

## **A FIRST-PRINCIPLE STUDY OF Cd-Zn BINARY ALLOY**

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*Received 21 July, 2010*

**Abstract:** The Harrison's First Principle (HFP) pseudopotential technique an orthogonalized plane wave (OPW) method has been applied to study the liquid electrical resistivity. Also, Knight shift, Fermi energy and electronic density of states (DOS) of liquid binary alloys of simple metals have been calculated. Reasonable agreement with experiment has been obtained. The binary alloy is regarded as being a quasi-single component system. We have also performed the first-principles calculation of the electronic band structure of Cd-Zn alloy employing full-potential Linearized augmented plane wave (FLAPW) method. Total energy minimization enables us to estimate the equilibrium volume, bulk modulus and its pressure derivative. We have also described the total density of states (DOS) and the partial DOS (PDOS) around the Fermi energy.

**Keywords:** Electrical conductivity; Knight shift; electronic density of states; binary alloy

### **1. Introduction**

The study of the transport properties of liquid metals binary alloys is important for various chemical as well as metallurgical purposes. The Cd-Zn alloys are a subject of matter of investigation since past few decades as this alloy consists of industrially important materials due to their application in nanocrystals (CdZnS) and optoelectronics (CdZnTe). Alcock calculated the thermodynamics of binary and dilute ternary alloys and discussed in terms of the electron theory of metals and the constant pair-wise binding model [1]. Landa et al. have calculated the velocity of sound in liquid Cd-Zn alloys [2]. Kumar et al. have presented the thermodynamic properties of mixing of Cd-Zn liquid alloy applying complex formation model (CFM) [3].

The well-known electrical conduction theory by Ziman (1961, 1967) [4, 5] for liquid metals and its extended form by Faber-Ziman (1965) [6] for liquid metal binary alloys using pseudopotential concept have been found very successful in predicting the electrical resistivity of several liquid metals and alloys. The presence of conduction electrons and their interaction with the background of positive ions is treated through the Harrison's First principle (HFP) pseudopotential technique which is a branch of orthogonalized plane wave formalism first proposed by Herring (1940) [7] and later developed by Philips and Kleinmann (1959) [8] and others. In the present paper, we have theoretically dealt with the structure, electrical resistivity, Knight shift, Fermi energy and electronic density of states of liquid binary Cd-Zn alloy. The structure factor  $S(\mathbf{k})$  needed for the present computation has been obtained through the hard sphere model via Percus-Yevik (PY) approximation along the lines of Ashcroft & Langreth [9] and Enderby & North [10].

The form factor  $w(\mathbf{k}, \mathbf{q})$  of the constituent metals has been derived through the well-known Harrison's First Principle (HFP) pseudopotential technique. From these two ingredients the properties under investigation have been computed. In the HFP pseudopotential technique, the

various interacting potentials are arrived at through fundamental considerations employing quantum mechanical and statistical mechanical approaches along with Poisson's equation. Although the technique was much rigorous than the model potential technique and also free from arbitrariness in choosing a model or its parameter, it lagged behind due to some cumbersome calculations involved. However, this was employed by King and Cutler [11] and Hafner [12] along with their co-workers. The HFP technique has been claimed to be superior to the model potential techniques as no arbitrary adjustable parameter is introduced and no arbitrary model is proposed. Further it has input requirements and is based on sound theoretical background (Harrison, 1966 [13]).

In spite of various favorable points regarding HFP technique the workers found that there are several considerations to be kept in mind while choosing the input parameters, the most significant among them was the energetic problem. In computation of the form factor the important input parameters are the eigenfunctions and eigenvalues of the core electrons represented by  $P_m(r)$  and  $\epsilon_m$ ,  $n$  and  $l$  being the quantum numbers of the core states. The basic characteristics of the pseudopotential technique which distinguishes it from the band structure calculations is the use of the first order perturbation theory and the factorization of crystal matrix elements into the form factor  $w(k,q)$  and the static structure factor  $S(k)$ . Both these ingredients are involved in all the physical properties studied in this project.

Usually, the researchers in this field obtained these input parameters from Herman-Skillman [14] or generated with some improvement in his program while some authors preferred to use the experimental eigenvalues. Clementi [15] also published his atomic structure calculations in which he provided the eigenfunctions and eigenvalues of elements of one-third of the periodic table.

In the present work, the HFP pseudopotential technique has been applied to evaluate the hard sphere diameters as a function of composition by minimizing the interionic pair potential for liquid binary alloys for the use in the determination of their partial structure factors. Then, in order to determine the physical aspects and explanation of the concentration dependence of the observed electrical resistivity in the liquid binary alloys of simple metals and other physical properties of the alloy considered for the study, we have also performed the first-principles calculation of the electronic band structure of Cd-Zn alloy employing the full-potential linearized augmented plane wave (FLAPW) method. Total energy minimization enables us to estimate the equilibrium volume, bulk modulus and its pressure derivative. This enables us to calculate the total density of states (DOS) and the partial DOS (PDOS) around the Fermi energy.

