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## Suppression of superconductivity by carbon addition to $\text{La}_3\text{X}$ ( $\text{X} \equiv \text{Al, Ga, In or Tl}$ )

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**Abstract.** The first theoretical attempt to explain the role of interstitials in the superconducting behaviour of intermetallic compounds is reported here. Further, the often-quoted correlation between stability and superconductivity in intermetallic compounds is also confirmed. Band-structure results obtained from our calculations on  $\text{La}_3\text{X}$  and  $\text{La}_3\text{XC}$  are compared with the available experimental results. The possible reasons for the experimentally observed suppression of the superconducting transition temperature  $T_c$  by carbon addition to  $\text{La}_3\text{X}$  compounds are also analysed.

### 1. Introduction

Carbon plays an important role in deciding the physical properties of rare-earth non-transition-metal compounds. For example,  $\text{Pr}_3\text{Al}$  is a ferromagnetic material with a Curie temperature of 11.3 K and the carbon-containing  $\text{Pr}_3\text{Al}$  (i.e.  $\text{Pr}_3\text{AlC}$ ) becomes an antiferromagnetic material with a Néel temperature of 5.1 K [1]. Recently, the carbides of rare-earth transition-metal borides with a high  $T_c$  have been reported [2–4] and the compounds in this series without carbon have been found to be non-superconductors or to have a low  $T_c$  [2, 5]. Studies on the Y–Pd–B system have shown that the addition of carbon drastically increases the  $T_c$  to a value of 23 K, higher than the  $T_c$ -values reported earlier for bulk intermetallic compounds [3]. Mazumdar *et al* [6] reported that about 2% of the Y–Ni–B system is superconducting with  $T_c = 12$  K, and their later studies [7] show that the superconductivity in this system may be due to the small amount of carbon present in their samples. Hence, they intentionally added carbon to the above system and enhanced its  $T_c$  [2]. Some of the very recent studies on the Y–Ni–B system show that the carbon, which is responsible for the small fraction of superconducting phase, creeps into the system via impure boron [5].

The  $T_c$ -values of  $\text{La}_3\text{X}$  compounds are in the range 5–11 K [8, 9]. The addition of carbon to these systems drastically reduces their  $T_c$ -values [10–12] and consequently the  $\text{La}_3\text{XC}$  compounds are found to be non-superconductors even at 1.02 K [10, 11]. Even though carbon plays an important role in deciding the  $T_c$ -values of the intermetallic compounds, no theoretical attempt has been made to understand the mechanism by which the carbon influences the superconducting behaviour. In view of the interesting influence of carbon on superconducting behaviour, we have attempted to explain the various reasons for the suppression of  $T_c$  in  $\text{La}_3\text{X}$  compounds by the addition of carbon.

The role of impurities in the physical properties of the rare-earth intermetallics has been experimentally studied [13]. In general, magnetic impurity atoms can depress the  $T_c$

of a host metal appreciably owing to the spin-exchange interaction, in contrast with non-magnetic impurities. On the contrary, the addition of non-magnetic carbon to the  $\text{La}_3\text{X}$  system decreases its  $T_c$  drastically [10, 12]. The depairing effect of magnetic impurities in conventional superconductors has been understood through the work of Abrikosov and Gor'kov [14]. Further, many experiments on the superconducting behaviour of systems with magnetic impurities, such as Gd and Ce in  $\text{La}_3\text{In}$ , have been performed to understand the magnetic pair-breaking mechanism [15]. Perovskite carbides ( $\text{La}_3\text{XC}$ ) have properties which are drastically different from those of the corresponding  $\text{La}_3\text{X}$  systems. In particular, they are found to be more stable and non-superconducting up to 1.02 K compared with  $\text{La}_3\text{X}$  systems [10]. This has led us to correlate the superconductivities of these systems with their structural stabilities. A considerable amount of theoretical studies has been made on A15, C15 and B1 superconductors [16]. Even though more than 45  $\text{L1}_2$  superconductors have been reported earlier [9], only limited theoretical studies have been made on  $\text{L1}_2$  superconductors [17]. Also, no attempt has been made so far to explain the variation in  $T_c$  by the influence of non-magnetic impurities in superconductors using band-structure results. In view of the potentially interesting behaviour of carbon on the superconductivity of intermetallics, we have undertaken investigations on the role of ternary alloying of carbon on the superconducting properties of  $\text{La}_3\text{X}$  compounds.

## 2. Details of calculations

The details of our calculations are similar to those in our previous studies [18]. The crystal structure of  $\text{La}_3\text{X}$  compounds is of the  $\text{Cu}_3\text{Au}$  type which is designated as  $\text{L1}_2$  and that of  $\text{La}_3\text{XC}$  is of  $\text{CaTiO}_3$  type which is designated as  $\text{E2}_1$ . We have used the LMTO ASA method [19] for the electronic structure, and  $T_c$  calculations and the TB LMTO method for the cohesive energy and heat-of-formation calculations [20]. In our calculations of the  $\text{La}_3\text{X}$  compounds, we have chosen the same radii for both the La and the X atomic spheres. Because the  $\text{L1}_2$ -type  $\text{AB}_3$  compounds are more stable in the vicinity of  $R_A/R_B \simeq 1$  [9]. For  $\text{La}_3\text{XC}$  compounds, we have chosen the sphere radii in such a way that the carbon atom should accept electrons (because of its higher electronegativity). The exchange potential is calculated using the exchange and correlation formalism of von Barth and Hedin. All angular momentum components up to  $l = 2$  have been retained. The calculations are self-consistent with an eigenvalue accuracy of  $10^{-3}$  Ryd in the LMTO ASA method and  $10^{-4}$  Ryd in the TB LMTO method. The eigenvalues are calculated in a uniform mesh of 84  $k$ -points in the irreducible wedge of the first Brillouin zone (1BZ) of the simple-cubic lattice for all the above compounds. For  $\text{La}_3\text{Al}$ , we have also considered the hexagonal  $\text{D0}_{19}$  structure with 64  $k$ -points in the 1BZ of the hexagonal lattice in order to view its relative stability between  $\text{L1}_2$  and  $\text{D0}_{19}$  structures. The heats of formation of  $\text{La}_3\text{X}$  and  $\text{La}_3\text{XC}$  are obtained from the difference between the total energies of the compounds and their corresponding weighted sums of their constituents.

