PHYSICAL REVIEW B VOLUME 44, NUMBER 5 1 AUGUST 1991-I

Electron energy bands and superconductivity of the intermetallics $BaRh_2$ and $LaRu_2$

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(Received 30 May 1990; revised manuscript received 25 January 1991)

We report the computation of electron energy bands of the intermetallic compounds $BaRh_2$ and $LaRu_2$. The energy bands were determined using the self-consistent linear muffin-tin-orbital method. The band-structure results were primarily used to calculate the electron-phonon coupling constant in order to explain the superconducting behavior. Further, the conduction bandwidth, electronic specific heat coefficient, and Pauli paramagnetic susceptibility obtained using the band-structure results are also reported. These results are compared with previously reported values for compounds of similar structure.

I. INTRODUCTION

It is interesting to note that there exist several intermetallic compounds with the $MgCu_2$-type structure exhibiting superconductivity.[1-3] Most of these superconducting compounds have a valence-electron concentration of 6.67. Their superconducting transition temperatures (T_c) lie in the range of 3 to 9 K. Among these compounds $BaRh_2$ and $LaRu_2$ have the values of T_c as 6 and 4.45 K,[1,4] respectively. It should be emphasized here that very little experimental work has been made for these compounds. In view of this, the theoretically calculated values such as the Fermi energy, the density of states, and conduction bandwidth that are reported here for $BaRh_2$ and $LaRu_2$ assume greater significance. However, different T_c values are quoted for $LaRu_2$ ranging from 1.6 to 4.5 K by various workers.[4-6] We report here band-structure calculations made on these materials and their calculated values of electron-phonon coupling coefficients (λ). The intermetallic ZrV_2 has the highest T_c of 8.8 K among the superconducting intermetallics of the AB_2 type. This serves as a test case, as its band structure and T_c calculations were available.[7,8] The linear muffin-tin-orbital (LMTO) method[9] was employed here to obtain the self-consistent band structures. The band-structure outputs were used in McMillan's formula to calculate the values of λ and T_c. In addition to the above, the conduction bandwidth, electronic specific-heat coefficient, and the Pauli paramagnetic susceptibility are calculated.

II. ELECTRON ENERGY BANDS OF $BaRh_2$ AND $LaRu_2$

A. Structural details of $BaRh_2$ and $LaRu_2$

Both these intermetallic compounds are known to crystallize in the $MgCu_2$-type structure. This is similar to the spinel structure without oxygen and with the ideal atomic radii ratio r_A/r_B is 1.225.[6,10] The unit cell contains 8 molecules of the AB_2 type. The positions of the basis[10] of six atoms or two molecules of the AB_2 type associated with the primitive cell given in terms of the lattice parameter are A: (0,0,0); (1/4,1/4,1/4) and B: (5/8,5/8,5/8); (5/8,7/8,7/8); (7/8,5/8,7/8); and (7/8,7/8,5/8). The lattice constants of $BaRh_2$ and $LaRu_2$ are 7.852 and 7.702 Å, respectively.[3,6] The volume of the average atomic sphere was obtained by equating the volume of the fcc cell to the volume of the Wigner-Seitz (WS) sphere.

B. LMTO method

The LMTO method is very well suited for the closely packed systems. In this method, the secular determinant is made up of two parts, one that depends on the crystal structure and the other on the crystal potential. The basis functions, which are energy independent, are constructed from the partial functions and its energy derivatives matched at the sphere boundaries. These orbitals are known as muffin-tin orbitals and the atomic-sphere approximation (ASA) was applied in order to reduce the interstitial region in which the kinetic energy is assumed to be zero. The structure constants which are independent of a crystal potential can be calculated and will be subsequently used for the energy-band calculations for the system of interest.