## 2. Formalism

### 2.1. Form Factor

The potential-dependent term is called the form factor  $w(\mathbf{k}, \mathbf{q}) = \langle \mathbf{k} + \mathbf{q} | w | \mathbf{k} \rangle$ . It is the Fourier transform of the crystal potential in the reciprocal lattice. The non-local screened form factor may be expressed as

$$w(\mathbf{k}, \mathbf{q}) = \left\{ \frac{v_q^{a,b} + v_q^c + v_q^d}{\varepsilon^*(q)} \right\} + \left\{ \frac{1 - G(q)}{\varepsilon^*(q)} \right\} v_q^f + W^R, \quad (1)$$

where  $v_q^{a,b}$ ,  $v_q^c$ ,  $v_q^d$ ,  $v_q^f$ ,  $W^R$ ,  $\varepsilon^*(q)$  and  $G(q)$  are the valence charge and core electron potential, conduction band-core exchange potential, conduction electron potential, screening potential, repulsive potential, the dielectric screening function and the exchange-correlation function respectively.

### 2.2. Structure Factor

The computation of partial structure factors through the formalism given by Ashcroft and Langreth [9] requires the hard sphere diameters  $\sigma_1$ ,  $\sigma_2$  of the first and second components of the alloy and packing density  $\eta$  which is related to  $\sigma_1$  and  $\sigma_2$  as given by

$$\eta = \frac{\pi}{6\Omega} \sum_{i=1}^2 C_i \sigma_i^3. \quad (2)$$

In the present work  $\sigma_1$  and  $\sigma_2$  have been evaluated by using the relation of Ashcroft and Langreth, 1967 [16]

$$V_{ip}(\sigma_i) = V_{\min} + \frac{3}{2} k_B T, \quad (3)$$

where  $\frac{3}{2} k_B T$  is the mean kinetic energy and  $V_{\min}$  the depth of the first minimum in the interionic pair potential given by Harrison, 1966 [10] as

$$V_{ip}(R_0) = \frac{Z_i^2 e^2}{R_0} \left[ 1 - \frac{2}{\pi} \int_0^\infty F_{ni}(q) \frac{\sin q R_0}{q} dq \right] \quad (i = 1, 2). \quad (4)$$

Here  $F_{ni}(q)$  is the normalized energy-wavenumber characteristic and is given by

$$F_{ni}(q) = - \left( \frac{q^2 \Omega}{2\pi Z_i^2 e^2} \right) F_i(q) \quad (5)$$

where  $F_i(q)$  in the local approximation is [13]

$$F_i(q) = - \left( \frac{\Omega q^2}{8\pi} \right) \left[ |W_i(q)|^2 \frac{\varepsilon^*(q) - 1}{\varepsilon^*(q)} \frac{1}{1 - G(q)} \right], \quad (6)$$

$\varepsilon^*(q)$  is the modified Hartree dielectric function given by

$$\varepsilon^*(q) = 1 + \{\varepsilon(q) - 1\} \{1 - G(q)\} \quad (7)$$

with  $\varepsilon(q)$  as the usual Hartree dielectric function.  $G(q)$  takes into account the correlation among the conduction electrons.

The three partial structure factors for a binary liquid mixture can be expressed in terms of the Fourier transform of direct correlation functions and are computed on the lines of Ashcroft and Langreth [9] and Enderby and North [10]:

$$S_{\alpha\alpha}(k) = [1 - n_\beta c_{\beta\beta}(q)] / D_d(q), \quad (8)$$

$$S_{\beta\beta}(k) = [1 - n_\alpha c_{\alpha\alpha}(q)] / D_d(q), \quad (9)$$

$$S_{\alpha\beta}(k) = (n_\alpha n_\beta)^{1/2} c_{\alpha\beta}(q) / D_d(q), \quad (10)$$

with

$$D_d(q) = [1 - n_\alpha c_{\alpha\alpha}(q)] [1 - n_\beta c_{\beta\beta}(q)] - n_\alpha n_\beta c_{\alpha\beta}^2. \quad (11)$$

$S_{\alpha\alpha}$ ,  $S_{\beta\beta}$  and  $S_{\alpha\beta}$  are called the Ashcroft-Langreth partial structure factors.

### 2.3. Electrical Resistivity

For the computation of resistivity of liquid metals, Ziman gave the diffraction model formula (Ziman, 1961 [4]), which has been quite successful especially when applied to simple metals. The derivation of the Ziman formula relies on the use of the relaxation time approximation for the Boltzmann equation and the use of pseudopotential for the interaction between an electron and an ion.

It was shown by Faber and Ziman (1965) [6] that the diffraction model formula for liquid metals proposed by Ziman (1961) [4] could easily be extended for binary alloys. For the sake of better representation, we express the resistivity of binary alloys as consisting of three distinct contributions, i.e.

$$R = R_{\alpha\alpha} + R_{\beta\beta} + R_{\alpha\beta}, \quad (12)$$

where the first two terms on right hand side arise due to the same particle correlation and the third term ( $R_{\alpha\beta}$ ) is due to the cross term scattering.  $\alpha$  and  $\beta$  represent here the constituent species of the binary alloys. The different contributions are given by

$$R_{\alpha\alpha} = (3\pi/\hbar|e|^2) (\Omega/Nv_F^2) 4 \int_0^1 c_1 |w_1(k, \eta)|^2 S_{11}(k) \eta^3 d\eta, \quad (13)$$

$$R_{\beta\beta} = (3\pi/\hbar|e|^2) (\Omega/Nv_F^2) 4 \int_0^1 c_2 |w_2(k, \eta)|^2 S_{22}(k) \eta^3 d\eta, \quad (14)$$

$$R_{\alpha\beta} = \left(3\pi/\hbar|e|^2\right)\left(\Omega/Nv_F^2\right)4\int_0^1 2(c_1c_2)^{1/2}|w_1(k,\eta)||w_2(k,\eta)|S_{12}(k)\eta^3d\eta. \quad (15)$$

