquid give rather similar values for E_g. The interpolation scheme of Nozières and Pines[29] gives

$$E_g = 2.21Z/r_s^2 - 0.916Z/r_s - (0.115 - 0.031\ln r_s)Z \quad . \tag{23}$$

For a bcc lattice the electrostatic energy is

$$E_{es} = -1.792Z^{5/3}/r_s \quad . \tag{24}$$

The Hartree term is given by

$$E_H = Z \lim_{q\to 0}\left(w_q + \frac{4\pi Z e^2}{\Omega q^2}\right)\frac{2\hbar^2}{me^4} \quad , \tag{25a}$$

which for the Ashcroft potential of Eq. (7) simplifies to

$$E_H = 3Zr_c^2/r_s^3 \quad . \tag{25b}$$

The band-structure term is given to second-order perturbation theory as

$$E_{bs} = {\sum_{\vec{H}}}' F_{\vec{H}} \quad , \tag{26}$$

where

$$F_h = -(4\pi Z^2 a_0/\Omega h^2)G(h) \quad . \tag{27}$$

Figure 12 shows the results of calculations for $m^* = 1.00$ and $r_c = 1.69$, the parameters used for Na in the dispersion-relation calculations. (The energy is calculated for the static crystal, so that the atomic mass does not enter. The zero-point motions of Na are expected to have an energy around 0.001 Ry/atom.[14]) The band-structure energy was calculated using the same four dielectric functions, but the energy is not very sensitive to the screening used and only the extremal results are shown – those with RPA and self-consistent screening.

A correct calculation of E should have the derivative $\partial E/\partial r_s$ zero at the observed value of r_s (3.93 for Na). As seen from Fig. 12, this is not satisfied by the calculated energy, nor is the energy at $r_s = 3.93$ in agreement with the observed cohesive energy of 0.459 ± 0.002 (heat of sublimation, plus first-ionization energy).[13] Ashcroft and Langreth in a similar calculation[35] assert that the least accurate part is the assumption that the form of Eq. (7) for the pseudopotential is still valid in the long-wavelength limit. Since the pseudopotential parameter is fitted to short-wavelength data such as band gaps (by Ashcroft) or phonon frequencies (by us), this seems plausible. We therefore follow Ashcroft and Langreth's example and adjust E_H by multiplying Eq. (25b) by a constant factor to make $\partial E/\partial r_s = 0$ at $r_s = 3.93$. The necessary constant is 1.218 (for the self-consistent screening calculation – it is not too different for the calculations with the other dielectric functions) and the results of the modification are shown as dashed lines in Fig. 12. It is seen that not only is the equilibrium condition satisfied, but also, the total energy is brought into agreement with the observed cohesive energy.

Brovman, Kagan, and Holas[13] have made similar calculations with a pseudopotential that has a form similar to Eq. (7) but with an additional parameter. The equilibrium condition and the observed value of the elastic constant c_{44} are used to fix the two parameters, and reasonable agreement with measured cohesive energy and dispersion curves are obtained. The second parameter thus appears to have an equivalent effect to that produced by modifying Eq. (25b).

VI. COMPRESSIBILITY

The inverse compressibility B is given by double differentiation of the crystal energy

$$\Omega B \equiv \Omega^2 \frac{\partial^2 E}{\partial \Omega^2} = \frac{1}{9}\left[r_s \frac{\partial}{\partial r_s}\left(r_s \frac{\partial E}{\partial r_s}\right) - 3 r_s \frac{\partial E}{\partial r_s}\right] . \qquad (28)$$

The evaluation of the contributions B_g, B_{es} and B_H is straightforward. The contribution B_{bs} is more complicated because Eq. (27) depends on r_s explicitly through Ω and implicitly through h (which is proportional to $2\pi/a$) and k_F, the latter in the dielectric function. We ignore the weak volume dependence of parameters such as k_{TF}, ξ, and A, B in the various expressions for $f(q/k_{\mathrm{F}})$. By applying the operation