C. Method of calculation

The electronic configurations considered for Ba and Rh, respectively, are the ⟨Xe⟩ core plus ($6s^2$) valence and ⟨Kr⟩ core plus ($4d^8 5s^1$) valence. The same for La and Ru are ⟨Xe⟩ core plus ($5d^1 6s^2$) valence and ⟨Kr⟩ core plus ($4d^7 5s^1$) valence, respectively. The total number of electrons per primitive cell are 40 and 38 for these compounds $BaRh_2$ and $LaRu_2$ and we need about 20 bands to accommodate these electrons. The charge densities were calculated with the above electronic configurations by solving the relativistic Hartree-Fock equation. The WS sphere radius of the respective atom is found out by minimizing both, the potential discontinuity at the sphere boundary and the charge transfer between the atoms. The Barth-Hedin exchange correlation scheme was used for constructing the potentials. The trial potential parameters for the individual atoms were constructed by solving the Dirac equation for the chosen E_ν's.[9] These trial potential parameters were used in the LMTO calculation to obtain the energy bands. To begin with the calculation 20 k points in the irreducible Brillouin zone (IBZ) were taken and the self-consistency was achieved after 40 iterations in which the E_ν's are fixed to be the center of the bands. The final few runs were made for 89 k points in the IBZ with an eigenvalue accuracy of 1 mRy.

D. Results and discussion

The band structure of $BaRh_2$ is shown in Fig. 1, and the 20-band cluster arises from the contributions coming from the Rh d electrons and s electrons of Ba. The majority of the bands are due to Rh d electrons and the Fermi level cuts the 20th band. These are reflected also from Fig. 2 in which the density of states, the number of states, and their partial components are shown. It is found from Table I and Fig. 2 that the density of states contribution is mainly due to the d orbitals of the Rh atoms in $BaRh_2$. The conduction bandwidth is found to be 0.303 Ry. Table II gives the sphere radii and the four self-consistent potential parameters used in the LMTO calculation. The electronic specific heat coefficient obtained is 6.047 mJ $mol^{-1}K^{-2}$ and a detailed comparison of the above values could not be made due to the nonavailability of the experimental data. To check the validity of the band-structure calculation it is desirable to compare the conduction bandwidth with that obtained from soft-x-ray emission data[11] as was done for elemental Mg (Ref. 12) or $MgCu_2$.[11]

The band structure and the density of states of $LaRu_2$

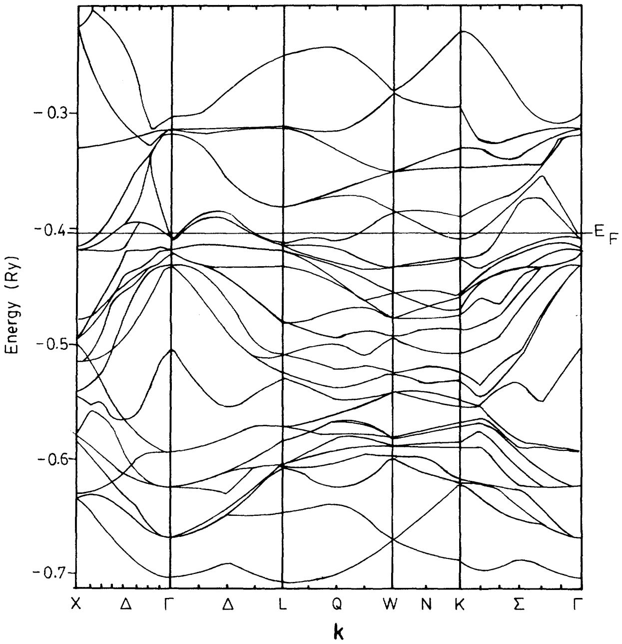

FIG. 1. The energy bands of $BaRh_2$.

