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Band Structures for Superconductors $LnBa_2Cu_3O_7$ (Ln=Ho, Er, Tm, Yb)

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Electronic energy band structures for the superconducting system given by substitutions of rare earth cations (Ho,Er,Tm,Yb) for Y in $YBa_2Cu_3O_7$ were investigated by employing the EHMO approach based on the tight-binding method. As compared, to the results of $YBa_2Cu_3O_7$, the substitutions of the rare earth cations dramatized the degree of complexity of the energy band structures at the Fermi surface and resulted in an increase in the number of bands crossing the Fermi level E_f and electronic densities of states, while those for $PrBa_2Cu_3O_7$ decreased. From the energy bands and the electronic densities of states obtained from calculations, it is explained why the substitutions of Ho, Er, Tm and Yb in $YBa_2Cu_3O_7$ can still maintain the high superconducting transition temperature T_c, while the substitution of Pr does not.

INTRODUCTION

In 1987, the Y–Ba–Cu–O superconducting system, for which the superconducting transition temperature T_c is from 90 to 100 K, was first reported by M. K. Wu and coworkers.[1] It was proved later that these superconductors were triply layered oxygen-deficient perovskites $YBa_2Cu_3O_y$, with y slightly less than 7. In their unit cell, two-dimensional (2D) Cu–O planes and one-dimensional (1D) Cu–O ribbons are included, and there are two O vacancies. It is now known that for the $YBa_2Cu_3O_y$ system, values of T_c in the range 90–100 K can be obtained by a wide variety of isoelectronic cation substitutions, for example, most rare earthes in place of Y in $YBa_2Cu_3O_y$.[2,3] The rare earthes are strongly magnetic ions. Generally speaking, substitutions of the strongly magnetic ions for Y in $YBa_2Cu_3O_y$ are of no advantage to superconductivity, that is, they can cause the superconducting transition temperature T_c to decrease or destroy the superconductivity. Why do the substitutions of the magnetic rare earthes, except for Pr ($PrBa_2Cu_3O_7$ is a semiconductor), for Y in the Y–Ba–Cu–O system still retain a high-T_c? It is explained as follows.[4] The ionic radii of the rare earthes and Y are very similar, the change in coupling strength between the positive and negative ions caused by the isoelectronic cation substitutions is very small, and so is that in crystal structures. There is, therefore, little change in the transition temperature. This explanation does not seem to be satisfactory. From the point of view of the quantum theory, the physical property of a system, for instance superconductivity, is in close relationship with its electronic structure. Thus, in order to attempt rationalizing the origin of the superconductivity for the Ln–Ba–Cu–O (Ln = Ho, Er, Tm and Yb) system, calculations are made on the electronic energy band structures for $HoBa_2Cu_3O_7$, $ErBa_2Cu_3O_7$, $TmBa_2Cu_3O_7$ and $YbBa_2Cu_3O_7$ by using the EHMO approach based on the tight-binding method. From the band structures and the electronic densities of states obtained, the reason why the rare earth cation substitution can maintain a high-T_c is given in the present paper.

CRYSTAL STRUCTURE AND CALCULATION

Crystal structures given by the full substitution of rare earth cations for Y in orthorhombic $YBa_2Cu_3O_7$ are similar to that of $YBa_2Cu_3O_7$. Like $YBa_2Cu_3O_7$, the low-temperature phases for $LnBa_2Cu_3O_7$ (Ln = Ho, Er, Tm, Yb) are orthorhombic and have the Pmmm ($D_4'h$) structures. The crystal structure of the orthorhombic $LnBa_2Cu_3O_7$ is shown in Figure 1. There are two O vacancies in the 15-site unit cell. One, which is presented by the *y*-site in Figure 1, lies in the Cu–O plane between the two Ba–O planes, and the other, presented by the *z*-site in Figure 1, in the Ln plane. Much work has been done in determining their structure parameters, which is not described in detail here. In the present calculations, the atomic coordinates of $LnBa_2Cu_3O_7$ (Ln = Ho, Er, Tm, Yb) are taken from Refs. 5–8.