The superconducting transition temperature is calculated using McMillan's formula which is

$$T_c = \frac{\Theta_D}{1.45} \exp\left(\frac{-1.04(1 + \lambda)}{\lambda - \mu^* (1 + 0.62\lambda)}\right) \quad (1)$$

where  $\lambda$  is the electron-phonon coupling constant,  $\Theta_D$  is the Debye temperature and  $\mu^*$  is the electron-electron interaction constant, which is taken to be 0.13 in the present work.

Various relations are used to calculate the average phonon frequency of the compounds [16, 17]. In general, if the constituents have a large mass difference, then the lighter atom will give rise to the optical phonon branches. Because of the above, we treat the constituents as independent oscillators and they vibrate with their characteristic frequencies. In this case,  $\lambda$  can be expressed as

$$\lambda = \sum_t \frac{N(E_F) \langle I_t^2 \rangle}{M_t \langle \omega_t^2 \rangle} \quad (2)$$

where  $M_t$  is the atomic mass,  $\langle \omega_t^2 \rangle$  is the average squared phonon frequency of the particular type and  $\langle I^2 \rangle$  is the square of the electron-phonon matrix element averaged over the Fermi surface. The parameters that enter into the calculation of  $\langle I^2 \rangle$  are taken from the band-structure results. The details of our  $T_c$  calculations are similar to our previous studies [18].

In the  $\text{La}_3\text{X}$  and  $\text{La}_3\text{XC}$  systems, the Debye temperatures are available only for  $\text{La}_3\text{In}$ ,  $\text{La}_3\text{Tl}$  and  $\text{La}_3\text{InC}$ . Hence we have assumed that the values of  $\Theta_D$  appearing in McMillan's formula for  $\text{La}_3\text{Al}$  and  $\text{La}_3\text{Ga}$  to be that of  $\text{La}_3\text{In}$  and for  $\text{La}_3\text{AlC}$ ,  $\text{La}_3\text{GaC}$  and  $\text{La}_3\text{TlC}$  to be that of  $\text{La}_3\text{InC}$ . Because the substitution of 30 at.% Ga in place of In in  $\text{La}_3\text{In}$  results in a negligible variation in  $\Theta_D$ , hence we expect not much variation in  $\Theta_D$  even though the whole of In is replaced by other X elements [10].

### 3. Structural stability and superconductivity

The stability of an intermetallic has been correlated with its superconducting behaviour; the more stable compounds will have a low  $T_c$  or non-superconductivity [21–23]. Moreover, the structural stability has been related to the electronic structure of an intermetallic; the materials for which  $E_F$  falls on the pseudo-gap (deep valley close to  $E_F$ ) in the density of states (DOS) curve will have low  $N(E_F)$ -values and high stabilities [24]. As discussed by Butler [25], a high  $N(E_F)$  reduces the stability indirectly since the high DOS at the Fermi energy tends to lower  $M(\omega^2)$  (lattice stiffness parameter or the effective force constant) through renormalization of the phonon frequencies [25]. Further, the superconductivities of A15 [26, 27] and C15 [28] systems have also been related to their structural phase transition. It is noteworthy that a few of the recently discovered high- $T_c$  rare-earth transition-metal borocarbides are also found to be metastable [29].

Regarding the stability of  $\text{La}_3\text{X}$  compounds, Buschow and von Vucht found that many of the  $\text{Cu}_3\text{Au}$  type phase of  $\text{R}_3\text{Al}$  ( $\text{R} \equiv$  rare earth) compounds do not stabilize unless some carbon is present [30]. The role of interstitial impurities in the structural stability of binary intermetallic compounds was extensively reviewed by Gschneidner [13]. He stated that the  $\text{La}_3\text{X}$  ( $\text{X} \equiv \text{Al, Ga, Pb or Sn}$ ) compounds do not exist in the stable phase and the  $\text{Cu}_3\text{Au}$ -type metastable phases are stabilized by interstitial impurities such as C or N [31]. It is experimentally observed that the small addition of interstitial elements such as B, Be or C to superconducting intermetallics changes their  $T_c$ -values drastically [2, 21]. Even though a considerable amount of qualitative analysis on the correlation between structural stability and superconductivity exists for intermetallics, there are no quantitative studies available so far. In order to understand the correlation between stability and superconductivity, we have performed total-energy and  $T_c$  calculations for all these compounds.  $-\Delta H$  (heat of formation) is a quantity which measures the stability of materials. Hence, we have calculated the value of  $-\Delta H$  for all the  $\text{La}_3\text{X}$  and  $\text{La}_3\text{XC}$  compounds from our total-energy studies. The calculated and experimental  $T_c$  and the calculated  $-\Delta H$  are given in tables 1 and 2.