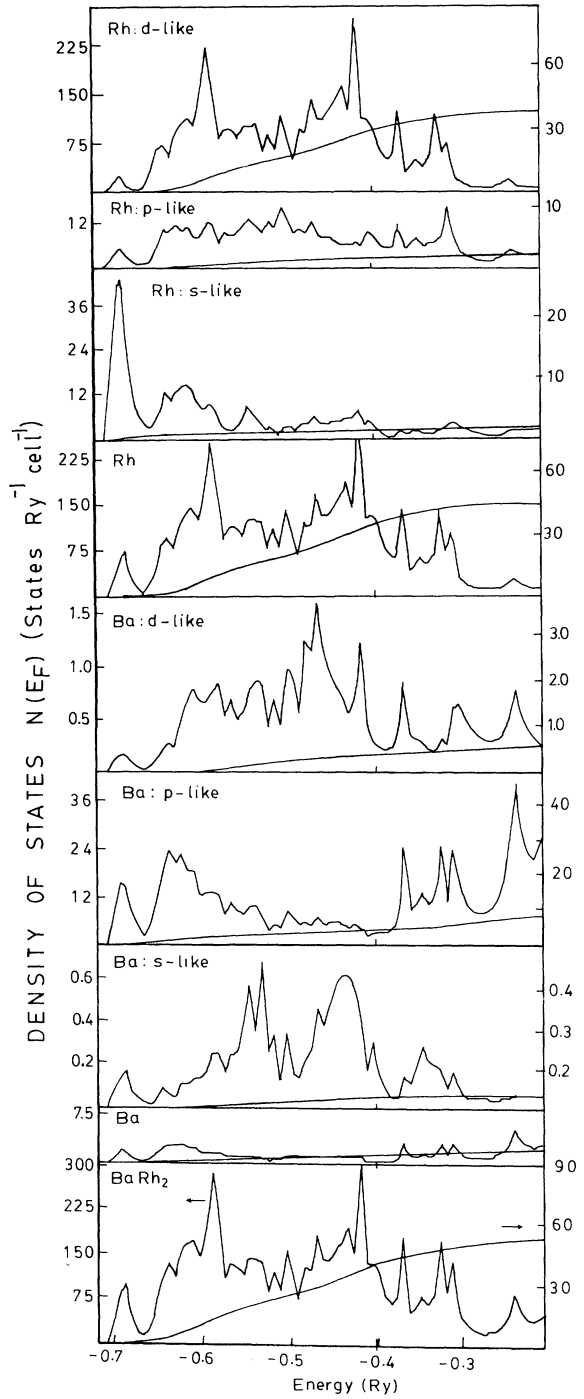

FIG. 2. The density of states, number of states, and their partial components of $BaRh_2$.

TABLE I. The density of states, number of states, their partial components, and the electronic configurations.

	Density of states (states $\text{Ry}^{-1}\,\text{cell}^{-1}\,\text{spin}^{-1}$)				Number of states			Configuration	
	s	p	d	Total	s	p	d	s	d
Ba	0.119	2.248	0.134	2.501	0.040	1.950	0.096	2	
2Rh	1.961	4.993	57.853	64.807	1.270	1.336	15.305	2	16
BaRh_2				67.308					
La	0.012	3.432	0.348	3.792	0.049	3.006	0.115	2	1
2Ru	0.673	1.899	81.167	83.739	1.202	1.555	13.071	2	14
LaRu_2				87.531					

are given in Figs. 3 and 4. Similar to the earlier case, there is a 20-band complex and the Fermi level cuts the bands arising from the d electrons of Ru and s electrons of La. The conduction bandwidth here is found out to be 0.382 Ry. The self-consistent potential parameters are given in Table II along with that of BaRh_2. The calculated electronic specific heat coefficient from the known density of states is 7.911 mJ $\text{mol}^{-1}\,\text{K}^{-2}$ while the experimental value is 8.5 mJ $\text{mol}^{-1}\,\text{K}^{-2}$.[4]

III. BAND STRUCTURE AND T_c CALCULATION OF ZrV_2

As the band structure of ZrV_2 has been performed using several techniques[7,8] and also its T_c has been calculated, it served as a test case. The band structure obtained by us for ZrV_2 for 89 k points in the irreducible wedge of the Brillouin zone is found to be very similar to that obtained by Huang *et al.* (1988) who have employed the LAPW method.[7] The electron-phonon coupling constant (λ), calculated using different methods of band-structure calculations, is found to lie in the range 1.36 to 1.7, whereas our value is 1.45. It is important to note that these λ values lead to fairly large T_c values. For instance, the value of T_c calculated by Huang *et al.* (1988) is 25 K which differs very much from the experimental value of 8.8 K. The expression used for T_c in their calculation is