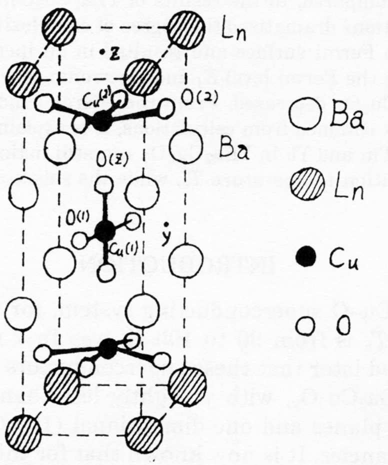

Figure 1. Crystal structure of $LnBa_2Cu_3O_7$

In this work, all the calculations of electronic energy band structures are carried out employing the EHMO approach based on the tight-binding method.[9–10] The non-diagonal elements, H_{ij}, in the $\boldsymbol{H}$ matrix are obtained from the following

$$H_{ij} = k_1 * (H_{ii} + H_{jj}) * S/2$$

$$k_1 = k + \Delta^2 + \Delta^4 * (1 - k),$$

$$\Delta = (H_{ii}) - H_{jj})/(H_{ii} + H_{jj})$$

where H_{ii} are taken as the negatives of atomic orbital ionization potentials and k = 1.75. The basis sets include the 4f, 5d, 6s, 6p atomic orbitals for the rare earth elements, the 3d, 4s, 4p for the Cu atom, the 6s, 6p for the Ba atom, and the 2s, 2p valence state orbitals for the O atom. L. Lemin and coworkers[11,12] from spectral data, give the orbital exponents and the atomic orbital ionization potentials for the rare earth elements. For the configuration $4f^{\alpha}\ 5d^{\beta}\ 6s^{\gamma}$, the atomic orbital ionization potentials are given by the following equation

$$\begin{aligned}\mathrm{VOIP}^i(\alpha,\beta,\gamma,q) = {} & B_o+B_1\alpha + B_2\alpha^2 + B_3\beta + B_4\beta^2 + B_5\gamma + B_6\gamma^2 + B_7q + \\ & B_8q^2 + B_9\alpha\beta + B_{10}\alpha\gamma + B_{11}\alpha q + B_{12}\beta\gamma + B_{13}\beta q + B_{14}\gamma q,\end{aligned}$$

$$(i = 4f,\ 5d,\ 6s)$$

where q is the electric charge of the rare earth ions and the coefficients B_o, B_1, $\cdots$ B_{14} were determined by least-squares fitting of VOIP obtained from spectral data. In the light of the above equation, the atomic orbital ionization potentials for the rare earth elements can be easily obtained. All the EHMO parameters used in the present calculations are summarized in Table I. Calculations of the electronic energy band structures are carried out along the high-symmetry directions in the first Brillouin zone shown in Figure 2, with 15 k-points in each 1/8 Brillouin zone.

TABLE I

EHMO parameters used in calculations

	$-H_{ii}$(eV)				Orbital Exponent			
	s	p	d	f	s	p	d	f
Pr	5.607	3.60	7.061	13.57	1.287	0.972	1.778	4.509
Ho	5.989	4.56	6.687	18.38	1.395	1.054	2.031	5.829
Er	6.134	4.68	6.471	18.59	1.408	1.064	2.062	5.968
Tm	6.301	4.80	6.217	18.72	1.420	1.073	2.090	6.106
Yb	6.490	4.92	5.925	18.76	1.432	1.082	2.119	6.259
Cu	9.101	6.06	16.45		1.541	1.541	3.813	
Ba	5.21	3.69			1.25	1.25		
O	32.44	15.86			2.189	2.029		
Y	11.99	6.60			1.8	1.8		

