

Computation of elastic constants and phonon frequencies in K-Cs melt

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Using experimental compressibility the elastic constant C_{11} of the alloy has been computed. C_{11} has also been computed through Schofield's equations and the computations have been iterated with various values of the empty-core radius r_c . Care, however, has been taken to ascertain that the values of r_c are near the free-ion value as given by Pauling. Thus a self-consistent method has been evolved in arriving at C_{11} . Further, the position of the effective-potential minima obtained through the empty-core model is found to be in good agreement with the maxima of the radial distribution function. The effective-potential functions at typical concentrations of Cs have been computed. The longitudinal and transverse phonon frequencies have been computed through the use of the Takeno-Goda equations. From the phonon frequencies the elastic constants have been computed. These values have been compared with those obtained from Schofield's I_1 and I_2 integrals. The elastic constants obtained by the two different methods are in fair agreement with each other. It is important to point out that the radial distribution functions are obtained from Fourier transformation of the total structure factors, which are found to be in very good agreement with experiment.

I. INTRODUCTION

Extensive theoretical and simulation studies of phonons in liquids have been made by Takeno and Goda,¹ Rahman,² Singwi, Skold, and Tosi,^{3,4} Chung and Yip,⁵ and Chihara.⁶ Recently Bhatia and Singh⁷ and Saxena and co-workers^{8,9} have made an extensive study of phonons in simple liquids, alloys, and amorphous solids. Liquids resemble amorphous solids in the sense that these substances lack long-range ordering as verified by neutron and x-ray scattering studies. Further Hafner made simulation and molecular dynamics studies of several glassy materials.^{10,11}

At this juncture it is important to point out that extensive experimental^{12,13} and theoretical investigations^{6,14,15} have been made on phonon dispersion calculations in liquid metals and glasses and not much work has been done in alloys. Thus the theoretical computations become all the more important in the investigation of phonons in alloys. Further it may be noted that Albas and his co-workers determined experimentally the structure factors of K-Cs liquid alloy¹⁶ and subsequently Rao and Das Gupta¹⁷ made theoretical calculations of the structure factors which are found to be in excellent agreement with the experimental results. Thus it is important to evaluate the dynamic properties of these alloys and use the radial distribution function obtained by Fourier transforming the total structure factor as computed by Rao and Das Gupta¹⁷ in evaluating the phonon frequencies and elastic constants. We choose two typical concentrations of K (60 and 40 at. % of K) in K-Cs alloy to investigate their properties.

II. METHOD

We use the pseudopotential method of approach in arriving at the partial and effective potentials of the alloys

in the computation of phonon dispersion curves and elastic constants. The required radial distribution function is obtained by Fourier transforming the computed total structure factors since these are found to be in excellent agreement with experiment.¹⁷

The total energy per ion U_T in the metal is given by¹⁸

$$U_T = U_{BS} + U_{es} , \quad (1)$$

where U_{BS} is the so-called band-structure energy. Enderby has given¹⁸ at great length the details of U_{BS} . He showed that

$$U_{BS} = \frac{1}{2N} \sum_{i,j} \phi_{ind}(|\mathbf{r}_i - \mathbf{r}_j|) + \frac{1}{N} \sum' F(k) , \quad (2)$$

where

$$\phi_{ind}(\mathbf{r}) = \frac{2}{N} \sum' F(k) \exp(-i\mathbf{k} \cdot \mathbf{r}) . \quad (3)$$

In the above equation the prime in the summation indicates that the self-part should be avoided. Further U_{es} is the direct electrostatic energy of interaction of the ions carrying a charge Z , $F(k)$ is the energy wave-number characteristic and the rest of the symbols have their usual significance. He finally showed that the effective interionic potential is given by

$$\phi(r) = \frac{Z^2 e^2}{r} + \frac{2}{\pi} \frac{Z^2 e^2}{r} \int F_N(k) \frac{\sin(kr)}{k} dk . \quad (4)$$

Here $F_N(k)$ is the normalized energy wave-number characteristic function and is given by

$$F(k) = \frac{2\pi Z^2 e^2}{k^2 \Omega} F_N(k) . \quad (5)$$

Some authors use Z^* in Eq. (5) as effective valence instead of Z . However, in the present calculations we used

the normal values of K and C_s which are taken as unity in the case of both the metals. Further $F_N(k)$ is given by

$$F_N(k) = \frac{k^4 \Omega^2}{16\pi^2 Z^2 e^4} \left[\frac{1}{\epsilon(k)} - 1 \right] |\psi_i(k)|^2. \quad (6)$$