**Table 1.** The equilibrium lattice parameters  $a_0$ , DOS  $N(E_F)$  at the Fermi level, heats of formation  $\Delta H$ , cohesive energies  $E_c$  and Debye temperatures  $\Theta_D$  for  $\text{La}_3\text{X}$  and  $\text{La}_3\text{XC}$  compounds.

System	$a_0$ (Å)	$N(E_F)$ (states $\text{Ryd}^{-1} \text{FU}^{-1}$ )		$\Delta H$ (kcal $\text{mol}^{-1}$ )	$E_c$ (kJ $\text{mol}^{-1}$ )	$\Theta_D$ (K)
		LMTO	TB LMTO			
$\text{La}_3\text{Al}$	5.06	56.76	58.49	-28.18	478.77	170
$\text{La}_3\text{Al} (\text{D0}_{19})$	$a = 7.195, c = 5.503$	61.87	71.12	-19.58	476.71	170
$\text{La}_3\text{Ga}$	5.66	88.89	95.18	+174.37	413.60	170
$\text{La}_3\text{Ga}$	5.064	74.86	91.62	+35.89	446.73	170
$\text{La}_3\text{In}$	5.07	60.05	85.30	-194.04	469.64	170
$\text{La}_3\text{Tl}$	5.13	64.60	93.04	-70.73	470.90	163
$\text{La}_3\text{AlC}$	5.12	36.99	36.41	-295.45	678.52	203
$\text{La}_3\text{GaC}$	5.17	34.55	30.12	-321.37	668.00	203
$\text{La}_3\text{InC}$	5.19	32.97	30.42	-461.91	669.53	203
$\text{La}_3\text{TlC}$	5.20	32.84	28.95	-343.63	671.99	203

#### 4. Results and discussion

From figures 1 and 2, it is clear that both  $\text{La}_3\text{X}$  and  $\text{La}_3\text{XC}$  exhibit metallic behaviour. In addition to this, it is found from the figures that the La d electrons mainly contribute to the conduction state. Because of the isoelectronic and isostructural nature of the  $\text{La}_3\text{X}$  compounds, the topologies of the DOS curves resemble each other. The DOS curve of  $\text{La}_3\text{X}$  compounds shows that  $E_F$  falls on a peak. This is in agreement with the conclusion drawn from the temperature-dependent nature of the Knight shift, susceptibility and specific-heat studies on  $\text{La}_3\text{In}$  and  $\text{La}_3\text{Tl}$  [10, 11]. For the same reason, the  $\Theta_D$ -values for these systems decrease suddenly at low temperatures [10] as in the case of A15 superconductors [32].  $E_F$  falls on the valley in the DOS curve of  $\text{La}_3\text{XC}$  compounds as shown in figure 2 and this is attributed to the temperature-independent Knight shift in these systems [10]. In the DOS curve of  $\text{La}_3\text{X}$  compounds shown in figure 1, the peak present in the low-energy region, which is well separated from the conduction band, mainly arises from the s states of X atoms. From our angular momentum and site-split DOS studies, we have found that the La d states and X p states are completely hybridized in the entire energy range of the conduction band. This indicates that there is a strong covalent bonding between La and the metal X in  $\text{La}_3\text{X}$  compounds.

Experimental observations of high- $T_c$  A15 superconductors [22, 33] showed that the resistivity reaches saturation in the high-temperature region. This can be attributed to the fall of  $E_F$  on the peak of the DOS curve [34]. Likewise, in our  $\text{La}_3\text{X}$  systems,  $E_F$  also falls on the peak in the DOS curve as shown in figure 1. So, it is expected that the resistivity reaches saturation at high temperatures, but there is no experimental temperature-dependent resistivity studies on these compounds to confirm our expectation.

The total bare DOS at the Fermi energy obtained from our band-structure calculation for  $\text{La}_3\text{In}$  and  $\text{La}_3\text{Tl}$  are 60.05 states  $\text{Ryd}^{-1} \text{FU}^{-1}$  and 64.6 states  $\text{Ryd}^{-1} \text{FU}^{-1}$ , respectively. These values are comparable with the corresponding experimental values of 81.6 states  $\text{Ryd}^{-1} \text{FU}^{-1}$  and 72.8 states  $\text{Ryd}^{-1} \text{FU}^{-1}$  obtained from the specific-heat measurements after carrying out the proper correction to the electron-phonon mass enhancement [11].

From the magnetic susceptibility measurements and NMR studies of  $\text{La}_3\text{X}_{1-y}\text{X}'_y$  ( $\text{X} \equiv \text{Tl}$  or  $\text{In}$ ;  $\text{X}' \equiv \text{Al, Ga, Sn}$  or  $\text{Pb}$ ) it has been suggested that the role of the d electrons from La is more significant than the electrons of the other constituents for the magnetic and superconducting properties of the  $\text{La}_3\text{X}$  compounds [10]; the above observation is consistent

Table 2. The important parameters used in the  $T_c$  calculations obtained from the self-consistent band-structure results: the electronic contributions  $\eta$  for  $T_c$  arising from various sites, the electron-phonon coupling constants  $\lambda$  for various sites and the experimental and theoretical  $T_c$ .