ENERGY-BAND STRUCTURE

In the unit cell of $LnBa_2Cu_3O_7$ (Ln=Ho, Er, Tm, Yb), the basis sets include 79 valence state orbitals, which lead to 79 electronic energy bands. 46, 47, 47 and 48 occupied bands are, respectively, included in the 79 bands for $HoBa_2Cu_3O_7$, $ErBa_2Cu_3O_7$, $TmBa_2Cu_3O_7$ and $YbBa_2Cu_3O_7$. The Fermi level, E_f, for $HoBa_2Cu_3O_7$ is −15.44 eV, −15.38

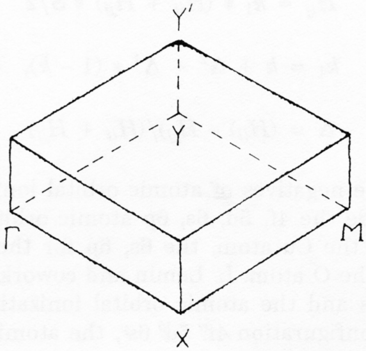

Figure 2. The 1/8 Brillouin zone of $LnBa_2Cu_3O_7$.

eV for $ErBa_2Cu_3O_7$, –15.35 eV for $TmBa_2Cu_3O_7$, and –15.33 eV for $YbBa_2Cu_3O_7$. The seven lowest O–2s valence bands in $LnBa_2Cu_3O_7$, for which the dispersions are very small, lie about 19 eV below E_f. These O– 2s bands are non-bonding in character. The seven rare earth 4f orbitals for the rare earthes do not participate in bond formation. These rare earth 4f bands, for which the dispersions are zero, are very flat. For $HoBa_2Cu_3O_7$, the 4f bands lie about 2.9 eV below E_f, 3.2 eV for $ErBa_2Cu_3O_7$, 3.3 eV for $TmBa_2Cu_3O_7$ and 3.4 eV for $Yba_2Cu_3O_7$. For each of $LnBa_2Cu_3O_7$, there are 36 bands, for which the total bandwidth is about 3 eV, spanning the energy range from –17.5 to –14.5 eV. These energy bands arise mostly from Cu3d–O2p overlaps. The electronic energy band structures of the orthorhombic $LnBa_2Cu_3O_7$ (Ln = Ho, Er, Tm, Yb) are shown in Figure 3, in which the zero energy is placed at the Fermi level. For comparison, that for $PrBa_2Cu_3O_7$ is also shown in Figure 3. It can be seen from Figure 3, on one hand, that the dispersions of all the energy bands of $LnBa_2Cu_3O_7$ along the

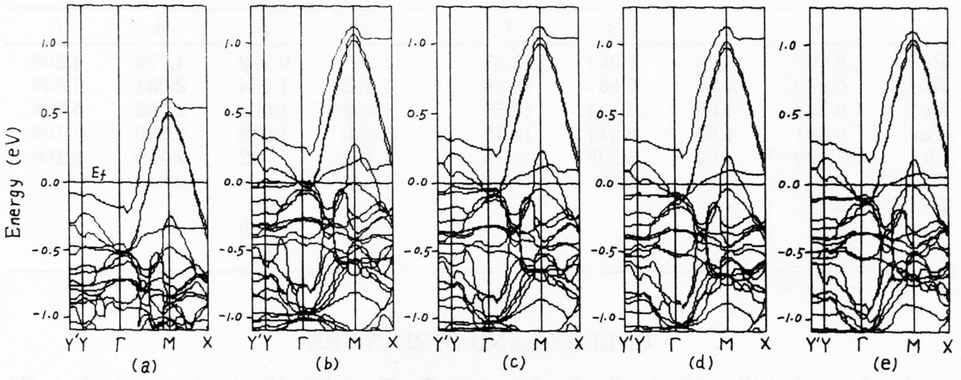

Figure 3. Energy band structures: (a) $PrBa_2Cu_3O_7$ (b) $HoBa_2Cu_3O_7$ (c) $ErBa_2Cu_3O_7$ (d) $TmBa_2Cu_3O_7$ (e) $YbBa_2Cu_3O_7$