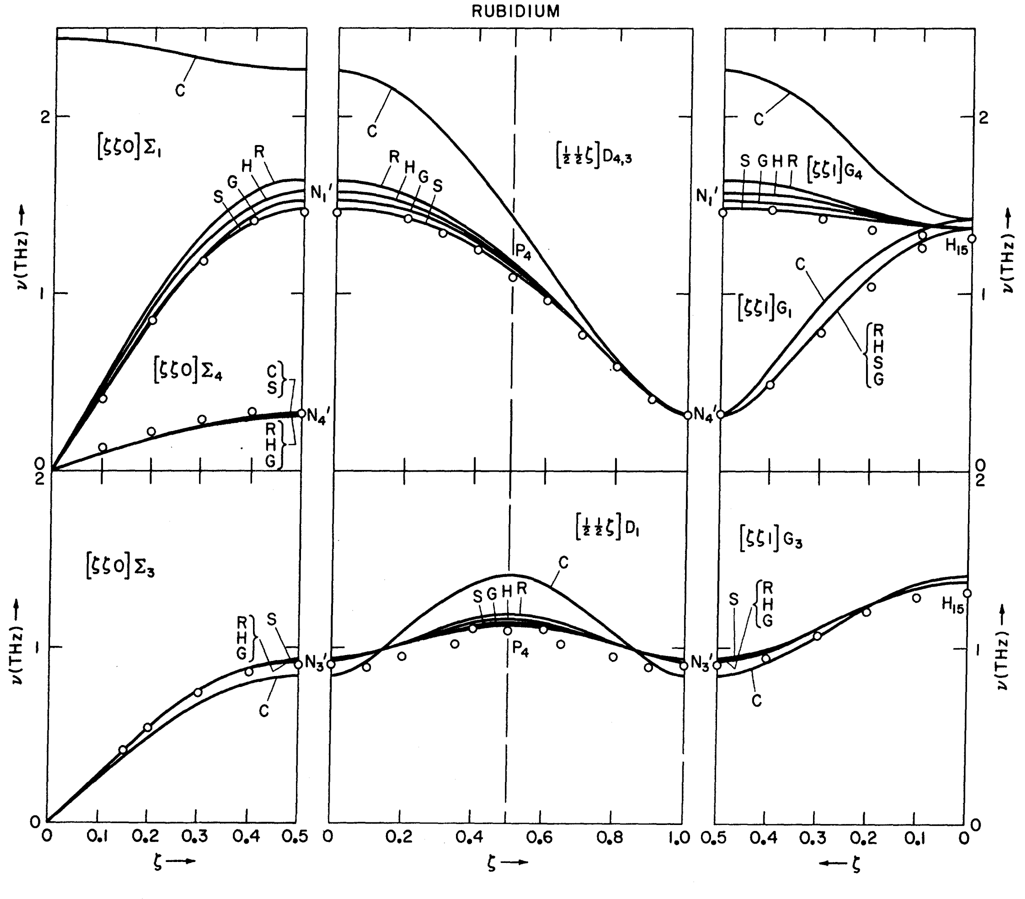

FIG. 8. Dispersion curves for Rb. Notation as for Fig. 1.