System	$\eta_{La}$ ( $eV \text{ \AA}^{-1}$ )	$\eta_X$ ( $eV \text{ \AA}^{-2}$ )	$\eta_C$ ( $eV \text{ \AA}^{-2}$ )	$\lambda_{La}$	$\lambda_X$	$\lambda_C$	$\eta$ ( $eV \text{ \AA}^{-2}$ )	$\lambda$	$T_c$ (K)	
									Theoretical	Experimental
La <sub>3</sub> Al	1.93	0.07	—	0.77	0.01	—	2.01	0.797	5.27	5.57, 6.16
La <sub>3</sub> Al (D0 <sub>19</sub> )	2.44	0.05	—	0.98	0.01	—	2.50	0.996	8.35	
La <sub>3</sub> Ga (Experimental $a_0$ )	0.60	0.06	—	0.24	0.01	—	0.67	0.255	0.00	
La <sub>3</sub> Ga (Theoretical $a_0$ )	2.69	0.20	—	1.08	0.03	—	2.90	1.115	10.05	5.84
La <sub>3</sub> In	1.84	0.74	—	0.74	0.61	—	2.59	1.360	13.11	9.83, 10.4
La <sub>3</sub> Tl	2.00	0.10	—	0.80	0.07	—	2.11	0.880	6.31	8.86, 9.04
La <sub>3</sub> AlC	1.11	0.09	0.31	0.44	0.02	0.18	1.51	0.651	2.51	<1.02
La <sub>3</sub> GaC	0.91	0.12	0.21	0.36	0.01	0.12	1.24	0.511	0.96	<1.02
La <sub>3</sub> InC	0.94	0.09	0.27	0.37	0.07	0.15	1.30	0.611	2.89	<1.02
La <sub>3</sub> TlC	0.91	0.09	0.24	0.36	0.06	0.14	1.25	0.578	1.64	<1.02

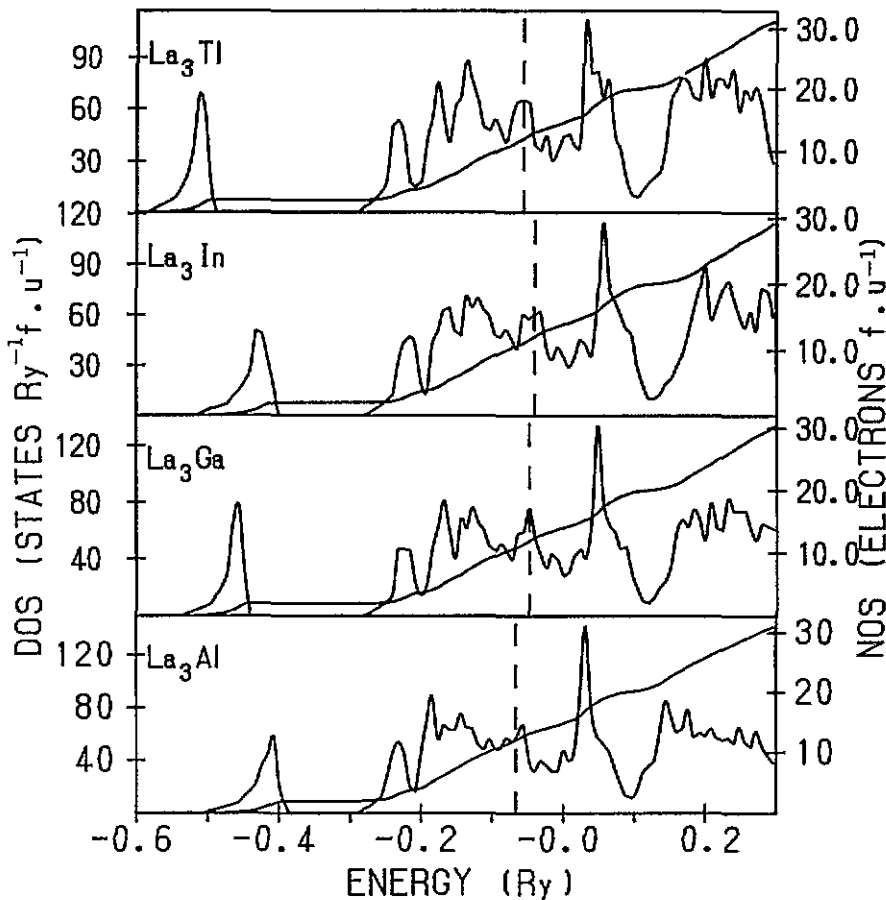


Figure 1. dos of  $\text{La}_3\text{X}$  ( $\text{X} \equiv \text{Al, Ga, In or Tl}$ ).

with our detailed band structure and  $T_c$  calculations in the sense that the DOS at  $E_F$  is mainly contributed by the La d electrons and also the La d electrons are mainly responsible for the electronic contribution to  $T_c$ .

It has been predicted from the measurements of the temperature-dependent NMR, susceptibility and specific heat that the  $E_F$  of  $\text{La}_3\text{In}$  and  $\text{La}_3\text{Tl}$  compounds should fall on the peak of their DOS curves [10, 11] and this is consistent with our theoretical findings (figure 1). However, there is a contradiction between the theoretical studies of recently found superconducting rare-earth transition-metal borocarbides that  $E_F$  should fall on the peak of the DOS curves [35] and the experimental findings according to which  $E_F$  does not fall on the peak of the DOS curve [36]. Hence, the present result is particularly important.

The overall topology of the DOS curve obtained from our calculations on  $\text{La}_3\text{In}$  is similar to that obtained from the earlier studies [17]. The heat of formation for  $\text{La}_3\text{In}$  is  $-0.14747 \text{ Ryd f.u.}^{-1}$  and this is in good agreement with the value obtained by Hackenbracht and Kubler [17]. Even though Hackenbracht and Kubler successfully explained the cohesive properties of this compound, they were unable to explain its superconducting behaviour. One of the possible reasons for this is that their calculated value of the electronic contribution to  $T_c$  arising from the In atom is very small ( $0.024 \text{ eV \AA}^2$ ) compared with our value ( $0.748336 \text{ eV \AA}^2$ ).