line Y′–Y in the Brillouin zone (see Figure 2) are relatively small and that several Cu3d–O2p bands, in which occupied bands are included, cross the Fermi level in all the directions of the wave vectors located in a*b* plane. It demonstrates that $LnBa_2Cu_3O_7$ have 2D metallic band structures. On the other hand, both the dispersions of the Cu3d–O2p bands for $LnBa_2Cu_3O_7$ (Ln = Ho, Er, Tm, Yb) and the interactions between these bands are very strong, and the concentration of the Cu3d–O2p bands near the Fermi level is large while that for $PrBa_2Cu_3O_7$ is not. Therefore, $LnBa_2Cu_3O_7$ (Ln = Ho, Er, Tm, Yb) are of a good metallic property while $PrBa_2Cu_3O_7$ is not. Actually, $PrBa_2Cu_3O_7$ is a semiconductor. In $PrBa_2Cu_3O_7$, there are three broad anisotropic bands crossing E_f, two of which correspond to the two 2D Cu–O planes and the third to the 1D Cu–O ribbons, but four bands corresponding to the 2D Cu–O planes and the 1D Cu–O ribbons in $LnBa_2Cu_3O_7$ (Ln = Ho, Er, Tm, Yb). one of which is the lowest unoccupied band, cross E_f. All of these bands arise from the Cu3d–O2p antibonding orbitals. In addition, it can be seen from Figure 3 that the energy band structures of $HoBa_2Cu_3O_7$, $ErBa_2Cu_3O_7$, $TmBa_2Cu_3O_7$ and $YbBa_2Cu_3O_7$ are quite complicated near the Fermi level, while that of $PrBa_2Cu_3O_7$ is not. The degree of complexity of the energy band structure at the Fermi surface can greatly influence the superconducting transition temperature T_c. It can be taken that, as the number of the Cu3d–O2p energy bands near the Fermi surface increases, densities of the hole-carriers in the 2D Cu–O planes and the 1D Cu–O ribbons increase considerably, and so also does the transition temperature T_c. From the point of view of multiband effects,[13,14] T_c can also be enhanced by the interactions between the Cu3d–O2p energy bands near the Fermi surface. It may be the reason why substitutions of strongly magnetic Ho,Er,Tm and Yb for Y in $YBa_2Cu_3O_7$ do not affect the superconducting transition temperature T_c, while T_c for $PrBa_2CU_3O_7$ is very low.

ELECTRONIC DENSITIES OF STATES

Total electronic densities of states (TDOS) for $LnBa_2Cu_3O_7$ (Ln = Pr,Ho,Er,Tm,Yb) and atomic projected densities of states (PDOS) for $HoBa_2Cu_3O_7$ are shown in Figure 4 and Figure 5, respectively. They are direct results of the energy band structures shown above. It can be seen that they have all strong peaks, which arise largely from the 2D Cu–O planes and the 1D Cu–O ribbons as demonstrated by the atomic projected densities of states shown in Figure 5, near the Fermi level except for $PrBa_2Cu_3O_7$. The total densities of states and the atomic projected densities of states at the Fermi level are summarized in Table II, in which those for $YBa_2Cu_3O_7$ are also listed for comparison. For the rare earthes and Ba, the atomic projected densities of states near the Fermi level are almost zero. Thus, their only role is in contributing electrons to the Cu–O planes and Cu–O ribbons. The total densities of states at E_f, $N(E_f)$ are 11.8 states/eV-unit cell for $HoBa_2Cu_3O_7$, 10.4 for $ErBa_2Cu_3O_7$, 9.6 for $TmBa_2Cu_3O_7$, 9.1 for $YbBa_2Cu_3O_7$, while those for $PrBa_2Cu_3O_7$ are only 2.7. Obviously, the densities of states for $LnBa_2Cu_3O_7$ (Ln = Ho,Er,Tm,Yb) are larger than those for $YBa_2Cu_3O_7$ (7.1 states/eV-unit cell), while those for $PrBa_2Cu_3O_7$ are much smaller. From the point of view of the BCS theory, densities of states at the Fermi level are in close relationship with superconductivity, that is, they can have a great influence on the transition temperature T_c.