In a composite form  $R$  can be expressed as

$$R = \left(3\pi/\hbar|e|^2\right)\left(\Omega/Nv_F^2\right)\left\langle\sum_{\alpha,\beta}(c_1c_2)^{1/2}S_{ij}(k)w_\alpha(k,\eta)w_\beta(k,\eta)\eta^3\right\rangle, \quad (16)$$

where  $\langle \rangle$  stands for

$$\begin{aligned} \langle \rangle = & 4\left[\int_0^1 c_1S_{11}(k)|w_1(k,\eta)|^2 + c_2S_{22}(k)|w_2(k,\eta)|^2 + \right. \\ & \left. + 2(c_1c_2)^{1/2}S_{12}(k)|w_1(k,\eta)||w_2(k,\eta)|\right]\eta^3d\eta, \end{aligned} \quad (17)$$

where  $w_1(k,\eta)$  and  $w_2(k,\eta)$  are the form factors of species 1 and 2 constituting the alloys;  $c_1, c_2$  are the concentrations  $S_{11}(k), S_{22}(k)$  and  $S_{12}(k)$  are the partial structure factors of the alloy, and  $\eta=q/2k_F$ .

#### 2.4. Knight shift

The frequency of nuclear magnetic resonance (NMR) associated with a metallic state is generally higher than the corresponding frequency for non-metallic state, such a shift of the NMR frequency is known as the Knight Shift. This arises due to the hyperfine contact interaction between the nucleus and the surrounding conduction electrons. The Knight shift (K%) is defined as the ratio of the frequency shift to the frequency at which the NMR is observed for the metallic state. The hyperfine interaction between conduction electrons and nuclear moment in metal provide a rich array of properties that can be studied through nuclear magnetic technique [Mahanti et al. (1970) [17], Knight (1956) [18] and Slater (1951) [19]]. Although the experimental techniques of measurement of the Knight shift have been developed much earlier, its theoretical development had been in a state of infancy and has been developed much later. The previous theoretical works (Ziman 1961 [4], Bradley et al. 1962 [20], Ziman 1964 [21], Muto et al. 1962 [22], Mishra and Roth 1969 [23], Mishra et al. 1990 [24], Tripathi et al. 1989 [25]) on the magnetic properties of metal substantiate the view that like electrical resistivity, the nearly free electron approximation is also valid for the theoretical treatment of various magnetic properties viz., Knight shift, magnetic susceptibility, Hall coefficient, etc. We shall now present its concise theory within the framework of pseudopotential technique. The Knight shift *vide* Pake (1955) [26] may be written as

$$K = \left(\frac{8\pi}{3}\right)\chi_P P_F \Omega. \quad (18)$$

Here  $\chi_P$  is the spin paramagnetic susceptibility of conduction electron per unit volume,  $\Omega$  is the volume of the crystal and  $P_F$  the average electron density at the site of the nucleus from the

conduction electrons with an energy  $E_F$ . Assuming the form factor  $w(\mathbf{k}, \mathbf{q})$  and structure factor  $S(\mathbf{k})$  to be spherically symmetric, we get

$$\frac{K_1}{K_0} = \frac{P_F^1}{P_F^0} = -\frac{3Z}{4E_F k_F^2} \int_0^\infty S(k) w(\mathbf{k}, \mathbf{q}) q \ln \left| \frac{q+2k_F}{q-2k_F} \right| dq, \quad (19)$$

where  $P_F^0$  and  $P_F^1$  are the zero-order and first-order terms,  $K_0$  and  $K_1$  are zero order and first-order terms,  $E_F$  is the Fermi energy,  $k_F$  is the Fermi wave vector and the other symbols have their usual significance. For the alloys the integrand of Eq. (19) is replaced by the expression

$$I_K = \int_0^\infty \left[ c_1 S_{11}(k) w_1(\mathbf{k}, \mathbf{q}) + c_2 S_{22}(k) w_2(\mathbf{k}, \mathbf{q}) + 2(c_1 c_2)^{\frac{1}{2}} w_1(\mathbf{k}, \mathbf{q}) w_2(\mathbf{k}, \mathbf{q}) S_{12}(k) \right] q \ln \left| \frac{q+2k_F}{q-2k_F} \right| dq \quad (20)$$

Also  $Z$ ,  $E_F$  and  $k_F$  are those of the alloys evaluated through  $X = c_1 X_1 + c_2 X_2$  where  $c_1$  and  $c_2$  are the concentrations of the constituents,  $X$ ,  $X_1$ ,  $X_2$  are the input parameters of the alloy viz.,  $Z$ ,  $E_F$ ,  $k_F$ ,  $\Omega_0$  etc.

