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Electron–phonon coupling and related properties of C16-structured Zr_2Ni intermetallics

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Abstract. The self-consistent potential parameters obtained from LDA-based LMTO electronic structure calculations and phonon dispersion relations obtained from lattice dynamical model calculations have been used to estimate the electron–phonon coupling constant (λ) for Zr_2Ni using the McMillan–Hopfield formula within the rigid-muffin-tin approximation. The theoretically calculated heat capacity parameters compare well with those fitted to the experimental data. The superconducting transition temperature T_c deviates from the experimental value, but is within the expectations of the strong-coupling theory.

1. Introduction

The C16-structured transition metal intermetallics, namely Zr_2TM (TM = Fe, Co, Ni, Rh and Ir), have been studied experimentally as well as theoretically [1–4] because of their superconducting properties and hydrogen affinity. Superconductivity in these compounds is observed to obey the Matthias rule of band filling with increasing electron-to-atom (e/a) ratio [3]. Detailed self-consistent electronic structure calculations performed on these compounds attributed such a variation in T_c to the shift in the Fermi level (E_F) from a peak to a valley in the density of states (DOS) [3]. Since the electron–phonon coupling constant (λ) is directly proportional to the DOS at E_F ($\rho(E_F)$), a shift of E_F from a peak to a valley of the DOS would imply a corresponding variation in λ, which would result in a concomitant variation in T_c via McMillan's strong-coupling formula [5]. McMillan's formula for the theoretical determination of T_c requires knowledge of Θ_D and the coupling constant λ. Whereas Θ_D can be estimated accurately from lattice dynamical calculations, the experimental and theoretical estimation of the coupling constant λ are controversial even for some elemental transition metals. The analysis is further complicated by possible parallel processes of spin fluctuations—for example, in the problem of renormalization of the specific heat and T_c [6], or proximity effects in the tunnelling data [7]. Therefore, in order to extract the quantities of interest such as the superconducting critical temperature T_c, one has to use some theoretical models for approximating λ. Nearly all attempts to date to compute the electron–phonon interaction have focused on calculating merely the electronic contribution to λ, while the phonon frequencies and the eigenvectors were usually taken from lattice dynamical calculations. In all of these studies, the self-consistent adjustment of

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the one-electron potential to the phonon-mediated distortion was replaced by either the rigid-ion approximation (RIA) [8] or the more popular rigid-muffin-tin approximation (RMTA) [9]. For transition metals and compounds having large DOSs at E_F, the RMTA often works well, since the efficient electronic screening limits the change of the potential in the immediate vicinity of the displaced atom. It may be remarked here that very recently Savrasov and co-workers [10, 11] have attempted an all-electron formulation based on the generalized Sternheimer method [12, 13] to obtain the phonon dispersion in some elemental transition metals. The method estimates the coupling constant λ to within 10% of the true value and hence claims to give much better estimates of physical quantities such as the superconducting transition temperature (T_c), electronic specific heat coefficient (γ) and low-temperature lattice contribution to the heat capacity (β) as compared to the existing conventional methods. However, the success of the new method still remains to be tested for transition metal intermetallics such as the C16-structured compounds, to which at present only conventional models can be applied.

In the absence of any data on the phonon dispersion relation for the C16 Zr-based intermetallics, our previous study of these compounds [3] was restricted to a comparison of the $\rho(E_F)$ obtained from first-principles LDA calculation with that estimated from low-temperature heat capacity data. Recently, however, lattice dynamical calculations have been performed on C16-structured Zr_2Ni [14], with reasonable agreement being obtained between theory and experiment. In view of these new results, we embarked upon a detailed investigation of Zr_2Ni combining a first-principles electronic structure calculation with a lattice dynamical calculation. Our aim in the present article is to calculate the coupling constant λ within the RMTA and then obtain the superconducting T_c and heat capacity parameters for Zr_2Ni. In section 2 we give a brief summary of the results on the phonon dispersion and electronic structure. Section 3 covers in detail the results of the theoretical calculation of the coupling constant λ, the critical temperature T_c and the heat capacity parameters γ and β, and in section 4 we summarize our findings.