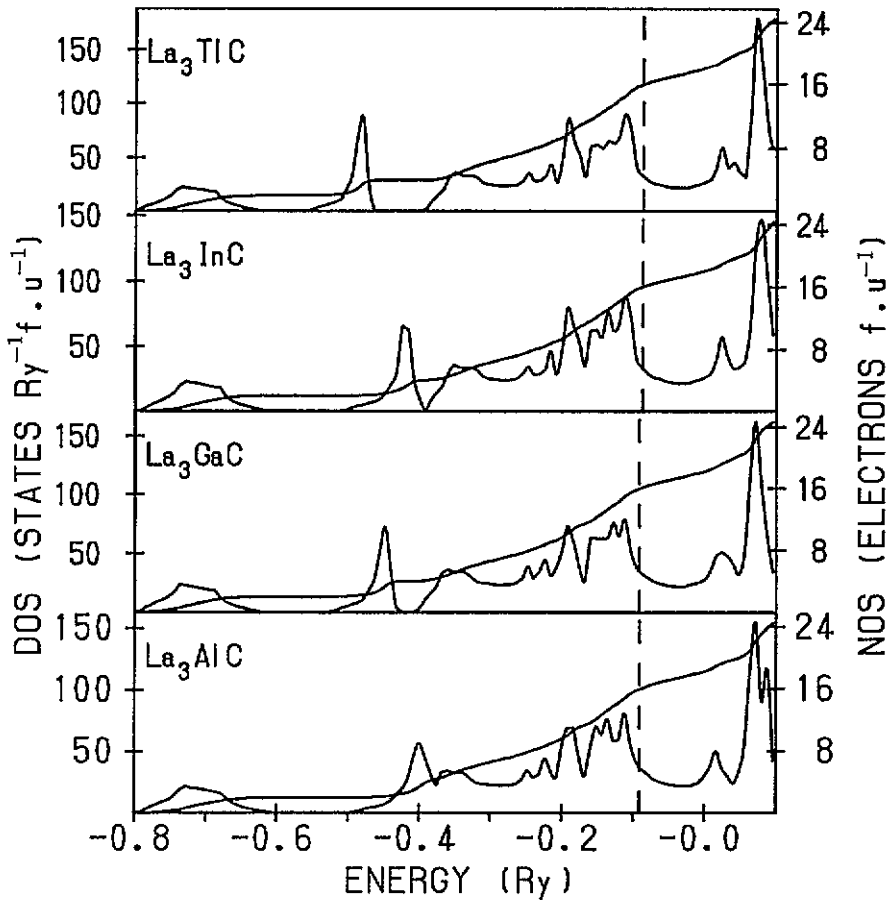


Figure 2. DOS of  $\text{La}_3\text{XC}$  ( $X \equiv \text{Al, Ga, In or Tl}$ ).

Our more recent studies on transition-metal aluminides show that  $E_F$  will fall on the peak in the DOS curve, if the material undergoes metastability or martensitic transformation [18]. It has been experimentally observed that the glass-forming ability of La–Al alloys is good and this is one of the reasons for the low heat of formation in these alloys compared with  $\text{La}_3\text{XC}$  systems [37]. The experimental  $\Delta H$ -value for  $\text{La}_3\text{Al}$  ( $L_{12}$ ) is  $-25 \pm 6 \text{ kJ mol}^{-1}$  and is in good agreement with our theoretical value of  $-28.18 \text{ kJ mol}^{-1}$ .

It is clear from figure 1 that, as  $E_F$  falls on the peak in the DOS curve of the  $\text{La}_3\text{Ti}$  system, it should be expected that the system should have metastability which is the reason for the non-identification of the  $L_{12}$  phase [38]. However, Iandelli [39] found that the crystal structure of  $\text{La}_3\text{Al}$  is of the cubic  $\text{Cu}_3\text{Au}$  type ( $L_{12}$ ), whereas Buschow and van Vucht [30] from their x-ray studies showed that  $\text{La}_3\text{Al}$  possesses the hexagonal structure of  $\text{Mg}_3\text{Cd}$  ( $\text{D}_{019}$ ) type. The heats of formation of  $\text{La}_3\text{Al}$  for both  $L_{12}$  and  $\text{D}_{019}$  structures given in table 1 show that the cubic  $L_{12}$  phase is more favourable than the hexagonal  $\text{D}_{019}$  phase. Regarding the experimentally observed discrepancies in the crystal structure of  $\text{La}_3\text{Al}$ , it should be understandable from our total-energy study that the total energies of the  $L_{12}$  and  $\text{D}_{019}$  structures are not very different ( $0.0065 \text{ Ryd f.u.}^{-1}$ ) and in this case it is possible for the system to stabilize in either phase.