## 2.5. Fermi energy and Density of states

The electronic structure of solids and liquids can be precisely described through an accurate knowledge of its electronic states. There are a number of theoretical methods of determining different aspects of electronic structure of liquid metals among which the density of states and the Fermi energy have significant bearing. The calculations of Fermi energy  $E_F$  and the density of states  $N(E_F)$  for simple liquid metals have been reported by Schneider and Stoll (1967) [27], Ashcroft (1968) [28], Shaw and Smith (1969) [29], Srivastava and Sharma (1969) [30], Jena and Halder (1971, 1972) [31, 32], Stoll et al. (1971) [33], Halder (1973) [34], Ichikawa (1973) [35], Dixit and Nigam (1973) [36], Srivastava (1974, 1975) [37, 38] and Kumar and Hemkar (1977) [39]. The study of density of states have been made by Watabe and Tanaka (1964) [40], Ballentine (1966) [41], Chan and Ballentine (1971, 1972) [42, 43], Itami and Shimoji (1972) [44], Ballentine and Chan (1973) [45] & Kuroha and Suzuki (1974) [46] using various pseudopotential and the Green function theory. It does not appear that the Harrison's first-principle pseudopotential has been used for the study of these properties except for Thakur (1980) [47] for alkali metals. We, therefore, present our work on the Fermi energy and density of states of multivalent liquid metals on the basis of the first-principle pseudopotential approach of Harrison. In the framework of conventional perturbation theory, the energy of liquid metal is expressed as (Harrison, 1966 [10]),

$$E(K) = \frac{\hbar^2 K^2}{2m} + \langle \mathbf{k} | w | \mathbf{k} \rangle + \frac{2m}{\hbar^2} \sum_q \frac{S(\mathbf{k}) |N \langle \mathbf{k} + \mathbf{q} | w | \mathbf{k} \rangle|^2}{|\mathbf{k}|^2 - |(\mathbf{k} + \mathbf{q})|^2}. \quad (21)$$

Here  $S(\mathbf{k})$  is the liquid structure factor and is non-zero for a liquid,  $\langle \mathbf{k} | w | \mathbf{k} \rangle$  are the matrix elements for the crystal potential (W),  $|N\langle \mathbf{k} + \mathbf{q} | w | \mathbf{k} \rangle|$  are the unscreened form factor,  $m$  is the electronic mass and  $\hbar = h/2\pi$ , where  $h$  is the Planck constant.

At the melting point, the above expression is reduced to (Schneider and Stoll, 1967 [27])

$$E(K) = \frac{\hbar^2 K^2}{2m} + \frac{2m}{\hbar^2} \sum_q \left( \frac{S(\mathbf{k}) w^2(\mathbf{q})}{|\mathbf{k}|^2 - |(\mathbf{k} + \mathbf{q})|^2} - \frac{S(\mathbf{k}) w^2(\mathbf{q})}{q^2} \right), \quad (22)$$

where  $w(\mathbf{k}, \mathbf{q}) = w(\mathbf{q})$ .

Replacing  $\Sigma$  by  $\frac{\Omega_0}{8\pi^3} \int d^3q$  and putting  $k = k_F$ , we obtain for the energy at the Fermi level,

$$E(k_F) = \left( \hbar^2 k_F^2 / 2m \right) + \Delta(k_F) - \Delta(0), \quad (23)$$

where

$$\Delta(k_F) = -\frac{m\Omega_0}{4\pi^2 \hbar^2 k_F^2} \int_0^\infty q S(k) w^2(\mathbf{q}) \ln \left| \frac{2k_F + q}{2k_F - q} \right| dq \quad (24)$$

and

$$\Delta(0) = -\frac{m\Omega_0}{4\pi^2 \hbar^2} \int_0^\infty S(k) w^2(\mathbf{q}) dq. \quad (25)$$

For the alloy the integrand of Eq. (24) is replaced by

$$I_E = \int_0^\infty \left[ c_1 S_{11}(k) |w_1(\mathbf{k}, \mathbf{q})|^2 + c_2 S_{22}(k) |w_2(\mathbf{k}, \mathbf{q})|^2 + 2(c_1 c_2)^{1/2} w_1(\mathbf{k}, \mathbf{q}) w_2(\mathbf{k}, \mathbf{q}) S_{12}(k) \right] q \ln \left| \frac{q + 2k_F}{q - 2k_F} \right| dq \quad (26)$$

and the integrand of Eq. (25) is replaced by

$$I'_E = \int_0^\infty \left[ c_1 S_{11}(k) |w_1(\mathbf{k}, \mathbf{q})|^2 + c_2 S_{22}(k) |w_2(\mathbf{k}, \mathbf{q})|^2 + 2(c_1 c_2)^{1/2} w_1(\mathbf{k}, \mathbf{q}) w_2(\mathbf{k}, \mathbf{q}) S_{12}(k) \right] dq. \quad (27)$$

Here  $\Omega_0$  is the atomic volume related to the Fermi wave vector  $k_F$  and valence  $Z$  by relation

$$\Omega_0 = 3\pi^2 Z / k_F^3. \quad (28)$$

It has been assumed that  $S(k)$  and  $w(q)$  are isotropic.