2. Details of the calculations

2.1. Electronic structure

Details of the atomic arrangement in Zr_2Ni and results of electronic structure calculations are given in our earlier work [3]. The calculations were for a body-centred tetragonal structure (space group D_{4h}^{18}), with $a = 6.481$ Å and $c/a = 0.812$. Self-consistent semi-relativistic electronic structure calculations have been performed [3] using the tight-binding linear muffin-tin orbital method within the atomic sphere approximation (TB-LMTO-ASA) [15, 16].

The calculated electronic densities of states (DOSs) are shown in figure 1. The Fermi level happens to lie in a valley of the DOS for Zr_2Ni (figure 1 (top panel)), unlike those of Zr_2Rh and Zr_2Co [3], which lie at peaks of the DOS. It may be noted here that Zr_2Ni has 6.0 valence electrons per atom (e/a) per formula unit as compared to 5.67 e/a in the case of Zr_2Rh and Zr_2Co. Therefore the shift in E_F from a peak to a valley of the DOS with increasing e/a can be described, within the rigid-band picture, as a filling of valence bands with the addition of electrons. The *l*-projected DOSs for Zr and Ni sites are shown in figure 1 (in the middle and lowest panels, respectively). The DOS at E_F is predominantly due to d-type electrons at the Zr and Ni sites, indicating that d electrons are involved in the superconductivity of the Zr_2Ni compound. Nevertheless, there is significant p character at the Fermi level, although in the atomic state both Zr and Ni atoms have only s and d