For the present purposes to estimate the transition temperature T_c approximately, let us adopt the simple BCS expression[15]

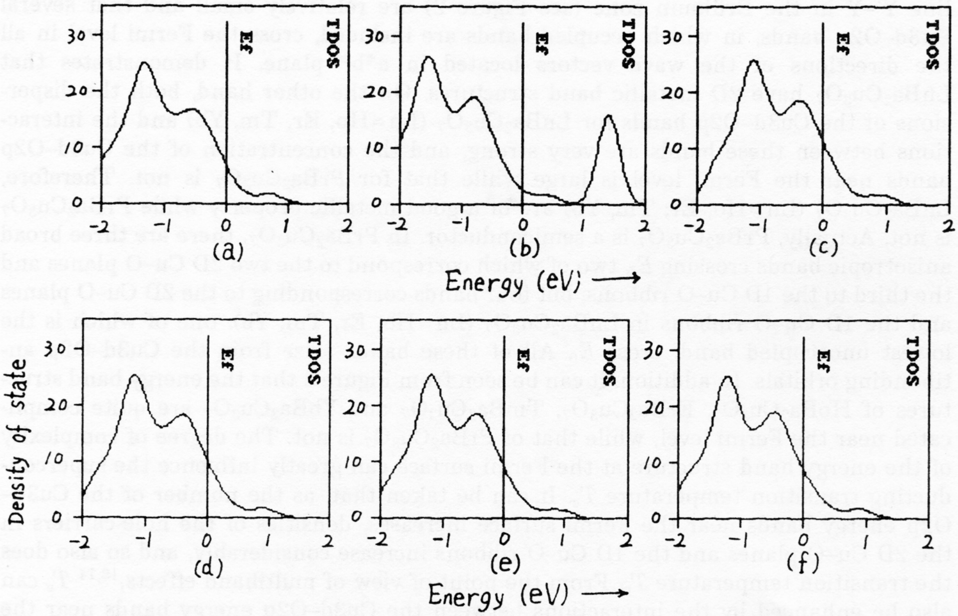

Figure 4. Total densities of states (states/eV-unit cell): (a) $YBa_2Cu_3O_7$ (b) $PrBa_2Cu_3O_7$ (c) $HoBa_2Cu_3O_7$ (d) $ErBa_2Cu_3O_7$ (e) $TmBa_2Cu_3O_7$ (f) $YbBa_2Cu_3O_7$

$$T_c = 1.14 \langle\omega\rangle \exp(-1/N(E_f)V)$$

where $\langle\omega\rangle$ is an average phonon energy (expressed in degrees K), V is an interaction parameter, and $N(E_f)$ is the total densities of states at the Fermi surface. Since the electronic structures of the rare earth elements are very similar and so also are their crystal structures given by their substitutions for Y in $YBa_2Cu_3O_7$, it is assumed that their $\langle\omega\rangle$ and V are equal. Obviously, based on this assumption and the BCS expression, it is indicated from the $N(E_f)$ given in Table II that sine the $N(E_f)$ for $HoBa_2Cu_3O_7$, $ErBa_2Cu_3O_7$, $TmBa_2Cu_3O_7$ and $YbBa_2Cu_3O_7$ are large compared with that for $YBa_2Cu_3O_7$, these systems can maintain a high-T_c although these rare earthes are strongly magnetic, while T_c for $PrBa_2Cu_3O_7$ is very low because of its small densities of states as compared to that for $YBa_2Cu_3O_7$.

