

Electrical Transport and Electronic Structure Calculation of Al–Ga Binary Alloys

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The Harrison first principle pseudopotential technique based on the concept of orthogonalized plane waves has been used to study the liquid electrical resistivity and other physical properties viz., Knight shift, Fermi energy and electronic density of states of liquid binary alloys of simple metals. We have also performed a first-principles calculation of the electronic band structure of Al–Ga binary alloy at equiatomic composition employing the full-potential linearized augmented plane wave 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 and the partial density of states around the Fermi energy.

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1. Introduction

Since the past few decades, Al, Ga and their alloys of very high purity have begun to play a pivotal role as materials for wide industrial use [1–6]. Straumal et al. studied the grain growth in high purity Al–Ga alloys at various Ga-concentrations. Also, the transition from normal to abnormal grain-growth was investigated in dependence of Ga-content and temperature [7]. Papastaikoudis et al. [8] studied the temperature dependent part of the phonon resistivity of dilute Al–Ga alloys. The electrical conduction theory in the liquid metal using the pseudopotential concept provides an alluring field for investigating the electrical transport properties of liquid metals. The presence of conduction electrons and their interaction with the background of positive ions is treated through the Harrison first principle (HFP) pseudopotential technique which is a branch of orthogonalised plane wave (OPW) formalism first proposed by Herring [9] and later developed by Philips and Kleinman [10] and others. In the present paper, we deal with the structure, electrical resistivity, the Knight shift, the Fermi energy and electronic density of states of liquid binary alloy Al–Ga. The structure factor $S(K)$ needed for the present computation has been obtained through the hard-sphere model via the Percus–Yevik (PY) approximation along the lines of Ashcroft and Langreth [11] and Enderby and North [12].

The form factor $w(\mathbf{k}, \mathbf{q})$ of the constituent metals has been derived through the well known HFP pseudopotential technique. From these two ingredients the properties

under investigation have been computed. In the HFP pseudopotential technique, the various interacting potentials arrive at thorough fundamental considerations employing quantum mechanical and statistical mechanical approaches along with Poisson's equation. Although the technique was more 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 [13] and Hafner [14] 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 [15]).

In spite of various favorable points regarding the HFP technique researchers found that there are several considerations to be kept in mind while choosing the input parameters, the most significant among them concerned the energetic problem. For the computation of the form factor the important input parameters are the eigenfunctions and eigenvalues of the core electrons represented by $P_{nl}(r)$ and ε_{nl} (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 a form factor $w(\mathbf{k}, \mathbf{q})$ and the static structure factor $S(k)$. Both these ingredients are involved in all the physical properties studied in this project.

Usually, the research groups in this field obtained these input parameters from the Herman–Skillman paper [16], or generated them with some improvement in his pro-

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gram while some authors preferred to use the experimental eigenvalues. Clementi [17] 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 partial structure factors and consequently the electrical resistivity (concentration dependence) and other physical properties of the alloy considered for the study. The full potential linearized augmented plane wave (FPLAPW) method has been employed to calculate the electronic structure of the binary alloy.

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

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

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 [18] requires the hard-sphere diameters σ_1 , σ_2 of the first and second components of the alloy and packing density η which is related to σ_1 and σ_2 as

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

In the present work σ_1 and σ_2 have been evaluated by using the relation as proposed by Ashcroft and Langreth [19]:

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

where $3/2 k_B T$ is the mean kinetic energy and V_{\min} is the depth of the first minimum in the interionic pair potential given by Harrison [15] as

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

$$i = 1, 2.$$

Here $F_{ni}(q)$ is the normalized energy-wave number characteristic

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

where $F_i(q)$ in the local approximation is [15]:

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

$\varepsilon^*(q)$ 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 [11] and Enderby and North [12]:

$$S_{11}(K) = [1 - n_2 c_{22}(q)] / D_d(q), \quad (8)$$

$$S_{22}(K) = [1 - n_1 c_{11}(q)] / D_d(q), \quad (9)$$

$$S_{12}(K) = (n_1 n_2)^{1/2} c_{12}(q) / D_d(q), \quad (10)$$

with

$$D_d(q) = [1 - n_1 c_{11}(q)][1 - n_2 c_{22}(q)] - n_1 n_2 c_{12}^2. \quad (11)$$

S_{11} , S_{22} and S_{12} are called the Ashcroft–Langreth partial structure factors.