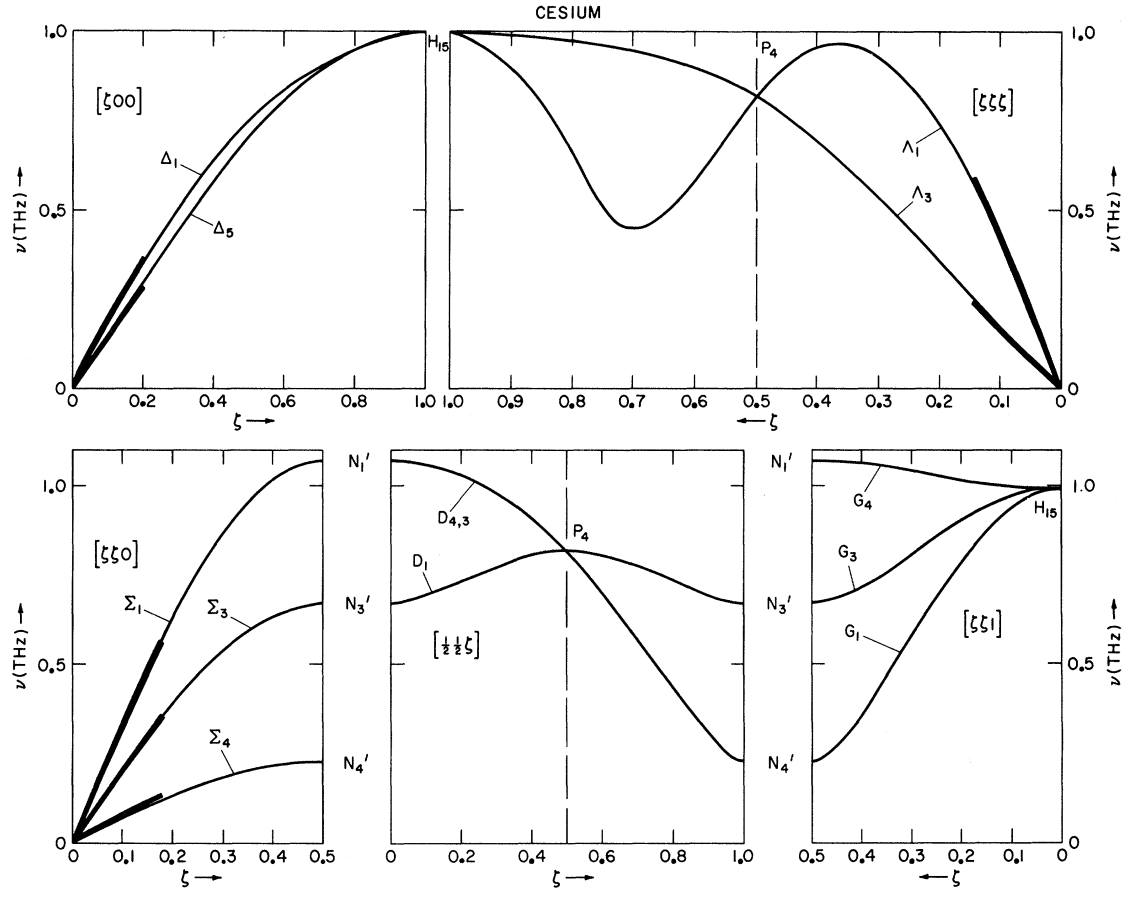

FIG. 9. Dispersion curves for Cs calculated with the self-consistent dielectric function. The heavy solid lines represent initial slopes derived from the measured elastic constants.

$$r_s \frac{\partial}{\partial r_s} = 3\Omega \frac{\Omega}{\partial \Omega} - h \frac{\partial}{\partial h} - k_F \frac{\partial}{\partial k_{\mathrm{F}}} \tag{29}$$

to E_{bs} in Eq. (26), we obtain

$$\Omega B_{\mathrm{bs}} = \tfrac{1}{9} \sum_{\vec{\mathrm{h}}}{}' \Big[4 - 12 h r_c \tan h r_c + 2 (h r_c)^2 (\tan^2 h r_c - 1) + \left(4 h r_c \tan h r_c + \frac{2}{\epsilon'(h)} - 6 \right) / \epsilon'(h) \Big] F_{\vec{\mathrm{h}}} \ , \tag{30}$$

where ϵ' is defined in Eq. (21b).

The question may now be asked: Is the compressibility evaluated from Eq. (28) equal to that evaluated from

$$\tilde{B} = \tfrac{1}{3}(c_{11} + 2c_{12}) \ , \tag{28$'$}$$

where the elastic constants are evaluated from the dispersion relation by the method of long waves?[40] This question for the crystal is analogous to that of the compressibility sum rule for the electron gas discussed in Sec. II C. Considered by Toya[1] but neglected by later workers, it has been conclusively answered by Lloyd and Sholl[41] and by Wallace[39] and considered in greater detail by Brovman and Kagan,[17] by Brovman, Kagan, and Holas,[42] and by Pethick.[18] These authors show that if the electron-phonon interaction is treated to second order in perturbation theory, Eq. (28) leads to the same result as Eq. (28′) only if the dielectric function obeys the compressibility sum rule and the term in k_{F} is left out of the differentiation in Eq. (29). Explicitly,