From table 2, it can be seen that there is a considerable difference between the  $N(E_F)$ -



values obtained by the LMTO and the TB LMTO methods for  $\text{La}_3\text{X}$  compounds. One of the reasons for the deviation is the fall of  $E_F$  on the peak of the DOS curve for these compounds (figure 1). Hence, a small disturbance in  $E_F$  will cause a large deviation in the  $N(E_F)$ -value. In contrast, the difference between the  $N(E_F)$ -values for  $\text{La}_3\text{XC}$  compounds obtained by the LMTO and TB LMTO methods is not large. Because  $E_F$  falls on the flat valley of the DOS curve for these compounds, a small perturbation in  $E_F$  will not affect the  $N(E_F)$ -value much. Further, on account of the slow convergence of the LMTO method, the eigenvalues are calculated with an accuracy of  $10^{-3}$  Ryd between two consecutive iterations to achieve self-consistency. Our previous studies show that this accuracy is sufficient to explain the superconductivity of intermetallics [18]. Owing to the fast convergence in the TB LMTO scheme, we are able to calculate the eigenvalues with an accuracy of  $10^{-4}$  Ryd within a shorter computational time. Apart from the above fact, the basis orbitals and structure constants used in the TB LMTO method are the screened versions of those used in the LMTO method. Hence the above two reasons may be responsible for the difference between the  $N(E_F)$ -values calculated by these two methods.

In general, in the calculation of  $T_c$  for the transition metals, the value of  $\mu^*$  is taken as 0.13 [40]. The electronic contribution to  $T_c$  (i.e.  $\eta$ ) arising from various sites of  $\text{La}_3\text{X}$  and  $\text{La}_3\text{XC}$  compounds given in table 2 clearly shows that the electronic contribution to  $T_c$  arises mainly from the La site ( $\eta_{\text{La}}$ ) which is responsible for superconductivity in these compounds. As La is a transition metal, the value of  $\mu^*$  used in the calculation of  $T_c$  for these compounds is quite justified. Although the  $\mu^*$ -value used in our calculation is justified, this may lead to some systematic error in the  $T_c$ -values for both the  $\text{La}_3\text{X}$  and the  $\text{La}_3\text{XC}$  systems, but this error is a minimum in the relative results in which we are interested.

The insertion of C into the  $\text{La}_3\text{X}$  compounds expands the lattice; this negative pressure on the La atoms shifts the bottom of the s band to lower energies more rapidly than the bottom of the d band. However, our angular-momentum-decomposed DOS study on  $\text{La}_3\text{XC}$  compounds shows that a strong covalent bonding exists between La d and C p states. Moreover, the more electronegative nature of C attracts electrons from La and hence the number of electrons in the La bands decreases on C addition. As suggested by Postural *et al* [41], because of the strong covalent hybridization and ionicity,  $E_F$  falls on the valley in the DOS curve of  $\text{La}_3\text{XC}$  compounds in figure 2. Since  $E_F$  falls on the pseudo-gap in the DOS curve, the heats of formation of  $\text{La}_3\text{XC}$  compounds obtained from our total-energy studies are larger (table 1) than those of  $\text{La}_3\text{X}$  compounds.

Because of the isostructural and isoelectronic nature of  $\text{La}_3\text{X}$  ( $\text{X} \equiv \text{Al, Ga, In or Tl}$ ) compounds, the atomic number is found to increase from Al to Tl, and hence one can expect the lattice parameter also to have a systematic increasing trend. Hence, we anticipate a lower  $a_0$  (equilibrium lattice constant) for  $\text{La}_3\text{Ga}$  than for  $\text{La}_3\text{In}$ . However, the experimentally observed lattice parameter of  $\text{La}_3\text{Ga}$  deviates greatly from the linear trend expected for  $\text{La}_3\text{X}$  compounds (see table 1). Moreover, only one report is available regarding the lattice parameter of  $\text{La}_3\text{Ga}$  [42]. Hence, similar to our previous studies on  $\text{Zr}_3\text{Al}$  [18], we have estimated the equilibrium lattice parameter of  $\text{La}_3\text{Ga}$ . This theoretically obtained lattice parameter was found to be in agreement with the expected linear trend. Also, the  $T_c$ -value calculated for  $\text{La}_3\text{Ga}$  with the experimental lattice parameter is negligible and that with the theoretical lattice parameter is found to be in good agreement with the experimental value, indicating that the experimental lattice parameter is somewhat erroneous. Further, the value for the heat of formation of  $\text{La}_3\text{Ga}$  estimated from our total-energy studies (table 1) is found to be positive among the compounds considered here. This indicates that  $\text{La}_3\text{Ga}$  is more metastable than other  $\text{La}_3\text{X}$  compounds. In addition to this, a strong correlation has

been observed between the La–La distance and the superconducting transition temperature of La-based superconductors [9,43]. According to this correlation, if the La–La distance is larger, then the system will have a low  $T_c$ . For the experimental lattice constant of  $\text{La}_3\text{Ga}$ , the La–La distance is larger than for the other  $\text{La}_3\text{X}$  compounds. Because of this, the theoretically calculated  $T_c$ -value is zero. However, for the theoretically estimated lattice parameter of  $\text{La}_3\text{Ga}$ , the La–La distance is comparable with those for other  $\text{La}_3\text{X}$  compounds and consequently the calculated  $T_c$ -value of the theoretically obtained lattice parameter is comparable with the experimental  $T_c$  (table 2).

Previous calculations have shown that the superconducting behaviour of solids is very sensitive to their crystal structure [18,44]. As mentioned earlier,  $\text{La}_3\text{Al}$  possesses both  $\text{L1}_2$  and  $\text{D0}_{19}$  structures. In order to understand the effect of the structures on the superconducting behaviour, we have performed band-structure and  $T_c$  calculations for both structures with their experimentally observed equilibrium lattice parameters (table 1). From our results, we have found that  $T_c$  is not sensitive to the various structures of  $\text{La}_3\text{Al}$ . Apart from this, there is not much variation between the value of  $N(E_F)$  for both phases of  $\text{La}_3\text{Al}$ . One of the possible reasons for the larger  $T_c$  for  $\text{La}_3\text{In}$  than for the other  $\text{La}_3\text{X}$  compounds is the larger pd scattering in In compared with other X atoms and also both La and In atoms contribute equally to  $\lambda$ .