2.3. Electrical resistivity

For the computation of the resistivity of liquid metals, Ziman gave a diffraction model formula (Ziman [20]), 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 [21] that the diffraction-model formula for liquid metals proposed by Ziman [20] 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.,

$$R = R_{11} + R_{22} + R_{12}, \quad (12)$$

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

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

$$R_{22} = (3\pi/\hbar|e|^2) (\Omega/Nv_F^2)$$

$$\times 4 \int_0^1 c_2 |w_2(\mathbf{k}, \mathbf{q})|^2 S_{22}(K) \eta^3 d\eta, \quad (14)$$

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

Here \hbar is the well-known Planck constant and is given by $\hbar = \frac{h}{2\pi}$.

In a composite form R can be expressed as

$$R = (3\pi/\hbar|e|^2) (\Omega/Nv_F^2) \\ \times \left\langle \sum_{\alpha,\beta} (c_1c_2)^{1/2} S_{ij}(K) w_1(\mathbf{k}, \mathbf{q}) w_2(\mathbf{k}, \mathbf{q}) \eta^3 \right\rangle, \quad (16)$$

where the expression in acute brackets, $\langle \dots \rangle$, stands precisely for the following integral:

$$\langle \dots \rangle = 4 \left[\int_0^1 c_1 S_{11}(K) |w_1(\mathbf{k}, \mathbf{q})|^2 \right. \\ \left. + c_2 S_{22}(K) |w_2(\mathbf{k}, \mathbf{q})|^2 \right. \\ \left. + 2(c_1c_2)^{1/2} S_{12}(K) |w_1(\mathbf{k}, \mathbf{q})| |w_2(\mathbf{k}, \mathbf{q})| \right] \eta^3 d\eta. \quad (17)$$

Here $w_1(\mathbf{k}, \mathbf{q})$ and $w_2(\mathbf{k}, \mathbf{q})$ are the form factors of species 1 and 2; 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 the 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 the conduction electrons and the nuclear moment in a metal provide a vast array of properties that can be studied through nuclear-magnetic technique [22–24]. Although the experimental techniques of the measurement of 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 work, [20, 25–30], on the magnetic properties of metal substantiate the view that like the electrical resistivity, the nearly-free-electron (NFE) approximation is also valid for the theoretical treatment of various magnetic properties viz., the Knight shift, magnetic susceptibility, the Hall coefficient etc. We shall now present its concise theory within the framework of pseudopotential technique. According to Pake [31] the Knight shift may be expressed as

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

Here χ_P is the spin paramagnetic susceptibility of a conduction electron per unit volume, Ω 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

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

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 meaning. For alloys the integrand of Eq. (19) is replaced by

$$I_K = \int_0^\infty \left[c_1 S_{11}(K) w_1(\mathbf{k}, \mathbf{q}) + c_2 S_{22}(K) w_2(\mathbf{k}, \mathbf{q}) \right. \\ \left. + 2(c_1c_2)^{1/2} w_1(\mathbf{k}, \mathbf{q}) w_2(\mathbf{k}, \mathbf{q}) S_{12}(K) \right] \\ \times q \ln \left| \frac{q + 2k_F}{q - 2k_F} \right| dq. \quad (20)$$

Also Z , E_F and k_F are such “alloy quantities” X , evaluated through Vegard’s rule i.e., $X = c_1 X_1 + c_2 X_2$, where c_1 and c_2 are the concentrations of the constituents.

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 the electronic structure of liquid metals among which the density of states and the Fermi energy have significant bearing. The calculations of the Fermi energy E_F and the density of states $N(E_F)$ for simple liquid metals have been reported by [32–51] using various pseudopotentials and the Green function theory. It does not appear that the Harrison first principle pseudopotential has been used for the study of these properties except by Thakur [52] 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 [15]):

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

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, as above.

At the melting point, the above expression reduces to (Schneider and Stoll [35])

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

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

$$E(k_F) = \frac{\hbar^2 k_F^2}{2m} + \Delta(k_F) - \Delta(0), \quad (23)$$

where

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

and

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

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

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

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 Ω_0 is the atomic volume related to the Fermi wave vector k_F and valence Z by the relation

$$\Omega_0 = \frac{3\pi^2 Z}{k_F^3}. \quad (28)$$

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

$$N(E_F) = \frac{k_F^3 \Omega_0}{\pi^2} \left[\left. \frac{\partial E(k)}{\partial k} \right|_{k=k_F} \right]^{-1} = \frac{k_F^2 \Omega_0}{\pi^2} \left[\frac{\hbar^2 k_F}{m} \right]$$

$$+ \frac{m\Omega_0}{4\pi^2 \hbar^2 k_F^2} \int_0^\infty q S(K) w^2(\mathbf{k}, \mathbf{q}) \ln \left| \frac{2k_F + q}{2k_F - q} \right| dq + \frac{m\Omega_0}{\pi^2 \hbar^2 k_F} \int_0^\infty \frac{S(K) w^2(\mathbf{k}, \mathbf{q}) q^2 dq}{4k_F^2 - q^2} \Big]^{-1}. \quad (29)$$