$$\Omega \tilde{B} = \Omega B - \Omega \Delta \ , \tag{31}$$

where

$$\Omega \Delta = \left[k_{\mathrm{F}} \frac{\partial}{\partial k_{\mathrm{F}}} + \frac{1}{9} k_{\mathrm{F}} \frac{\partial}{\partial k_{\mathrm{F}}} \left(k_{\mathrm{F}} \frac{\partial}{\partial k_{\mathrm{F}}} \right) + \frac{2}{9} k_{\mathrm{F}} \frac{\partial}{\partial k_{\mathrm{F}}} \left(h \frac{\partial}{\partial h} \right) \right] E_{\mathrm{bs}} \tag{32}$$

represents the terms arising from differentiation with respect to k_{F}. In the notation of Sec. II, $\Omega\Delta$

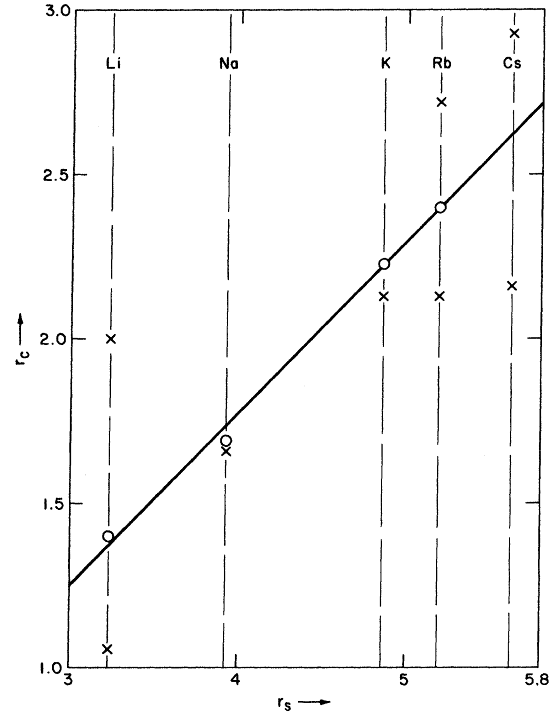

FIG. 10. Optimal values for r_c (open circles) plotted against r_s; the straight line is an approximate fit to these values. The crosses represent values fitted by Ashcroft to other physical data.

is given by

$$\Omega\Delta = \frac{1}{9}\sum_{\vec{h}}{}' \Big[-4hr_c \tanh hr_c \left(1 - \frac{\mathfrak{F}_1}{\mathfrak{F}} - Q_0 f_1\right) - \frac{\mathfrak{F}_2}{\mathfrak{F}} - 2\left(\frac{\mathfrak{F}_1}{\mathfrak{F}}\right)^2 - 9\left(\frac{\mathfrak{F}_1}{\mathfrak{F}}\right) - Q_0 f_2 - 5Q_0 f_1 + 8 - 2\left(1 - \frac{\mathfrak{F}_1}{\mathfrak{F}} - Q_0 f_1\right)\left(3 - \frac{\mathfrak{F}_1}{\mathfrak{F}} - Q_0 f_1\right)\Big/\epsilon' \Big] \frac{F_h}{\epsilon'} \ . \tag{33}$$

The subscripts 1 and 2 refer to single and double differentiations of the form $k_F\, \partial/\partial k_F$. Table II shows the quantities ΩB and $\Omega\Delta$ evaluated for Na from Eq. (28), (30), and (33), and $\Omega\bar{B}$ evaluated through Eq. (28′) from the long-wavelength limit of the dispersion relations calculated as described in Sec. III. It can be seen that Eq. (31) is satisfied for the Geldart and Vosko dielectric function and approximately satisfied for the self-consistent one. This is because the Geldart and Vosko screening is adjusted to obey the compressibility sum rule for the electron gas; the discrepancy in the case of the self-consistent screening is consistent with the small violation of the rule shown in Ref. 20, Fig. 4.