The expression for the density of states of liquid metal is given as

$$N(E_F) = \frac{k_F^3 \Omega_0}{\pi^2} \left[ \left| \frac{\partial E(k)}{\partial k} \right|_{k=k_F} \right]^{-1} = \frac{k_F^2 \Omega_0}{\pi^2} \left[ \frac{\hbar^2 k_F}{m} + \frac{m\Omega_0}{4\pi^2 \hbar^2 k_F^2} \int_0^\infty q S(k) w^2(\mathbf{q}) \ln \left| \frac{2k_F + q}{2k_F - q} \right| dq + \frac{m\Omega_0}{\pi^2 \hbar^2 k_F} \int_0^\infty \frac{S(k) w^2(q) q^2 dq}{(4k_F^2 - q^2)} \right]^{-1}. \quad (29)$$

The first integrand of Eq. (29) is the same as  $I_E$  and the second integrand for alloy becomes

$$I_N = \int_0^\infty \left[ c_1 S_{11}(k) |w_1(\mathbf{k}, \mathbf{q})|^2 + c_2 S_{22}(k) |w_2(\mathbf{k}, \mathbf{q})|^2 + 2(c_1 c_2)^{1/2} w_1(\mathbf{k}, \mathbf{q}) w_2(\mathbf{k}, \mathbf{q}) S_{12}(k) \right] \frac{q^2}{(4k_F^2 - q^2)} dq. \quad (30)$$

Also  $Z$ ,  $E_F$  and  $k_F$  are those of the alloys evaluated through  $X = c_1 X_1 + c_2 X_2$  where  $c_1$  and  $c_2$  are the concentrations of the constituents,  $X$  are the input parameters of the alloy viz.,  $Z$ ,  $E_F$ ,  $k_F$ ,  $\Omega_0$ , etc. and  $X_1$ ,  $X_2$  are those of the constituents.

### 3. Results and Discussion

#### 3.1 Structure

The values of  $R_0$  that satisfy (3) have been taken as the hard sphere diameters.  $\sigma_1$  and  $\sigma_2$ , as a function of composition, have been evaluated for the system. The partial structure factors have been computed using these hard sphere diameters through the expression given by Ashcroft and Langreth, 1967 [16].

The partial structure factors of Cd-Zn at  $T = 450^\circ\text{C}$  have been computed. The equiatomic structure factors have been graphically represented in Fig. 1. The characteristic nature of the partial structure factors has been reproduced. The principal peaks of  $S_{11}(k)$  and  $S_{22}(k)$  lie near  $k / k_F = 1.8$  and that of  $S_{12}(k)$  lies between them. Their principal peak heights are 1.906, 1.782 and 0.848, respectively.

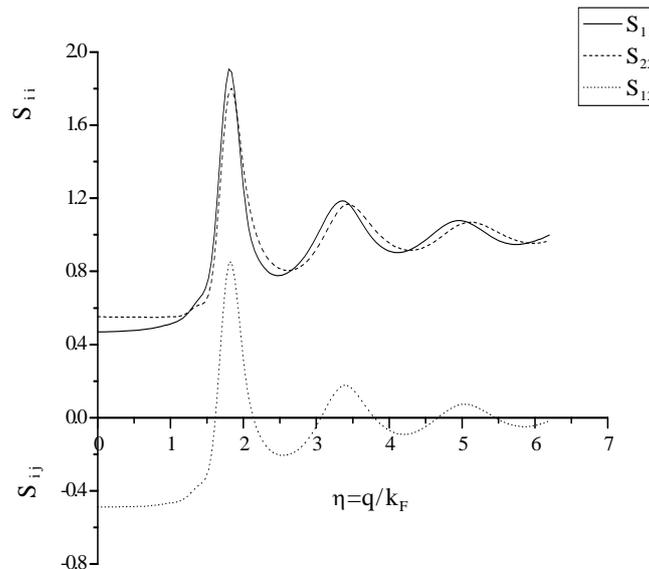


Fig. 1. Partial Structure Factors of Cd-Zn at equiatomic composition.

The computed structure factors show the behavior of random mixing without a subpeak or asymmetry of the first peak. The position of the first principal peak of the partial structure factors

and the crossover point  $q_0$  of the form factor decides the range of  $\eta = q / k_F$  which is most contributing to the resistivity integrands for the alloy.

### 3.2 Electrical resistivity

For the study of the electrical resistivity of liquid alloys we need for the partial structure factors at the melting temperature for different concentrations. Since the experimental knowledge on partial structure factors is limited to a few systems only at the equiatomic composition, we undertake a theoretical approach based on Percus-Yevik (PY) approximation on the lines of Ashcroft and Langreth (1967) [9] and Enderby & North (1968) [10]. Their natures have been shown in Fig. 1 for the alloy Cd-Zn at the equiatomic composition.

The form factors required for this computation were computed from Eq. (1). But it was found that some form factors, which reproduced good electrical resistivity with the experimental structure factors in case of metals, did not perform well in alloys. However, slight change in the choice of input parameters, e.g.,  $\beta$  or exchange correlation function improved the agreement in case of Cd-Zn. For Zn the form factor evaluated through eigenvalues of Clementi with  $\alpha = \alpha_{vt}$  and  $\beta = 5/8$  using V-S exchange correlation gave satisfactory agreement in case of Cd-Zn whereas that with HS eigenvalues  $\alpha = 2/3$ ,  $\beta = 5/8$  and Shaw form of exchange reproduced the resistivity of pure Zn more satisfactorily.