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

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

3. Results and discussion

3.1. Structure

The hard-sphere diameters σ_1 and σ_2 , as a function of composition, have been evaluated for the system according to the relation (3). The partial structure factors have been computed using these hard-sphere diameters through the expression given by Ashcroft and Langreth [18].

The partial structure factors of this system have been presented at 700 °C for equiatomic composition as shown in Fig. 1. The desired nature of the structure factors has been reproduced with a very small pre-peak in $S_{11}(k)$ and $S_{12}(k)$ which is a characteristic of gallium. A slight dip in $S_{22}(k)$ before the principal peak and that in $S_{11}(k)$ after the principal peak also appears. The principal peak heights of $S_{11}(k)$, $S_{22}(k)$ and $S_{12}(k)$ are 2.248, 2.145, and 1.215, respectively.

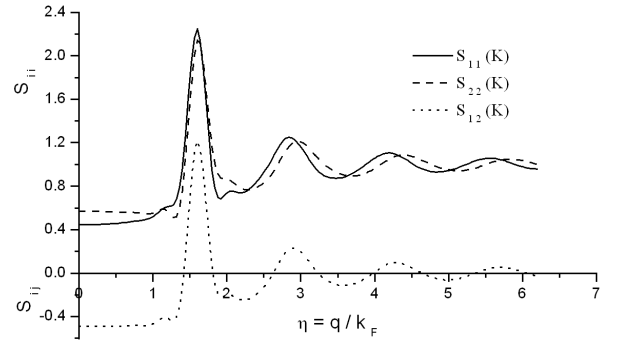


Fig. 1. Partial structure factors of liquid Al-Ga (just above the melting point) at equiatomic composition.

In case of Al-Ga, the computed structure factors do not show the behaviour of random mixing without a sub-peak 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

$\eta = q/2k_F$ which is most contributing to the resistivity integrands for the alloy.

3.2. Electrical resistivity

For the study of the electrical resistivity of the liquid alloys we need 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 the Percus–Yevik (PY) approximation on the lines of Ashcroft and Langreth [11] and Enderby and North [12].

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., β or exchange correlation function improved the agreement in case of Al–Ga.

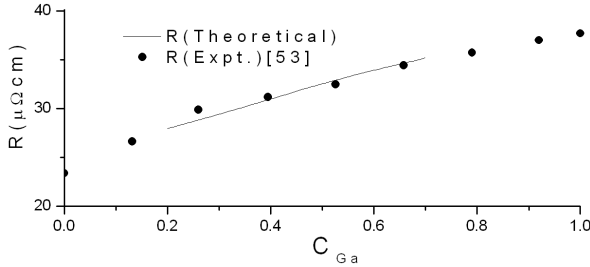


Fig. 2. Concentration dependence of the electrical resistivity of Al–Ga.

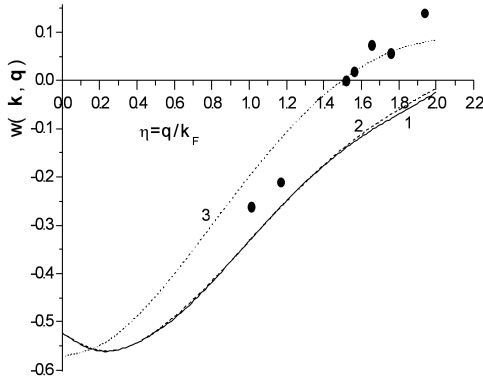


Fig. 3. Form factor of aluminium. • — data from [54].

For Al–Ga, the form factor of the Al component (Fig. 3) has been calculated by Hubbard–Sham (HS) while for Ga component (Fig. 4) the Shaw (SH) form of exchange has been used to obtain better agreement with the experiment. The good agreement may be indicative of the free-electron behaviour of these alloys. The slight discrepancies wherever they occur may be attributed to the failure of approximations involved in the

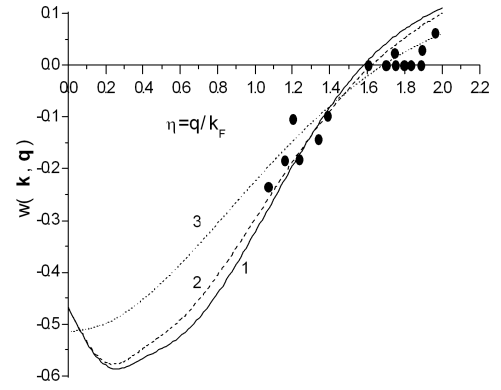


Fig. 4. Form factor of gallium. • — data from [54].