Here Ω is the volume per electron and $\psi_i(k)$ is the Fourier transform of the Ashcroft pseudopotential which is given by^{19,20}

$$\psi_i(k) = -\frac{4\pi Z e^2}{\Omega k^2} \cos(Kr_c) \quad (7)$$

where r_c is the core radius. Further the dielectric response function $\epsilon(k)$ is given by

$$\epsilon(k) = 1 + \frac{f(\eta)}{2\pi a_0 k_F \eta^2 - f(\eta)G(\eta)}. \quad (8)$$

Here a_0 is the Bohr radius and $\eta = k/2k_F$. k_F is the Fermi wave vector. The function $f(\eta)$ is given by¹

$$f(\eta) = 1 + \frac{1+\eta^2}{2\eta} \ln \left| \frac{1+\eta}{1-\eta} \right|. \quad (9)$$

Further, the function $G(\eta)$ in Eq. (8) takes into account the exchange and correlation effects and is given by

$$G(\eta) = A [1 - \exp(-4B\eta^2)]$$

where $\eta = k/2k_F$ and A and B are parameters taken from the table given by Vashista and Singwi²¹ and these are functions of r_s , the average volume containing one electron. The values are taken from Table IV of Vashista and Singwi's paper.²¹ The exact values of A and B are inter-

TABLE I. Input parameters for K-Cs melt.

Metals	A	B	r_c (Å)
K	1.381	0.2370	1.15
Cs	1.311	0.2490	1.73

polated using Lagrange's formula and these are given in Table I.

As has been done by other workers²² we now obtain the effective potential to be used in the computation of phonon frequencies as

$$\phi_{\text{eff}}(r) = c_1^2 \phi_{11}(r) + 2c_1 c_2 \phi_{12}(r) + c_2^2 \phi_{22}(r). \quad (10)$$

Here c_i stands for the concentration of the i th species. Further we have to also modify Eq. (4) for the alloys as

$$\phi_{ij}(r) = \frac{Z_{ij}^2 e^2}{r_{ij}} + \frac{2}{\pi} \frac{Z_{ij}^2 e^2}{r_{ij}} \int F_{N,ij}(k) \frac{\sin(kr_{ij})}{k} dk \quad (11)$$

where $F_{N,ij}(k)$ is the corresponding normalized energy wave-number characteristic for the alloy and is given by

$$F_{N,ij}(k) = \frac{k^2 \Omega^2}{16\pi^2 Z_i Z_j e^4} \left[\frac{1}{\epsilon} - 1 \right] |\psi_i(k)\psi_j(k)| \quad (12)$$

and

$$k_F^{(12)} = (3\pi^2 \bar{Z} \rho^{(12)})^{1/3}. \quad (13)$$

Here \bar{Z} is the mean valency in the liquid alloy and $\rho^{(12)}$ is the mean number density.

We use Takeno-Goda equations in the evaluation of phonon frequencies and these are given by

$$\omega_L(k) = \frac{4\pi \rho^{(12)}}{M^{(12)}} \int dr g(r) \left[r \phi'_{\text{eff}}(r) \left[1 - \frac{\sin(kr)}{kr} \right] + [r^2 \phi''_{\text{eff}}(r) - r \phi'_{\text{eff}}(r)] \left[\frac{1}{3} - \frac{\sin(kr)}{kr} - \frac{2 \cos(kr)}{(kr)^2} + \frac{2 \sin(kr)}{(kr)^3} \right] \right], \quad (14)$$

$$\omega_T(k) = \frac{4\pi \rho^{(12)}}{M^{(12)}} \int dr g(r) \left[r \phi'_{\text{eff}}(r) \left[1 - \frac{\sin(kr)}{kr} \right] + [r^2 \phi''_{\text{eff}}(r) - r \phi'_{\text{eff}}(r)] \times \left[\frac{1}{3} + \frac{\cos(kr)}{(kr)^2} - \frac{\sin(kr)}{(kr)^3} \right] \right]. \quad (15)$$

Here $\phi'_{\text{eff}}(r)$ and $\phi''_{\text{eff}}(r)$ are the first and second derivatives of $\phi_{\text{eff}}(r)$ and $M^{(12)}$ is the mean mass.