For Cd-Zn the form factor of Cd component is that evaluated through the Hubbard–Sham form of exchange, the other inputs being the same as the previous computations. However, for Zinc the form factor has been evaluated with C eigenvalues along with  $\alpha = \alpha_{vt}$ ,  $\beta = 5/8$  and V-S form of exchange correlation to yield the better agreement of the calculated values with the experimental resistivity of the alloy. The experimental data have been read from graph of [48].

The good agreement may be indicative of the free electron behavior of these alloys. The slight discrepancies wherever they occur may be attributed to the failure of approximations involved in the theoretical framework or to the formation of chemical complexes, which is quasistable in nature. For further improvement the complex formation model proposed by Bhatia and Thornton may be used. The resistivity in Cd-Zn varies almost linearly with concentration (Fig. 2). Since, in this case  $Z_m = 2$  (i.e.,  $Z_m = c_\alpha Z_\alpha + c_\beta Z_\beta$ ) so this system may have either negative or positive (weakly temperature dependent) one coefficient of resistance. Also, this is supported by the fact that this alloy is regarded as being a quasi-single component system, i.e., a negative temperature coefficient is expected when  $2k_F$  is close to the position of main peak in the structure factor (or  $Z_m \approx 2$ ) and that is what we have observed in this case.

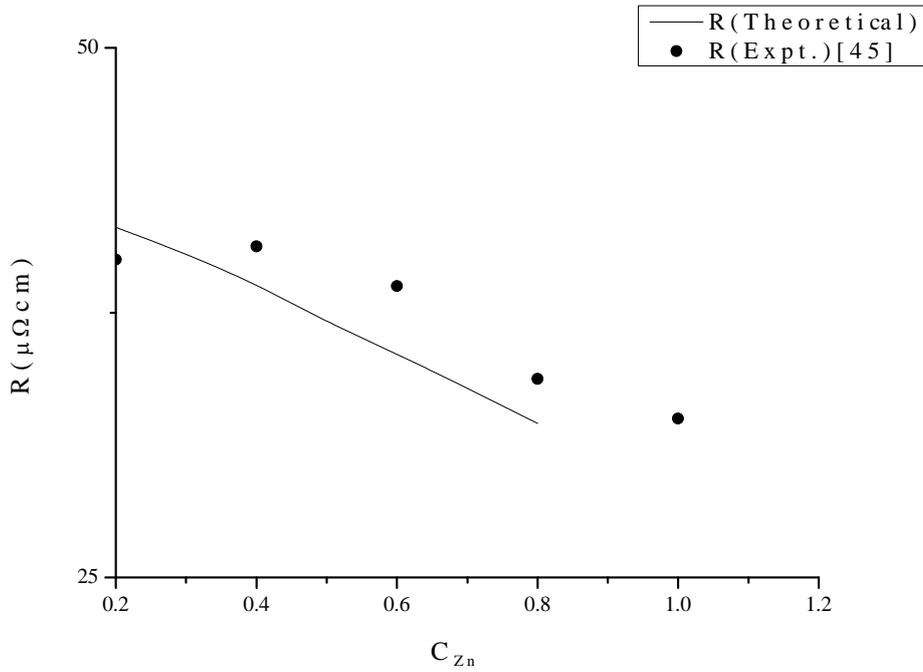


Fig. 2. Concentration dependence of electrical resistivity of Cd-Zn.

### 3.3 Physical Properties

The computed form factors, which have been found suitable for the evaluation of electrical resistivities of the alloys under investigation, have been further put to test through the computation of the Knight shift ( $K\%$ ), its concentration dependence and the Fermi energy ( $E_F$ ) in eV along with the electronic density of states for the alloys under investigation. It is to be mentioned that the integrand of the Knight shift involves within itself the form factor  $w(\mathbf{k}, \mathbf{q})$  linearly. Hence the computed Knight shift may be taken as a test for the accuracy of the form factor both in respect of magnitude and sign. Other physical quantities like electrical resistivity, Fermi energy and density of states have their integrands involving the square of the form factor and thus they are only concerned with the magnitude of the form factor. At the equiatomic composition, the Knight shifts are in fairly good agreement with their ideal values obtained through experimental data viz., for Cd-Zn  $(K\%)_{th} = 0.716$ ,  $(K\%)^{id} = 0.566$ .

The study of computed results reveals that for Cd-Zn  $(K\%)_{th} = 0.716$  against  $(K\%)_A = 0.795$ ,  $(K\%)_B = 0.337$  and  $(K\%)^{id} = 0.586$ . The Fermi energy  $(E_F)_{th} = 8.06$  whereas  $(E_F^0)_A = 7.46$ ,  $(E_F^0)_B = 9.39$ , and  $(E_F^0)^{id} = 8.425$  eV. The electronic density of states  $N(E_F)_{th} = 0.346$  whereas  $N(E_F^0)_A = 0.402$ ,  $N(E_F^0)_B = 0.319$  and  $N(E_F^0)^{id} = 0.36$  eV<sup>-1</sup>. The  $K_0$  value of the constituent metals is that evaluated through zero-order OPW method (Faber, 1972 [49]; Shimoji, 1977 [50]).