TABLE

Parameters to curves on figures.

Figure	Curve	ε_{nl}	α	β	Exchange	R	R_{exp}
3	1	C	VT	5/8	H–S	23.7	24.7
	2	C	VT	5/8	H–S	23.7	24.7
	3	Appapillai & Williams [55]					
4	1	HS	VT	1.0	SH	26.3	25.8
	2	HS	VT	1.0	V–S	19.1	
	3	Appapillai & Williams [55]					

theoretical framework or to the formation of chemical complexes, which are quasi-stable in nature. For further improvement the complex formation model proposed by Bhatia and Thornton may be used. The experimental data have been read from a graph of [53]. The electrical resistivity of the alloy has been shown in Figs. 2–4 and Table. It can be inferred from the figures that the system shows a positive temperature-coefficient of the resistance. The study reveals that as Z_m is larger than 2 (where $Z_m = c_\alpha Z_\alpha + c_\beta Z_\beta$), the system shows a positive temperature-coefficient of resistance.

3.3. Physical properties

The computed form factors, which have been found suitable for the 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 should 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, the 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 Al–Ga $(K\%)_{\text{th.}} = 0.456$ while $(K\%)^{\text{id}} = 0.306$.

Our results show for Al–Ga the Knight shift $(K\%)_{\text{th.}} = 0.456$ whereas $(K\%)_{\text{A}} = 0.164$, $(K\%)_{\text{B}} = 0.449$ and $(K\%)^{\text{id}} = 0.306$. The computed Fermi energy is $(E_{\text{F}})_{\text{th.}} = 11.02$ whereas $(E_{\text{F}}^0)_{\text{A}} = 11.63$, $(E_{\text{F}}^0)_{\text{B}} = 10.35$ and $(E_{\text{F}}^0)^{\text{id}} = 10.99$ eV. The computed electronic density of states is $N(E_{\text{F}})_{\text{th.}} = 0.414$ whereas $N(E_{\text{F}}^0)_{\text{A}} = 0.387$, $N(E_{\text{F}}^0)_{\text{B}} = 0.435$ and $N(E_{\text{F}}^0)^{\text{id}} = 0.411$ eV⁻¹. Here (id) is the ideal value of the properties for the binary alloys. The K_0 of the constituent metals is that evaluated through the zero-order OPW method (Faber [56]; Shimoji [57]).

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 [58]).

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 the 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 the 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, the Ziman formalism, the Knight formalism and the Fermi energy formalisms fairly reasonable agreement has been obtained in the present work.

3.4. Electronic structure calculation

A different *ab initio* electronic structure calculation of Al–Ga alloy has been performed using the FPLAPW method within the generalized gradient approximation (GGA) [58]. In our calculation, the crystal structure of Al–Ga has the space-group symmetry $Pm-3m$ with Al at (0, 0, 0) and Ga at (0.5, 0.5, 0.5) in the unit cell. The radii of the muffin-tin spheres were 1.5 a.u. and 2.0 a.u. for Al and Ga, respectively. The total energy with respect to the volume has been calculated and minimized as shown in Fig. 5. Thus, whereas the previous calculation considered real liquid metal alloys just above the melting point, the present calculation considers one single–single 50%–50% crystal corresponding to these liquids, or to an associated amorphous solid. However, as we will see, the present survey augments the above calculation in an important way, because of certain statements concerning the *s*- and *p*-levels (Al) and the *d*-level (Ga).