The  $-\Delta H$ -values of  $\text{La}_3\text{X}$  and  $\text{La}_3\text{XC}$  compounds are given in table 1, which clearly shows that the  $-\Delta H$ -values of the carbide systems are larger than those of non-carbide systems. It is well known that materials having a large  $-\Delta H$ -value will be more stable. Hence, the  $\text{La}_3\text{XC}$  systems are more stable than the  $\text{La}_3\text{X}$  compounds. Our heat-of-formation values agree with the experimental results in the sense that the  $\text{La}_3\text{XC}$  systems are more stable than the  $\text{La}_3\text{X}$  systems [10]. The experimental and the theoretical  $T_c$ -values given in table 2 clearly show that the stable compounds (i.e.  $\text{La}_3\text{XC}$ ) invariably have a low  $T_c$ . Hence, the general belief that a high stability and a low  $T_c$  should go hand in hand in intermetallic compounds is quantitatively established through our total-energy calculations.

## 5. Conclusions

In intermetallic compounds, the carbon behaves as a stabilizer as well as an electronic properties tuner. We have found several interesting and important results and, in particular, the following.

(i) The NMR, magnetic susceptibility and specific-heat measurements show that the Fermi level should fall on the peak of the DOS curve of  $\text{La}_3\text{In}$  and  $\text{La}_3\text{Tl}$  and this is confirmed by our theoretical studies as shown in figure 1.

(ii) The electron–phonon coupling constant calculated from the band-structure results shows that  $\text{La}_3\text{X}$  systems belong to the class of strong-coupling superconductors and it is consistent with experimental observations.

(iii) The superconducting behaviour of  $\text{La}_3\text{X}$  compounds is sensitive to volume of the unit cell. For the experimental lattice parameter, the theoretically calculated  $T_c$ -value of  $\text{La}_3\text{Ga}$  is very small whereas, for the theoretically obtained equilibrium lattice constant, the calculated  $T_c$ -value is found to be comparable with the experimental value.

(iv) Our previous calculations on  $\text{Zr}_3\text{Al}$  in the  $\text{L1}_2$  and  $\text{D0}_{19}$  structures show that the  $T_c$ -value is sensitive to the structures. However, for  $\text{La}_3\text{Al}$ , the  $T_c$  and  $N(E_F)$ -values are not much affected by the variation in crystal structure.

(v) The insertion of C into  $\text{La}_3\text{X}$  systems results in the following effects which suppress the  $T_c$  in  $\text{La}_3\text{X}$  systems.

(a) Expansion of the lattice by carbon addition is one of the causes of the suppression of the  $T_c$  of  $\text{La}_3\text{XC}$  compounds.

(b) Because of the more electronegative nature of carbon, finite La d electrons are transferred to C and further there is a strong covalent hybridization between C and La in  $\text{La}_3\text{XC}$ , which causes  $E_F$  to fall on the pseudo-gap. Hence, the La  $\eta_{pd}$  contribution decreases and correspondingly  $T_c$  for  $\text{La}_3\text{X}$  compounds decreases owing to the carbon addition.

(c) The  $\text{La}_3\text{XC}$  systems are more stable than  $\text{La}_3\text{X}$  compounds are (table 1). The metastability present in  $\text{La}_3\text{X}$  systems is the main cause of the higher  $T_c$  in these compounds.

(d) Because of the strong covalency existing in the  $\text{La}_3\text{XC}$  compounds, the cohesive energy, bond strength and hence  $\Theta_D$  of these compounds are higher. The phonon stiffening due to the above facts weakens  $\lambda$  and hence  $T_c$ .

Further, our more recent studies on  $\text{La}_3\text{Y}$  and  $\text{La}_3\text{YC}$  ( $\text{Y} \equiv \text{Sn}$  or  $\text{Pb}$ ) systems show that the carbon suppresses the superconductivity and this is consistent with the available experimental results [10, 11].

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### References

- [1] Andres K, Bucher E, Darack S and Maita J P 1972 *Phys. Rev. B* **4** 2716
- [2] Nagarajan R, Mazumdar C, Hossain Z, Dhar S K, Gopalakrishnan K V, Gupta L C, Godart C, Padalia B D and Vijayaraghavan R 1994 *Phys. Rev. Lett.* **72** 274
- [3] Cava R J *et al* 1994 *Nature* **367** 146, 252
- [4] Slegrist T, Zandbergen H W, Cava R J, Krajewski J J and Peck W F Jr 1994 *Nature* **367** 254
- [5] Hong N M, Michor H, Vybomov M, Holubar T, Hundegger P, Perthold W, Hilscher G and Rogl P 1994 *Physica C* **227** 85
- [6] Mazdumar C, Nagarajan R, Godant C, Gupta L C, Latroche M, Dhar S K, Leny-Clement C, Padalia B D and Vijayaraghavan R 1993 *Solid State Commun.* **87** 413
- [7] Gupta L C 1995 Personal communication
- [8] Matthias B T, Compton V B and Corenzwit E 1961 *J. Phys. Chem. Solids* **19** 130
- [9] Wang Rong-Yao 1986 *Phys. Status Solidi a* **94** 445
- [10] Heinigner F, Bucher E, Maita J P and Descouts P 1974 *Phys. Rev. B* **8** 3194
- [11] Descouts P, Perrin B, Dupanloup A and Treyvand A 1978 *J. Phys. Chem. Solids* **39** 161
- [12] Gschneidner K A Jr 1978 *J. Less Common Met.* **62** 167  
Gschneidner K A, McMasters O D and Ostenson J E 1973 *Proc. 10th Rare Earth Research Conf. (1973) (Conference Publication CONF-730402-p2)* vol 2, ed J K Clement and M Therald (Springfield, VA: National Technical and Information Service) p 721
- [13] Gschneider K A Jr 1993 *J. Alloys Compounds* **190** 83
- [14] Abrikosov A A and Gor'kov L P 1981 *Zh. Eksp. Teor. Fiz.* **39** 1781 (Engl. Transl. 1961 *Sov. Phys.-JETP* **12** 1242)
- [15] Guertin R P, Crow J E and Parks R D 1966 *Phys. Rev. Lett.* **16** 1095  
Mapple M B and Kang-Soo Kim 1969 *Phys. Rev. Lett.* **23** 118
- [16] Radousky H B, Jarlborg T, Knapp G S and Freeman A J 1982 *Phys. Rev. B* **26** 1208
- [17] Hackenbracht D and Kubler J 1979 *Z. Phys.* **B 35** 27