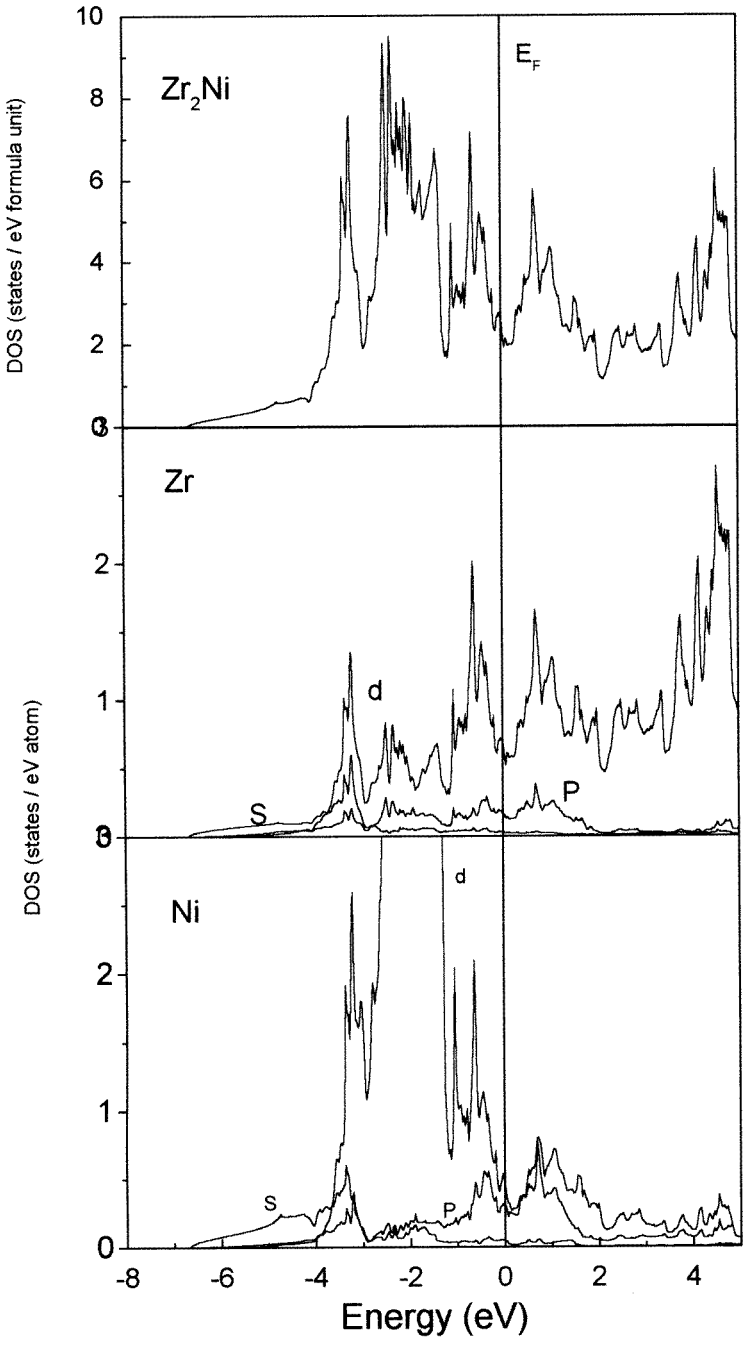

Figure 1. The total electronic density of states for Zr_2Ni, and the *l*-projected DOSs for Zr and Ni sites.

electrons. The magnitudes of the DOSs at E_F for Zr and Ni are comparable, implying that both Zr and Ni contribute significantly to the superconductivity of this compound; this is contrary to the earlier conjecture of Sinha and Harmon [17] that Ni chains are responsible for the superconductivity of this compound. The relationship between T_c, λ and $\rho(E_F)$ indicates that a low DOS at E_F implies a smaller λ, which in turn implies a lower T_c, as can be seen in the following section.

2.2. Lattice dynamics

Lattice dynamical calculations for Zr_2Ni have been performed [14] using a semi-empirical n-body potential [18] which is constructed in the framework of the second-moment approximation of the tight-binding scheme for the d band, which is well adapted to the transition metals. The parameters appearing in this semi-empirical n-body potential [14] are associated with the Zr–Zr, Ni–Ni and Zr–Ni pairs of atoms for Zr_2Ni and were obtained by fitting to the cohesive energy, equilibrium conditions and elastic constants of Ni, Zr and Zr_2Ni.

The lattice dynamical calculation was used to arrive at the total phonon DOS (figure 1), the partial DOSs for the Zr and Ni atoms and the neutron-cross-section-weighted phonon DOS. The calculated neutron-weighted DOS was found to be in good agreement with experiment [14]. The calculated total DOS was used to derive the lattice specific heat coefficient β as discussed in section 3.2. We have used the partial density of states (figure 2) to calculate $\langle\omega^2\rangle$ corresponding to Zr and Ni sites separately, and these values were then used to calculate the electron–phonon coupling constant for Zr_2Ni.

3. Results and discussion

3.1. Superconducting parameters: λ and T_c

Using RMTA, the McMillan–Hopfield expression for the electron–phonon coupling constant can be written as the ratio of the purely electronic part to the purely phononic part [19], $\eta/M\langle\omega^2\rangle$, where M is the mass of the constituent metal, $\langle\omega^2\rangle$ is the average square of the phonon frequencies and η is the so-called Hopfield parameter. Within RMTA it is therefore possible to calculate $\eta/M\langle\omega^2\rangle$ separately for Zr and Ni sites in the Zr_2Ni compound, and the electron–phonon coupling constant for the intermetallic may be written as the weighted average of their constituents:

$$\lambda = \frac{2}{3}\left[\frac{\eta}{M\langle\omega^2\rangle}\right]_{\mathrm{Zr}} + \frac{1}{3}\left[\frac{\eta}{M\langle\omega^2\rangle}\right]_{\mathrm{Ni}}. \tag{1}$$