However, while $\Omega\bar{B}$ is in reasonable agreement with the measured inverse compressibility (obtained by extrapolating ultrasonic measurements to low temperature[39]) – which we expect because the calculated dispersion curves agree quite well with the neutron data even at smaller q – the full inverse compressibility ΩB is much too low. If we take account of the modification to the Hartree energy introduced in Sec. V to satisfy the equilibrium condition, we see from the last two lines of Table II that we then get reasonable agreement for the full compressibility. We have no estimates of the effect of terms beyond second order in E_{bs}.

If the same modification is applied to the calculation of $\Omega\bar{B}$, the result of course will be too high. This is due to the neglect of the (negative) term $\Omega\Delta$ which arises from terms in the dynamical matrix involving the electron-ion interaction to third and fourth order which contribute to second order in the long-wavelength limit. These terms arise when one takes into account the influence of the periodic lattice on the electron response function.[17,18] Thus, we have an estimate, within the limits of our formulation, of the effects of third- and fourth-order terms in the dynamical matrix *at long wavelengths*. If their contribution is much smaller further out in the Brillouin zone, our fitting of the parameter r_c to the dispersion curves as a whole on the basis of second-order perturbation theory will not be too seriously in error. An increasing contribution of the third- and fourth-order terms as q decreases would mean that, if we were to include them, we would have to modify the potential at small q to maintain agreement with experiment. This modification could be done either by introducing a second parameter[13] or by an *ad hoc* adjustment as we made in Sec. V, and which we showed brought the observed lattice parameter and cohesive energy into agreement with observation.

However, the situation is different if the third- and fourth-order terms remain significant over the entire Brillouin zone. In that case, our use of second-order perturbation theory in fitting to the observed dispersion relation will lead to an effective value of r_c which attempts to allow for the effects of the higher-order terms. If these terms have the same sign for larger q as for small q, i.e., negative, the effective value of r_c will be lower than the true one. The true value however should be used in the Hartree and band-structure terms in the cohesive energy. This would be consistent with the fact that we had to use a higher value of r_c in the Hartree term (which is much more sensitive to r_c than the band-structure term) to bring the equilibrium value of the lattice parameter into agreement with the observed one. However, a value increased