In this connection it will be interesting to evaluate the elastic constants from the computed phonon frequencies and compare them with those obtained from other methods. An interesting and important set of equations that can be used in the evaluation of elastic constants are those of Schofield. Schofield derived the elastic constants in terms of two important integrals called I_1 and I_2 . These are defined by²³

$$I_1 = \frac{\rho}{2k_B T} \int_v g(r) r \frac{d\phi_{\text{eff}}(r)}{dr} d\mathbf{r}, \quad (16)$$

$$I_2 = \frac{\rho}{2k_B T} \int_v g(r) r^2 \frac{d^2\phi_{\text{eff}}(r)}{dr^2} d\mathbf{r}. \quad (17)$$

He further obtained equations for the elastic constants in terms of I_1 and I_2 integrals and these are

$$C_{11} = \rho k_B T (3 + 2I_1/15 + I_2/5), \quad (18)$$

$$C_{44} = \rho k_B T (1 + 4I_1/15 + I_2/15), \quad (19)$$

$$C_{12} = \rho k_B T (1 - 2I_1/5 + I_2/15). \quad (20)$$

It may be pointed out that I_1 and I_2 integrals are also connected to the first and second derivatives of the effective-potential function and the total radial distribution function obtained by the Fourier transformation of the total structure factor.

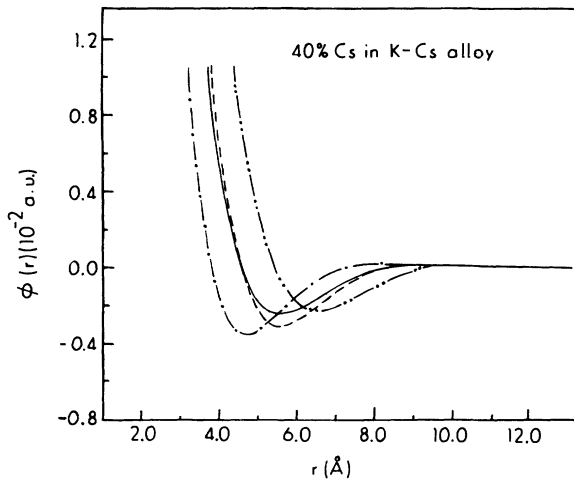


FIG. 1. Partial and effective-potential functions at 40 at. % Cs concentration in K-Cs alloy. $\phi_{K-K}(r)$ vs r graph is denoted by $\cdots\cdots\cdots$. $\phi_{Cs-Cs}(r)$ vs r graph is denoted by $-\cdots-\cdots-$. $\phi_{K-Cs}(r)$ vs r graph is denoted by $---$. $\phi_{eff}(r)$ vs r graph is denoted by $---$.

III. RESULTS AND DISCUSSION

The partial pair potentials have been computed from Eq. (11). The ionic radii have been chosen as suggested by Ashcroft^{19,20} and are nearly equal to those of the free ions. The pair potentials have been calculated for two typical concentrations, namely, 40 and 60 at. % of Cs. At this juncture it is important to point out that the experimental compressibilities of the alloy are known at different concentrations of Cs.¹⁶ Hence a set of r_c values have been scanned and the corresponding potential functions have been evaluated and were used to generate I_1 and I_2 integrals which in turn have been utilized to com-

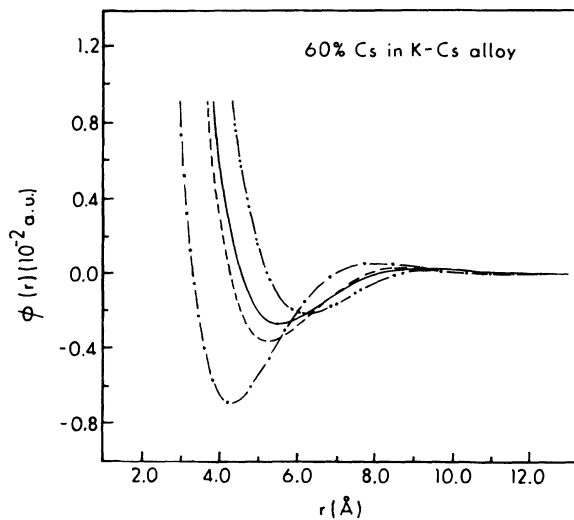


FIG. 2. Partial and effective-potential functions at 60 at. % Cs concentration in K-Cs alloy. The notation of the graphs is the same as in Fig. 1.