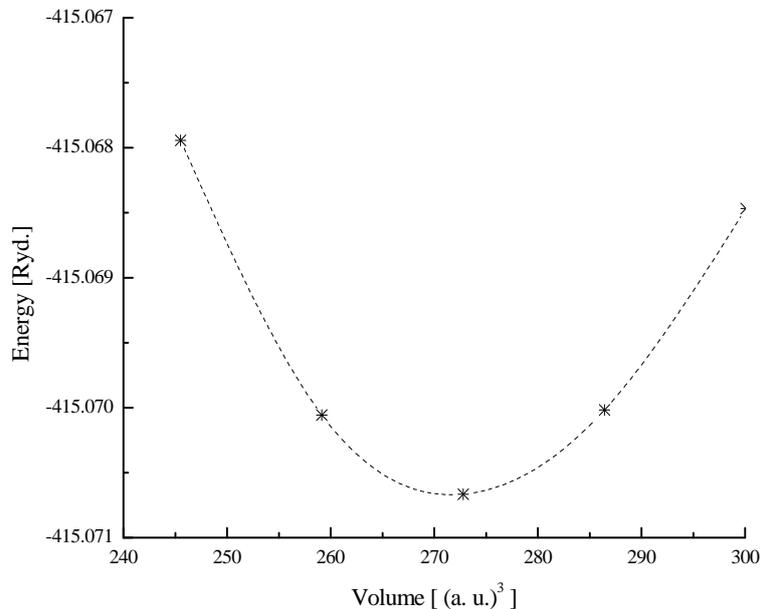
Such calculations are very sensitive to the structure factors and the pseudopotential form factor. Thus the results are not always in quantitative agreement with experiment (Shimoji, 1977 [50]).

Also it should be mentioned that the integrand of electrical resistivity involves the square of the form factors. This is also true for the integrands of Fermi energy and density of states. However, the integrand of the Knight shift involves the form factor linearly. Hence, the sign of the form factor is quite material in the computation of Knight Shift. Thus a form factor reproducing good electrical resistivity may not reproduce the Knight shift so nicely.

In spite of the above mentioned facts and the inherent approximations of the HFP technique, Ziman formalism, Knight formalism and Fermi energy formalisms, a fairly reasonable agreement has been obtained in the present work.

### 3.4 Electronic Structure Calculation

The ab-initio electronic structure calculation of Cd-Zn alloy has been performed using FLAPW method within the generalized gradient approximation (GGA) [51]. In our calculation, the crystal structure of Cd-Zn has the space group symmetry Pm-3m with Cd at (0, 0, 0) and Zn at (0.5, 0.5, 0.5) in the unit cell. The radii of the muffin tin spheres were 2.0 a.u. each for Cd and Zn, respectively. The total energy with respect to the volume has been calculated and minimized as shown in Fig. 3.



**Fig. 3.** Total energy of Cd-Zn as a function of cell volume.

The Birch-Murnaghan relation for equation of state (EOS) is used to get the static equilibrium volume  $V_0$  (=274.08) as well as the bulk modulus  $B_0$  (= 29.05 GPa) and its pressure derivative  $B'$  (=

3.834) at zero pressure. The pressure derivative of bulk modulus at zero pressure  $B_0'$  is a parameter of great physical significance in high pressure physics. It is related to a few other important thermophysical properties (like phase transitions, interphase energy, adsorption energy etc.) [52].

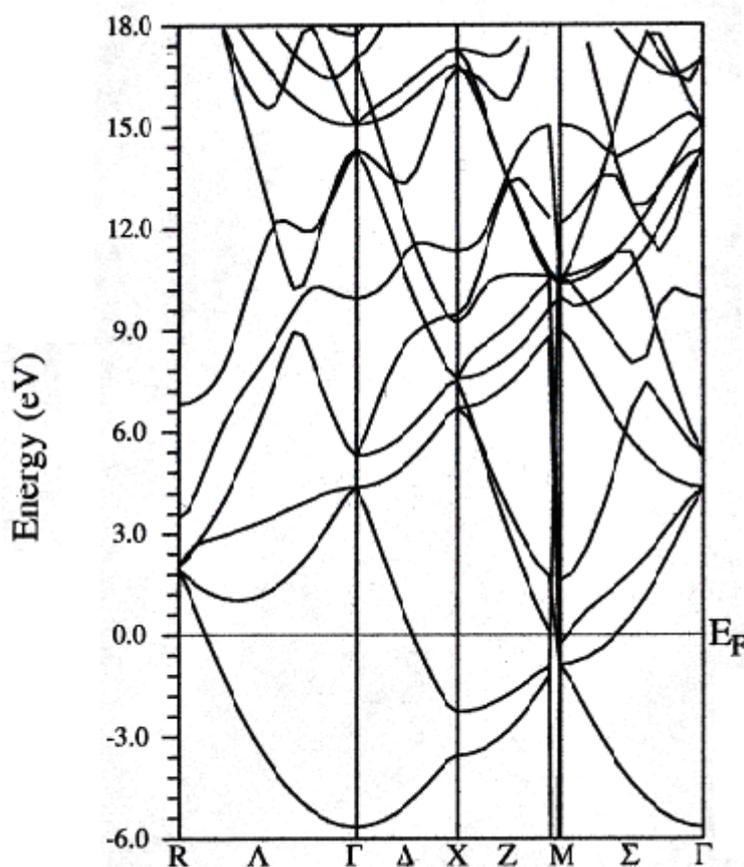


Fig. 4. The electronic band structure of Cd-Zn along high symmetry directions.