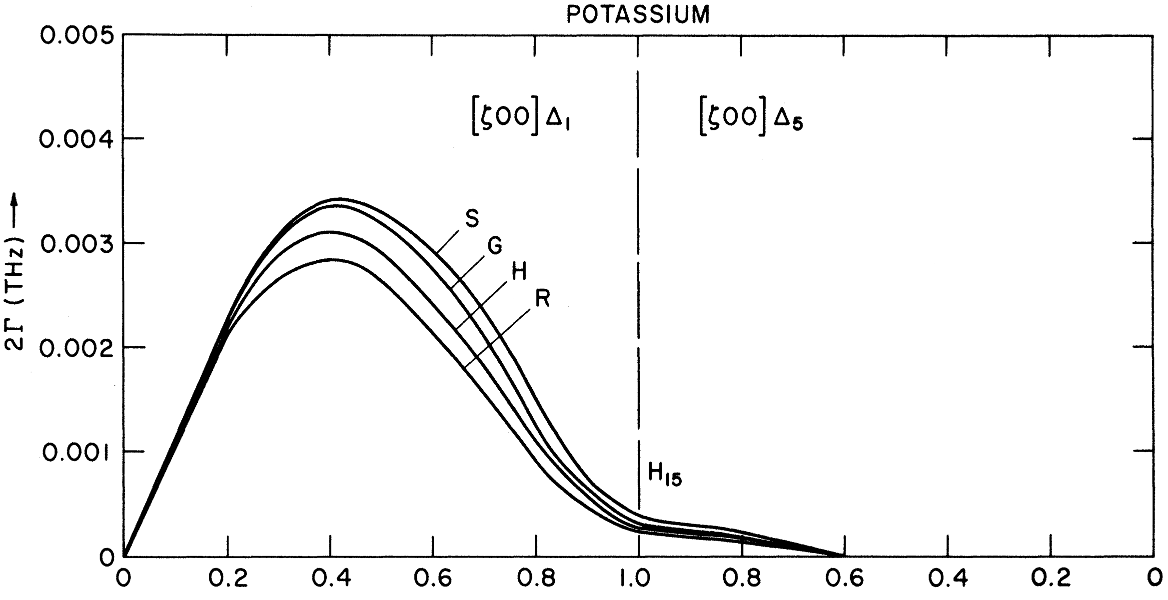

FIG. 11. Phonon widths due to the electron-phonon interaction for the [ζ00] direction in K.

by this amount – about 10% – would be in considerable disagreement with the values fitted to Fermi-surface and liquid-resistivity data. Our first explanation is thus perhaps more satisfactory in that all the data which refer to wave vectors of the order of the distances to the zone boundary are consistent with roughly similar values of the Ashcroft parameter.

VII. CONCLUSIONS

We have shown in Sec. III that the self-consistent dielectric function (used in conjunction with the harmonic approximation, second-order perturbation theory for the electron-ion interaction, and the Ashcroft pseudopotential) gives reasonable fits to the dispersion relations in the four alkali metals measured so far. For Na and K, the metals where a local pseudopotential is expected to be most applicable, the fitted values of the core radius parameter r_c are near those fitted to other data; the discrepancies, a few percent, are however significant since the dispersion relations are highly sensitive to r_c. For Li and Rb, where band effects are expected to play a greater role, there is a considerable spread in the values fitted to other data and ours lie somewhere in between.

In order to decide which of the dielectric functions gives the best agreement with the measured dispersion curves, one should look at the cases of Na and K where band effects are small, and so m^* must be approximately 1. Here we find that the self-consistent dielectric function gives considerably better agreement with the values of r_c used. None of the other dielectric functions would give as good agreement even if r_c was adjusted, since varying r_c has a very different effect from using another dielectric function, as is evident from the results shown in Figs. 3–6. However, in view of the uncertainties about the other items in the theory (see Sec. I), it

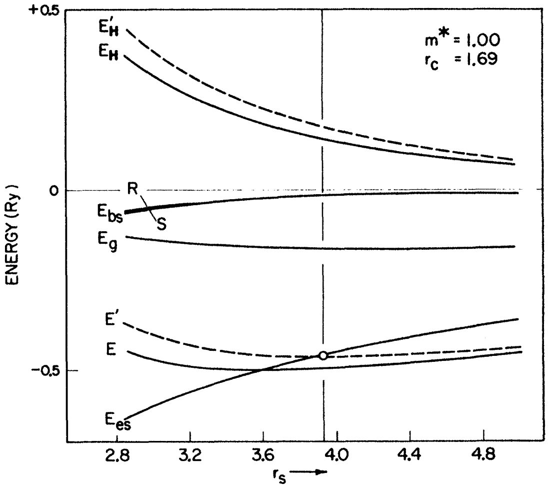

FIG. 12. Total crystal energy E and it components [Eqs. (22)–(27) of text]. The labels R and S for E_{bs} refer to evaluations with RPA and self-consistent screening, respectively. The dashed curves show the modification of E_H necessary to achieve the right equilibrium lattice parameter and the resulting total energy. The open circle shows the observed lattice parameter and cohesive energy.

TABLE II. Evaluation of inverse compressibility for Na (in Ry/atom).

Dielectric function	RPA	Hubbard	Geldart and Vosko	Self-consistent
ΩB[Eqs. (28) and (30)]	0.058	0.056	0.055	0.052
$\Omega\Delta$[Eq. (33)]	−0.052	−0.054	−0.056	−0.060
$\Omega B - \Omega\Delta$	0.110	0.111	0.111	0.112
$\Omega\tilde{B}$[Eq. (28′)]	0.224	0.166	0.111	0.118
$\Omega B'$ (modified E_H)	0.115	0.114	0.114	0.113
$\Omega\tilde{B}$ (observed[a])	0.129			

[a] See Ref. 14.

is impossible at present to use phonon dispersion curves in these metals as a rigorous test of a dielectric function.