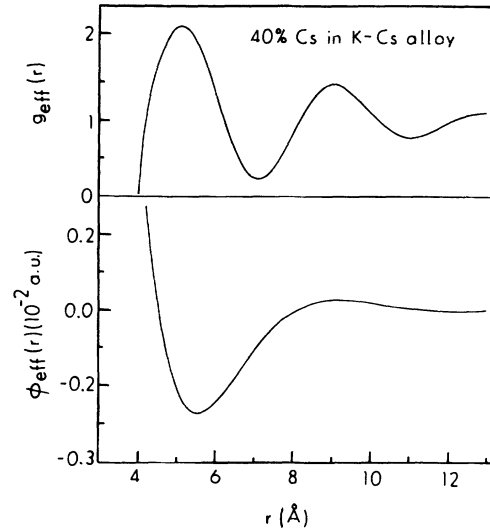


FIG. 3. Radial distribution function and the effective-potential function at 40 at. % Cs in K-Cs alloy.

pute C_{11} . This value of C_{11} is then compared with that obtained from experimental compressibilities¹⁶ (since $C_{11} = \gamma/\beta_T$). Thus the r_c is chosen in such a way as to give the correct C_{11} . Thus all the needed data for the computation of phonon frequencies have been verified indirectly with experiment. The input parameters are given in Table I. At this juncture it may be pointed out that at 60 at. % of Cs an increase in r_c for both the metals by 10% increases the elastic constant C_{11} by about 23% while a decrease of γ_c by 10% decreases the value of C_{11} by about 30%. On the other hand, at 40 at. % of Cs an increase or decrease in the r_c values increases or decreases the C_{11} values by about 30%. Thus it may be approximately concluded that a 10% increase in r_c values increases the C_{11} by about 25% while a decrease in 10% in r_c decreases the C_{11} values by about 30%.

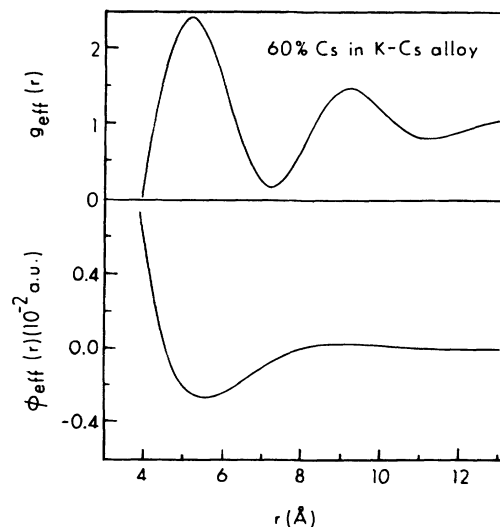


FIG. 4. Radial distribution function and the effective-potential function at 60 at. % Cs in K-Cs alloy.

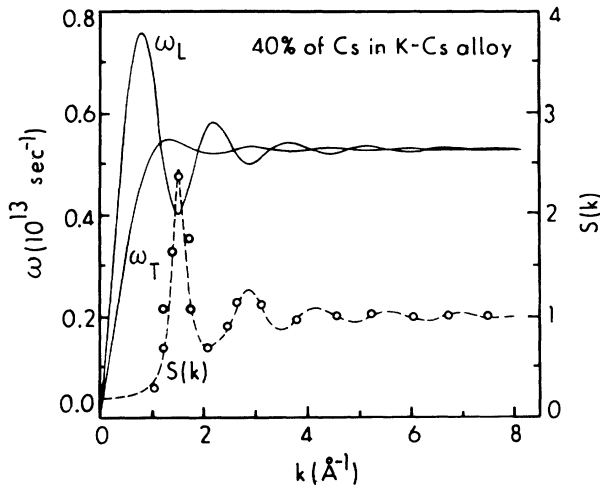


FIG. 5. Longitudinal and transverse phonon dispersion for 40 at. % Cs concentration in K-Cs alloy. Total structure factor $S(k)$ vs k for 40 at. % Cs concentration in K-Cs alloy; present calculated results, ----; $\circ \circ \circ \circ$, experimental results.