The Birch–Murnaghan relation for equation of state (EOS) is used to get the static equilibrium volume V_0 ($= 270.06$) as well as the bulk modulus B_0 ($= 27.05$ GPa) and its pressure derivative B' ($= 3.382$) at zero pressure. The pressure derivative of the 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 thermo-physical properties (like phase transitions,

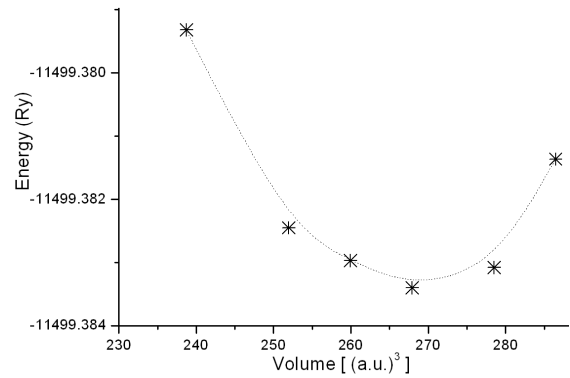


Fig. 5. Total energy of Al–Ga as a function of cell volume.

interphase energy, adsorption energy etc.) [59].

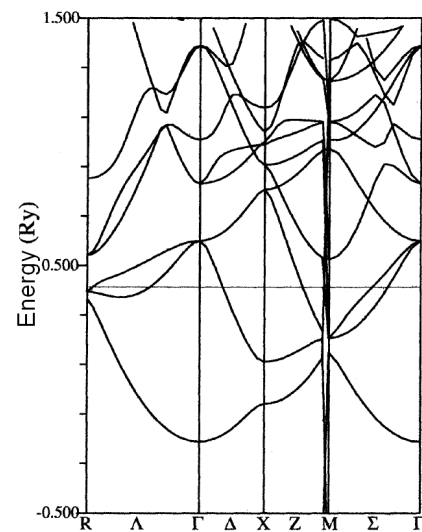


Fig. 6. The electronic band structure of Al–Ga along high symmetry directions.

The calculated band structure for Al–Ga in the high symmetry direction in the Brillouin zone is shown in Fig. 6. In this figure, we find a large dispersion of the bands.

The angular-momentum projected densities of states were obtained by using 2000-*k* points inside the irreducible Brillouin zone for integration. The full geometrical optimization gives an in-plane lattice constant $a = b = c = 3.24$, and $c/a = 1.0$ of pure Al–Ga alloy.

Figure 7 shows the total DOS along with the partial DOS of Al *s*, Al *p* and Ga *d* states of Al–Ga alloy. It is observed that the main contribution in the valence band comes from Al *p* state near the Fermi level. The hybridization between Al *s* and Al *p* state gives rise to the splitting of the peak into two subbands in the total density of states. A deep pseudogap (Ga *d*) appears near the Fermi level and causes electrons near the Fermi level to

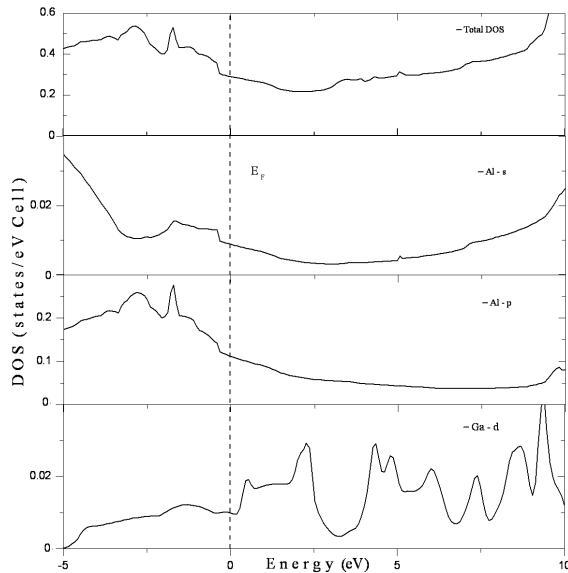


Fig. 7. Total DOS and PDOS around Fermi energy of Al-Ga alloys calculated for the optimized lattice constant.

push into higher binding energies. Such a pseudogap corresponds to a well-known criterion of Nagel and Taue [60].

4. Conclusion

- 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 Al-Ga alloys.
- 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.
- The accuracy of resistivity values are sensitive to the accuracy of the structure factor $S(k)$ and form factor $\langle k + q | w | k \rangle$. The resistivity in Al-Ga varies almost linearly with concentration. The resistivity curve shows positive temperature-coefficient of resistance.
- The sharp peaks in liquid alloys result from the formation of compounds or complexes. This is certainly suggestive for describing energetically favourable configuration of ions in liquid alloys.
- A related electronic band structure calculation of $\text{Al}_{0.5}\text{-Ga}_{0.5}$ has been performed using the FPLAPW method. The equilibrium volume, bulk modulus, and its pressure derivative have been estimated through energy minimization of the alloy.
- The main contribution in the valence band comes from Al p states. The Ga d states generate a pseudogap.

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