The values of $M\langle\omega^2\rangle$ for the Zr and Ni sites are respectively 0.15 and 0.13 Ryd au^{-2}, while the Hopfield parameter, which gives the electronic contribution, is written as [19]

$$\eta = \rho(E_F)\sum_l \frac{(l+1)}{(2l+1)(2l+3)} M_{l,l+1}^2 \frac{\rho_l(E_F)\rho_{l+1}(E_F)}{\rho(E_F)\rho(E_F)} \tag{2}$$

where $M_{l,l+1}$ describes the amplitude of the transition from state l to state $l+1$. $M_{l,l+1}$ is expressible in terms of the muffin-tin solutions ϕ_l and their logarithmic derivatives, D_l, at the sphere boundary:

$$M_{l,l+1} = -\phi_l\phi_{l+1}[(D_l(E_F) - l)(D_{l+1}(E_F) + l + 2) + (E_F - V(R))R^2]. \tag{3}$$

Using the potential parameters generated from a self-consistent electronic structure calculated for Zr_2Ni, it is possible to estimate $M_{l,l+1}$ [20, 21] and hence η for the Zr

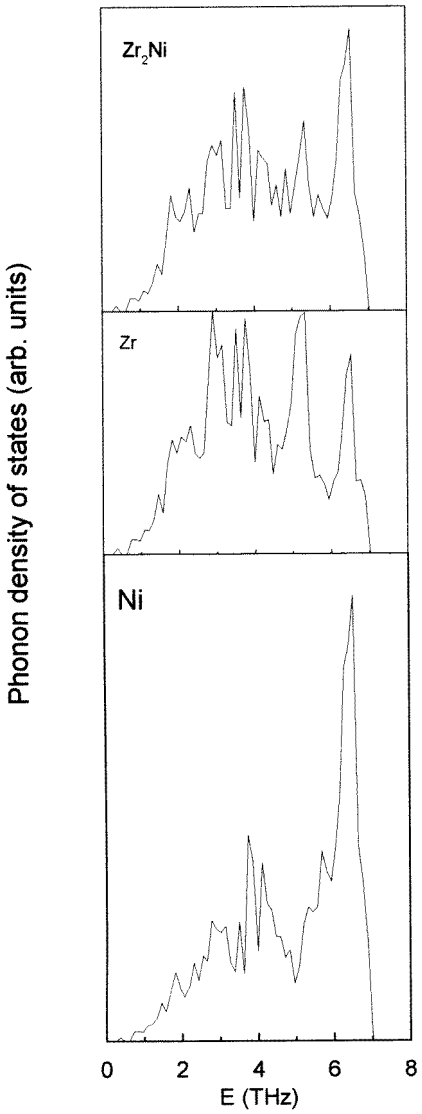

Figure 2. Partial phonon densities of states for Zr and Ni sites and the total phonon density of states for Zr_2Ni calculated from the lattice dynamics (1 THz = 4.136 meV).

and Ni sites. The values of the Hopfield parameter for Zr and Ni are 5.55×10^{-3} and 3.83×10^{-3} Ryd au^{-2} respectively. Using the values of η and $M\langle\omega^2\rangle$ in equation (1), we estimate λ for Zr_2Ni. The value of λ thus obtained is compared in table 1 with that estimated from the heat capacity measurement [3]. Considering the approximations involved in calculating λ and the errors present in the measurement of the heat capacity data, the agreement between theory and experiment is quite fair. The calculated value of λ can now be used to estimate T_c via the McMillan equation [5]. We obtain the theoretical value $T_c = 0.4$ K which is less than the experimentally observed value of $\sim$2.0 K. This is because T_c is related to λ through an exponential relation, and any approximations in the calculation

Table 1. Comparison of theoretically calculated values of γ, β, λ and T_c with those estimated from the heat capacity measurement for Zr_2Ni.