- [18] Ravindran P and Asokamani R 1994 *Phys. Rev. B* **50** 668
- [19] Andersen O K 1975 *Phys. Rev. B* **12** 3060
- [20] Andersen O K and Jepsen O 1984 *Phys. Rev. Lett.* **53** 2571
- [21] Kuentzler R and Waterstrat R M 1988 *Solid State Commun.* **68** 85
- [22] Dew-Hughes D 1974 *Cryogenics* **14** 435
- [23] Kuentzler R and Waterstrat R M 1988 *J. Less-Common Met.* **125** 261
- [24] Xu J H and Freeman A J 1990 *Phys. Rev. B* **41** 12553  
Carlsson A E and Meschter P J 1990 *J. Mater. Res.* **5** 2813  
Hong T, Watson-Yang T J, Guo X Q, Freeman A J, Oguchi T and Xu J H 1991 *Phys. Rev. B* **43** 1940  
Xu H and Freeman A J 1991 *J. Mater. Res.* **6** 1188
- [25] Butler W H 1981 *Treatise Mater. Sci. Technol.* **21** 165–221
- [26] Testardi L R, Meek R L, Poate J M, Royer W A, Storm A R and Wernick J H 1975 *Phys. Rev. B* **11** 4304
- [27] Izyumov Y A and Kurmaev E Z 1976 *Usp. Fiz. Nauk* **118** 53 (Engl. transl. 1976 *Sov. Phys.-Usp.* **17** 26)
- [28] Marchenco V A and Polovov V M 1980 *Sov. Phys.-JETP* **51** 535
- [29] Cava R J, Botlogg B, Siegrist T, Krajewski J J, Peck W F Jr, Carter S, Felder R J, Takaji H and van Dover R B 1994 *Phys. Rev. B* **49** 12384
- [30] Buschow K H J and van Vucht J H H 1967 *Philips Res. Rep.* **22** 233
- [31] Gschneidner K A Jr 1995 Private communication
- [32] Knapp G S, Bader S D and Fisk Z 1976 *Phys. Rev. B* **13** 3783
- [33] Lee T K, Birman J L and Williamson S J 1977 *Phys. Rev. Lett.* **39** 839
- [34] Fisk Z and Webb G 1976 *Superconductivity in d- and f- band Metals* ed D H Doughlass (New York: Plenum) p 545
- [35] Pickett W E and Singh D J 1994 *Phys. Rev. Lett.* **72** 3702  
Matthies L F 1994 *Phys. Rev. B* **49** 13279  
Lee J I, Zhao T S, Kim I G, Min B I and Youn S J 1994 *Phys. Rev. B* **50** 4030  
Coehoorn R 1994 *Physica C* **228** 331  
Singh D J 1994 *Phys. Rev. B* **50** 6486
- [36] Fujimori A *et al* 1994 *Phys. Rev. B* **50** 9660  
Pellegrin E, Meigs G, Chen C T, Cava R J, Krajewski J J and Peck W F Jr 1995 *Phys. Rev. B* submitted  
Golden M S, Knupfer M, Kielwein M, Buchgeister M, Fink J, Teehan D, Pickett W E and Singh D J 1995 *Europhys. Lett.* **218** 369
- [37] Sommer F, Keita M, Krull H G, Predel B and Lee J J 1988 *J. Less Common Met.* **137** 267
- [38] Delfino S, Saccone A, Gacciamani G and Ferro R 1985 *Z. Metallk.* **76** 7
- [39] Iandelli A 1959 *The Physical Chemistry of Metallic Solutions and Intermetallic Compounds* (London: HMSO) p 3F
- [40] Papaconstantopoulos D A, Boyer L L, Klein B M, Williams A R, Moruzzi V L and Janak J F 1977 *Phys. Rev. B* **15** 4221
- [41] Pastoral A, Colinet C and Hicter P 1985 *Physica B* **132** 177
- [42] Shunk F A 1969 *Constitution of Binary Alloys, Second Supplement* (New York: McGraw-Hill)
- [43] Smith T F and Luo H L 1967 *J. Phys. Chem. Solids* **28** 569  
Zarubia O A 1973 *Sov. Phys.-Solid State* **14** 2497
- [44] Papaconstantopoulos D A, Boyer L L, Klein B M, Williams A R, Moruzzi V L and Janak J F 1977 *Phys. Rev. B* **15** 4221