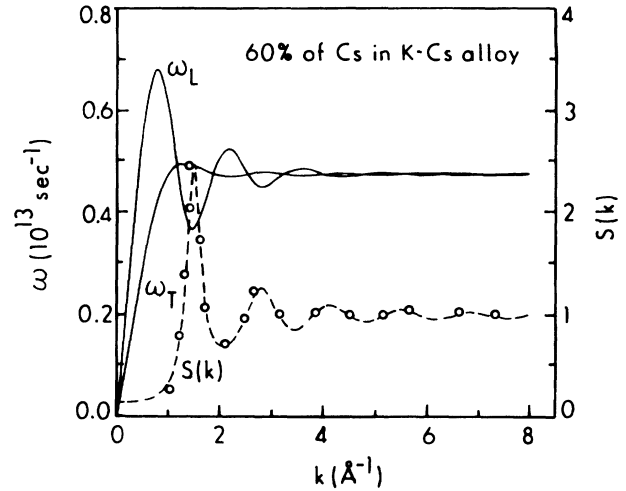


FIG. 6. Longitudinal and transverse phonon dispersion for 60 at. % Cs concentration in K-Cs alloy. Total structure factor $S(k)$ vs k for 40 at. % Cs concentration in K-Cs alloy; present calculated results, ----; $\circ \circ \circ \circ$, experimental results.

The effective and partial potentials at the two different concentrations are given in Figs. 1 and 2. For clarity the effective potential and the total radial distribution functions are shown in Figs. 3 and 4. It may be observed that the position of the potential minima and the corresponding radial distribution function maxima are nearly the same. Thus, for example, at 60 at. % of Cs the radial distribution function maximum and the potential minimum comes at 5.3 and 5.5 Å, respectively, while the corresponding values with 40 at. % of Cs are 5.1 and 5.4 Å, respectively. It may be observed that the effective-potential minimum and that of $\phi_{12}(r)$ at both the concentrations is found to lie in between $\phi_{11}(r)$ and $\phi_{22}(r)$. The potential-energy minimum of the smaller ion is greater in depth than that of the larger one. A similar trend can also be observed from the calculations of Hafner²⁴ on Na-K alloy. The phonon frequencies have been calculated with the help of Eqs. (14) and (15). It may be observed from Figs. 5 and 6 that the principal peak of the structure factor coincides nearly with the first minimum of $\omega_L(k)$ as

predicted by Bhatia and Singh.⁷ Further the $\omega_L(k)$ shows significant oscillations up to large values of k , while the transverse phonon frequencies reach the maximum at a larger value of k than the longitudinal phonons. The oscillations in $\omega_L(k)$ at large k clearly indicate the existence of collective excitations while the transverse phonons show no such oscillatory behavior. At low values of " k " both $\omega_L(k)$ and $\omega_T(k)$ change linearly with k and we compute C_{11} and C_{44} from the slopes of $\omega_L(k)$ and $\omega_T(k)$. As mentioned already we calculated C_{11} and C_{44} from I_1 and I_2 integrals and these values are also given in Table II. It is gratifying to find that they are in good agreement with each other. We also tabulate C_{11} as calculated from compressibilities. In these cases we assumed the specific-heat ratio γ as unity as experimental values are not available.

At this juncture it may be mentioned that C_{12} may be calculated if Cauchy's relation is assumed. This value may then be compared with that obtained from I_1 and I_2 integrals. These values are also given in Table II.

TABLE II. Elastic constants of K-Cs alloy at different concentrations obtained by different methods.

	From compressibility	From I_1 and I_2 integrals in units of 10^{10} dynes/cm ²	From phonon frequencies
Concentration of Cs in K-Cs alloy = 60 at. %			
C_{11}	1.84	1.84	1.90
C_{44}		0.55	0.54
C_{12}		0.73	0.82
Compressibility ¹⁶	54.4×10^{-12} cm ² /dynes		
Concentration of Cs in K-Cs alloy = 40 at. %			
C_{11}	2.32	1.94	2.10
C_{44}		0.57	0.57
C_{12}		0.80	0.96
Compressibility ¹⁶	43.1×10^{-12} cm ² dynes		

We also calculate C_{11} from compressibilities computed from Kirkwood-Buff's equation²⁵ which in turn is related with the partial direct correlation functions. The value so calculated is also given in Table II. Thus we arrive at an interconsistent method in the evaluation of elastic constants for the alloy at different concentrations of Cs.

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