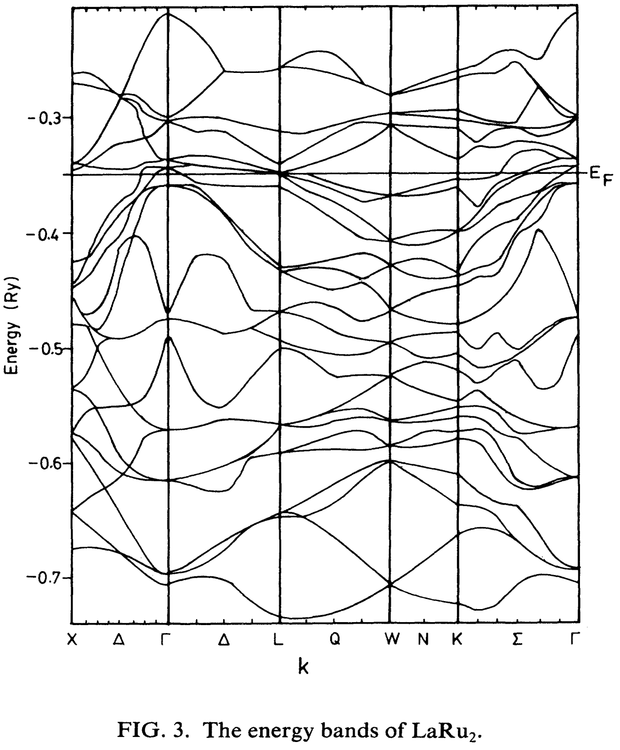

FIG. 3. The energy bands of LaRu_2.

$$T_c=\frac{\langle w^2\rangle^{1/2}}{1.20}\exp\left[\frac{-1.04(1+\lambda+\mu_{\text{sp}})}{\lambda-(\mu^*+\mu_{\text{sp}})(1+0.62\lambda)}\right], \tag{1}$$

where $\langle w^2\rangle$ is the mean-square phonon frequency, μ_{sp} is the electron-spin interaction parameter, and μ^* is the electron-electron interaction parameter. In order to achieve better agreement between the theoretical and the experimental value for T_c, the value for μ_{sp} is arbitrarily assigned[7] as 0.1 or 0.2, whereas in the case of the Chevrel phase compounds the value of μ_{sp} was taken as zero.[13] In our calculation of T_c for BaRh_2 and LaRu_2, we make use of the well-known McMillan equation[14] obtained from Eq. (1) when $\mu_{\text{sp}}=0.0$. We want to emphasize the fact that our calculation does not contain the parameter μ_{sp} whose value was arbitrarily varied in the above-mentioned calculations.

IV. T_c CALCULATION OF BaRh_2 AND LaRu_2

The electron-phonon coupling constant λ for the AB_2 type is calculated using the expression[15,16]

$$\lambda=\frac{\eta}{M\langle w^2\rangle}=\frac{\eta_A}{M_A\langle w^2\rangle}+\frac{\eta_B}{M_B\langle w^2\rangle}, \tag{2}$$

where the Hopfield parameter $\eta=N(E_F)\,\langle I^2\rangle$, M is the atomic mass, and the suffixes A and B represent the type of atoms. As we use the atomic-sphere approximation in our band-structure calculation, the e-ph matrix element $M_{l,l+1}$ is expressed in terms of logarithmic derivatives D_l instead of phase shifts. The latter procedure has been adopted in our earlier calculations[17,18] to calculate λ and hence T_c. The matrix element is given as[19]

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

In the above, D_l and D_{l+1} are the logarithmic derivatives of the wave functions ϕ_l and ϕ_{l+1}. All these parameters are evaluated at the sphere radius S and corresponding to the Fermi energy E_F. $V(S)$ is the potential at the sphere radius. The mean-square phonon frequency $\langle w^2 \rangle$ is approximated by the relation $\langle w^2 \rangle = 0.5\Theta_D^2$ as has been