The calculated band structure for Cd-Zn in the high symmetry direction in the Brillouin zone is shown in Fig. 4. In this figure we find a large dispersion of the bands.

The angular momentum projected densities of states were obtained by using 1000-k points inside the irreducible Brillouin zone for integration. The full geometrical optimization gives an in-plane lattice constant  $a = b = c = 3.74$  and  $c/a = 1.0$  of pure Cd-Zn alloy.

Fig. 5 shows the total DOS along with partial DOS of Cd-d and Zn-s states of Cd-Zn alloy. It is observed that the main contribution in the valence band comes from Cd-d state near the Fermi level. The density of state of Cd-d shows a sharp peak near the edge of the Brillouin zone after which it shows a rapid decline in the density of states. It can be interpreted as when the Fermi surface get contacted with the Jones zone planes, electrons would fill the corners of the Jones zone thereby resulting in a rapid decline in the density of states. The formation of the peak signifies the overlap of electrons across the  $\{100\}$  zone planes coupled with contact with the  $\{101\}$  zone planes in the hcp Brillouin zone. The narrow 3d band of Zn-metal can be ignored as it is positioned slightly below the bottom of the valence band and is scarcely hybridized with the valence electrons.

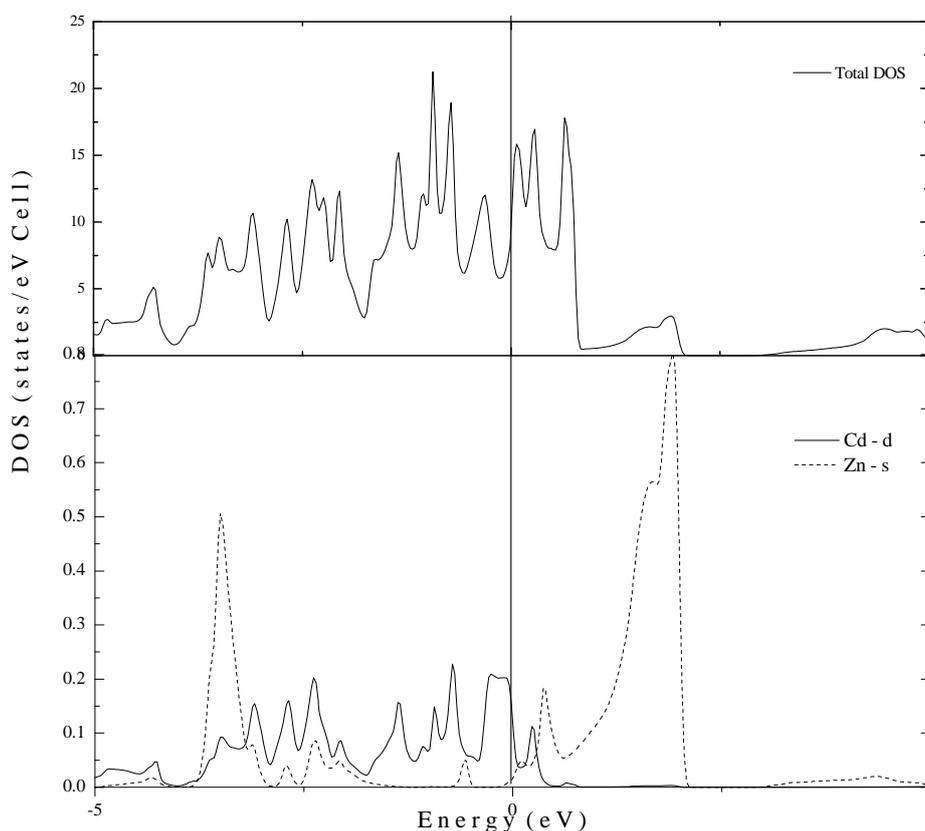


Fig. 5. Total DOS and PDOS around Fermi energy of Cd-Zn alloy calculated for the optimized lattice constant.

#### 4. Conclusion

1. The Harrison's First Principle technique in conjunction with the hard sphere technique of Ashcroft and Langreth can be safely used for the study of transport property (viz., electrical resistivity) of Cd-Zn alloy.
2. The partial structure factors play a key role in binary alloys due to the randomness of various scattering centers A, B and AB where A and B are the species.
3. The accuracy of resistivity values are sensitive to the accuracy of structure factor  $S(k)$  and form factor  $\langle k + q | w | k \rangle$ . The resistivity in Cd-Zn varies almost linearly with the Zn concentration. The resistivity curve shows a negative temperature coefficient of resistance. Hence, this alloy is regarded as being a quasi-single component system.
4. The sharp peaks in liquid alloys result from the formation of compounds or complexes. This is certainly suggestive for describing energetically favorable configuration of ions in liquid alloys.
5. The electronic band structure calculation of Cd-Zn has been performed using FLAPW method. The equilibrium volume, bulk modulus, and its pressure derivative have been estimated through energy minimization of the alloy.
6. The main contribution in the valence band comes from Cd-d and Zn-s states.

## Acknowledgement

The financial support rendered by DAE-BRNS, Mumbai; UGC, CSIR, DST, New Delhi, Govt. of India is gratefully acknowledged.

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