	γ (mJ mol^{-1} K^{-2})	β (mJ mol^{-1} K^{-4})	λ	T_c (K)
Theory	15.6	0.434	0.38	0.4
Experiment	20.1 ± 2	0.365 ± 0.04	0.49	1.7 ± 0.3

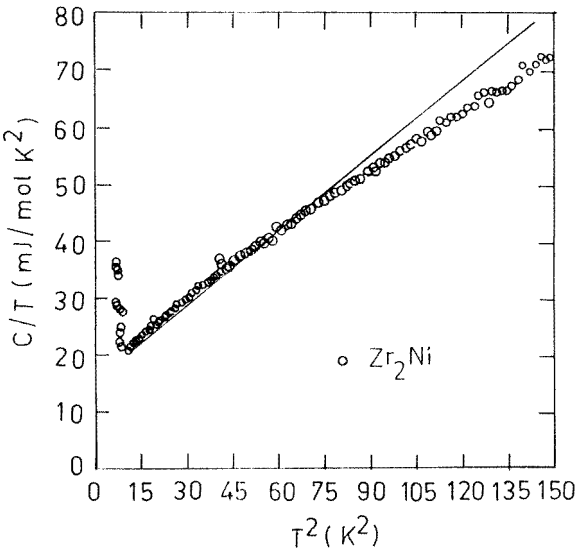

Figure 3. Comparison of the measured heat capacity data with those obtained from lattice dynamics and electronic structure calculations.

of λ are greatly magnified. This has in fact been the case for all theoretical estimations of T_c so far, and in view of this our results do conform with the existing trend.

3.2. Heat capacity parameters: γ and β

Using the value of λ calculated using a 'weighted average' and the electronic density of states, we estimate electronic specific heat coefficient using the Sommerfeld expression, $\gamma = \frac{2}{3}\pi^2 k_B^2 \rho(E_F)(1+\lambda)$. Table 1 gives a comparison of the electronic specific heat coefficient obtained from theory with that estimated from experiment. We find reasonable agreement between our calculated value and the experimental value.

Similarly, from lattice dynamical calculation of the phonon density of states $g(\omega)$ we compute the lattice specific heat as a function of temperature. The lattice specific heat C_v is given by [14]

$$C_v = \frac{\mathrm{d}}{\mathrm{d}T}\int \mathrm{d}\omega\ g(\omega)(n+1/2)\bar{h}\omega \tag{4}$$

where $n = [\exp(\bar{h}\omega/k_BT) - 1]^{-1}$. The value of β is obtained by fitting $C_v = \beta T^3$ to the calculated low-temperature lattice specific heat in the temperature range of 0–20 K. Table 1 gives a comparison of β calculated from the phonon DOS with that estimated from the heat

capacity measurement. The match is in fact quite good, implying that using a semi-empirical n-body potential leads to a fair explanation of the lattice specific heat in Zr_2Ni.

Using γ estimated from an electronic structure calculation and β calculated from the lattice dynamics, we calculate the specific heat C_v as a function of temperature from the relation $C_v/T = \gamma + \beta T^2$. Figure 3 shows a comparison of the theoretically estimated C_v with the experimentally measured heat capacity [22]. The comparison is extremely good in the low-temperature regime near T_c, and this indicates the success of our model calculation, which is based on the RMTA and a strong-coupling argument.

4. Summary

We have presented a theoretical approach for estimating the electron–phonon coupling constant of C16-structured Zr_2Ni compounds, whose electronic and phononic densities of states have been calculated separately. Using self-consistent LMTO electronic structure calculations on the one hand, and a semi-empirical lattice dynamical calculation based on an n-body potential on the other, we have derived the site-projected λs whose weighted average yields an estimate of the effective λ for the compound. This λ can then be used to calculate the heat capacity parameters and T_c. The reasonably good agreement of our results with the heat capacity data demonstrates the viability of our hybrid approach for the C16-structured transition metal intermetallics.

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[22] The Zr_2Ni sample was prepared by Drs P Raj, K Shasikala and A Sathyamoorthy, of the Chemistry Division, BARC, India, while the low-temperature heat capacity was measured by Dr S K Dhar, TIFR, India, using the semi-adiabatic heat pulse method on an automated apparatus.