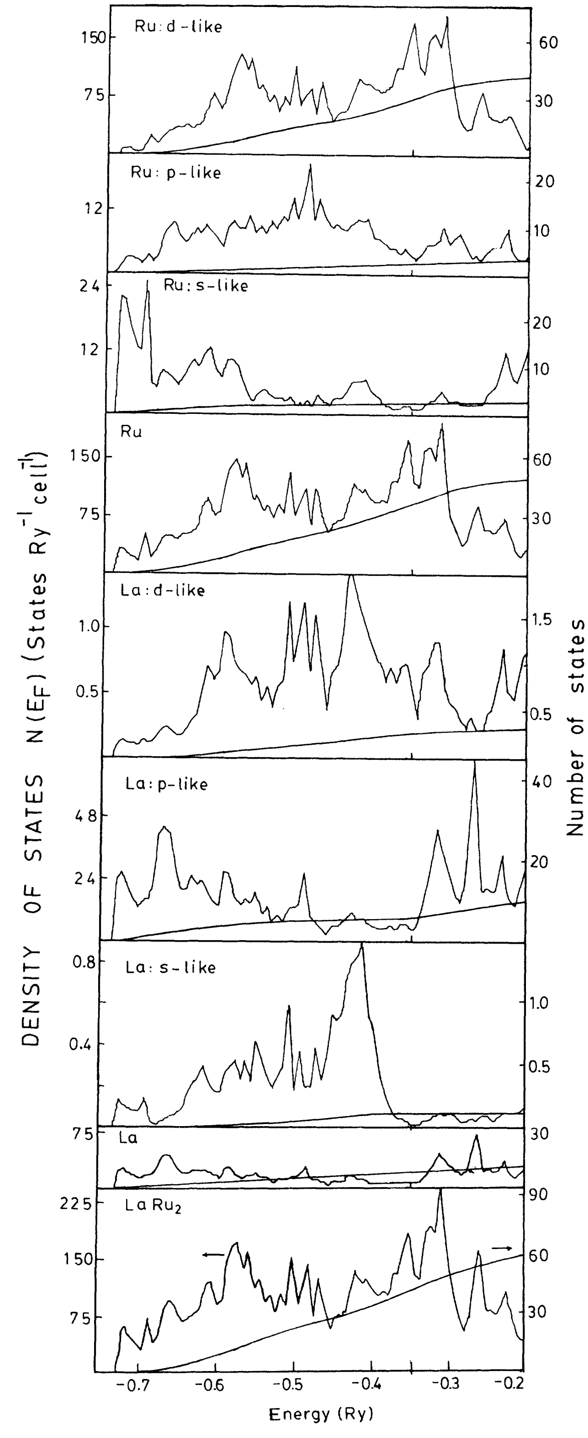

FIG. 4. The density of states, number of states, and their partial components of LaRu$_2$.

TABLE II. The atomic-sphere radii and the four potential parameters at the center of the bands of BaRh$_2$ and LaRu$_2$.

	S (a.u.)	E_ν (Ry)			$S\phi^2(-)$			$\phi(-)/\phi(+)$			$\langle \dot{\phi}^2 \rangle^{-1/2}$ (Ry)		
		s	p	d	s	p	d	s	p	d	s	p	d
Ba	2.901	2.310	0.212	1.771	0.401	0.139	0.181	0.934	0.479	0.319	0.218	0.459	0.306
Rh	3.318	0.148	0.858	0.163	0.210	0.194	0.018	0.839	0.589	0.057	0.379	0.330	1.710
La	2.820	2.368	0.170	1.828	0.429	0.139	0.185	0.930	0.473	0.309	0.202	0.451	0.300
Ru	3.264	0.210	0.954	0.254	0.230	0.210	0.023	0.845	0.600	0.056	0.340	0.301	1.477

TABLE III. Fermi energy (E_F), partial wave functions (ϕ_l), logarithmic derivatives D_l, electron stiffness constant (η), electron-phonon coupling constant (λ), T_c, specific heat coefficient (γ), and Pauli paramagnetic susceptibility χ.