Agreement with the observed cohesive energy, lattice parameter, and compressibility is, at least for Na, only achieved by means of an adjustment to the Hartree energy. This corresponds to an increase of about 10% in the value of r_c effective in the long-wavelength limit of the pseudopotential. Since the Ashcroft potential has generally been used to explain data involving shorter wavelengths, it is not too surprising for it to be somewhat inadequate at long wavelengths. It is satisfactory that a single adjustment brings all three quantities into reasonable agreement with the experimental values.

The difference between the values calculated for the compressibility by static and dynamic methods is quite large – nearly a factor of 2. Such discrepancies have been recently shown to be due to terms in the dynamical matrix involving the electron-ion interaction to third and fourth order which contribute to second order in the long-wavelength limit. We have no estimates of the contributions of the higher-order terms at shorter wavelengths. If these are significant, the values of r_c fitted to the measurements on the basis of the second-order theory will be effective rather than true values; this would contribute to the modification of r_c necessary in the cohesive energy calculation.

In conclusion, the self-consistent dielectric function appears to give a satisfactory formulation of the lattice dynamics of alkali metals as far as screening effects are concerned. It would be reasonable to use this formulation in calculations taking a more fundamental approach with regard to the pseudopotential and including higher-order terms in the electron-phonon interaction and anharmonic effects.

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PHYSICAL REVIEW B VOLUME 2, NUMBER 8 15 OCTOBER 1970

Magnetization Measurements of 0, 5, 10, and 20 at.% Al- Substituted First-Transition-Series Alloys

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Precision measurements on saturation moments of Cr-Fe, Fe-Co, Fe-Ni, and Co-Ni alloys with 0, 5, 10, and 20 at.% Al substitutions are reported; they show linear decrease of the mean atomic moment M at low Al concentration c. The negative slopes $-dM/dc$ vary with the electron to atom ratio $\mathfrak{z}$ of the transition metal: They show a maximum near $\mathfrak{z} \simeq 8.3$, as does the Slater-Pauling curve, and decrease to $-dM/dc \simeq 3.0\mu_B/$(Al atom) near pure nickel. At concentrations close to pure Fe, there is a sharp drop to $-dM/dc = 2.2\mu_B/$(Al atom). The moment decrease due to the Al solute is found to be in qualitative accord with $M = M_0(1-c) - c(V-n_s)\mu_B$, where $-(V-n_s)\mu_B$ is the moment induced by an impurity atom with valence V in the surrounding transition matrix with free-electron density n_s. This law takes for Ni as a particular case the known form $M = M_0 - cV\mu_B$. In the (Fe-Cr)-Al series the observed magnetic behavior is correlated with electronic-specific-heat data and critical concentrations for appearance of ferromagnetism.

I. INTRODUCTION

It is well known[1] that if Ni is alloyed with a nontransition metal which has V outer electrons, the mean atomic magnetic moment M decreases with the concentration c of the solute according to $M = M_0 - cV\mu_B$. Thus in the Ni alloys with Al, which has three valence electrons, $dM/dc = -3.0\mu_B/$(Al atom). On the other hand, if Fe is alloyed with Al or Si, the observed moment is known to decrease independently of the solute valence as $dM/dc = -2.2 = -M_0$, so that the effect on M seems to be only one of dilution. These two different kinds of behavior were also recently observed by neutron scattering measurements.[2,3] These observations would seem to indicate that a magnetic defect of roughly $-V\mu_B$ is formed in a Ni matrix around an Al impurity whereas an iron matrix is nearly unaffected by substituted Al atoms, which in this case behave as magnetic vacancies. On the other hand, magnetic investigations of several (Fe-Ni)-Al series lead to dM/dc values ranging from -2.5 to $-4.0\mu_B/$(Al atom).[4,5] In some series of these alloys, the moment decrease due to the Al impurity has values which are smaller than the expected valence value of $-3.0\mu_B/$(Al atom) observed in Ni-Al alloys.

Complementary conclusions indicating the complexity of the situation were reached by Srinivasan