	E_F (Ry)	$\phi(E_F)$			$D_l(E_F)$			η (a.u.)	λ	T_c (K)		γ (mJ mol^{-1} K^{-2})		χ (10^{-4}), emu/mol
		s	p	d	s	p	d			Expt	Theor	Expt	Theor	
Ba		−0.675	−0.602	1.354	4.637	−2.304	1.242	0.036	0.011					
Rh		0.767	−1.105	−0.048	−1.532	0.242	−84.601	1.379	0.561					
$BaRh_2$	−0.404							1.415	0.572	6.00	1.82		6.047	1.598
La		−0.860	−0.483	1.335	3.631	−3.620	1.107	0.151	0.045					
Ru		0.785	−1.110	−0.085	−1.645	0.137	−17.138	0.112	0.047					
$LaRu_2$	−0.350							0.263	0.092	4.45		8.5	7.911	2.078

done in our earlier calculations.[17,18] The values of η_A, η_B, λ_A, and λ_B calculated for both systems are given in Table III.

A. Results and discussion

The experimental value of Θ_D is not known for $BaRh_2$ and hence we use the same value of Θ_D which is available for $LaRu_2$. We are justified in using the same Θ_D, as the elements Ba and La as well as Rh and Ru are adjacent elements. The value of Θ_D quoted in the literature for $LaRu_2$ ranges from 146 to 164 K.[4,5,20] The parameters $N(E_F)$, ϕ_l, D_l, η, and λ are tabulated in Table III. The latest Θ_D which has been claimed to be more accurate is 164 K. Using this value the T_c calculated is 1.82 K whereas the experimental value is 6 K. We would like to emphasize here that the parameter u_{sp} which was varied arbitrarily in the case of ZrV_2 was not at all used here. We did not find T_c to be very sensitive to the small variation of Θ_D ranging from 146 to 164 K. Apart from the above, in view of the fact that λ is found inside the exponential and even a small variation of λ will considerably change the value of T_c, it is satisfactory to note that the theoretical estimate of T_c is fairly in good agreement with the experimental value.

A similar procedure was adopted for $LaRu_2$ to calculate λ and its value turned out to be 0.092. A comparison between the theoretical and the experimental electronic specific heat coefficients using the expression,[21]

$$\gamma_{\mathrm{expt}}=\gamma_{\mathrm{theor}}(1+\lambda) \tag{4}$$

also yielded a λ value of 0.074. It is satisfactory to note that the value of λ obtained from first-principle calculations which makes use of the band-structure outputs is in good agreement with that deduced from Eq. (4). However, this low-λ value gives rise to an enormously high value of T_c because of the fact that the denominator found in the exponential becomes negative as the second term in the denominator dominates over the first term. It is well known that λ should always be greater than the second term otherwise, the term inside the exponential will become positive which will in turn blowup the value of T_c.

The Pauli paramagnetic susceptibilities are calculated using the density of states values for the both compounds and are shown in Table III. The area under the ESR curve will give an experimental estimate of χ_{Pauli}. As such experiments have not been performed for these solids our theoretical values could not be checked.

V. CONCLUSION

The first band-structure calculations performed on $BaRh_2$ and $LaRu_2$ have been reported here. The density of states, the number of states, and their partial contributions coming from different atoms have been given in great detail (Figs. 1–4). As $BaRh_2$ and $LaRu_2$ have identical crystal structures of the type AB_2 of which the pairs of A and B atoms differ by just one atomic number, we made a systematic and detailed comparison of the parameters involved in the calculation of λ in Table III. It is found that the partial wave functions and their logarithmic derivatives are of the same magnitude except for the *d* component of the logarithmic derivative of Rh and Ru. This is due to the rapid change in the wave function near the Fermi energy.

With regard to the band-structure calculation, our experience shows that the choice of the sphere radii and the potential continuity are easily achieved in AB_2 and ABO_3 structures rather than the A_2BO_4 structure because of the fact that the latter is crystallizing in layered perovskite structure.[22,23]

ACKNOWLEDGMENTS

The authors wish to thank UGC and CSIR, India for financial support.

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