CONCLUSION

In conclusion, substitutions of Ho, Er, Tm and Yb for Y in orthorhombic $YBa_2Cu_3O_7$ can dramatize the degree of complexity of electronic energy band structures at the Fermi surface, compared with the results for $YBa_2Cu_3O_7$, and result in an increase in electronic densities of states at the Fermi level. Therefore, $LnBa_2Cu_3O_7$ (Ln = Ho, Er, Tm and Yb) superconductors can maintain a high superconducting transition temperature T_c. $PrBa_2Cu_3O_7$, which is similar in its crystal structure to that of $YBa_2Cu_3O_7$, has electronic densities of states at the Fermi level much smaller than

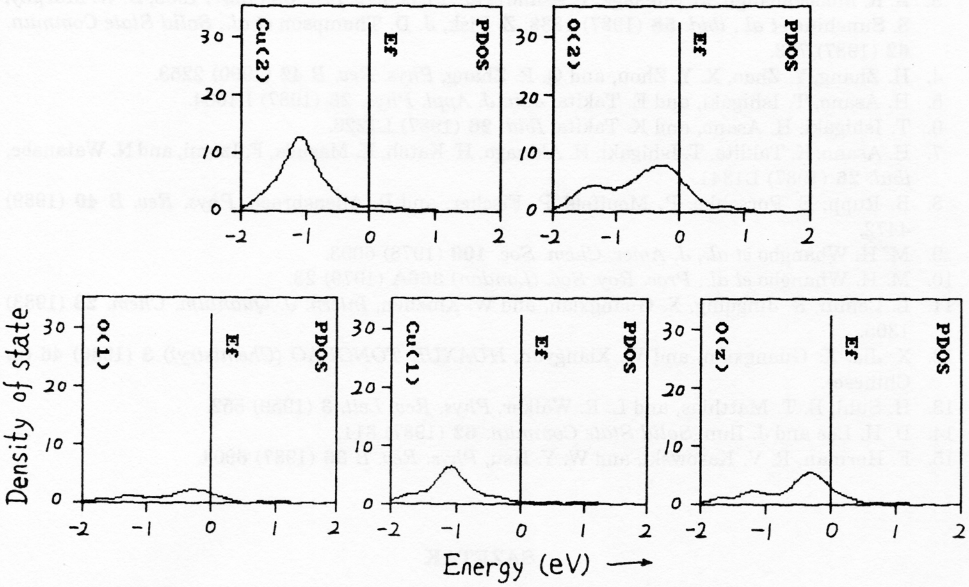

Figure 5. Atomic projected densities of states (states/3V-atom) for $HoBa_2Cu_3O_7$

TABLE II

Total and atomic projected densities of states at the Fermi level

$LnBa_2Cu_3O_7$	TDOS	PDOS						
		Ln	Ba	Cu(2)	O(2)	Cu(1)	O(1)	O(z)
$YBa_2Cu_3O_7$	7.14	0.01	0.00	0.45	0.94	0.39	0.84	0.75
$PrBa_2Cu_3O_7$	2.67	0.00	0.00	0.24	0.27	0.35	0.16	0.30
$HoBa_2Cu_3O_7$	11.80	0.06	0.01	0.45	1.50	0.36	1.68	1.52
$ErBa_2Cu_3O_7$	10.37	0.05	0.01	0.44	1.32	0.31	1.53	1.29
$TmBa_2Cu_3O_7$	9.56	0.04	0.00	0.43	1.25	0.28	1.46	1.18
$YbBa_2Cu_3O_7$	9.05	0.04	0.00	0.41	1.14	0.29	1.40	1.12

those of $YBa_2Cu_3O_7$. Its transitions temperature T_c is very low. It must be pointed out that although the present study cannot account for the reason why $PrBa_2Cu_3O_7$ is a semiconductor, it does provide the result that its T_c is very low.

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SAŽETAK

Strukture pojasa za supravodiče $LnBa_2Cu_3O_7$ (Ln = Ho,Er,Tm,Yb)

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Strukture elektronskih energijskih pojasa za sustave supravodiča dobivenih supstitucijom kationa lantanoida (Ho,Er,Tm,Yb) umjesto Y u V istraživana su medodom EHMO zasnovanom na metodi stegnutih veza (tight binding). U usporedbi s V, supstitucija kationima lantanoida dramatično je usložilla strukturu energijskih pojasa Fermijeve površine. Rezultat je povećanje broja pojasa koji križaju Fermijeve razine E_f i gustoće elektronskih stanja, dok one za $PrBa_2Cu_3O_7$ smanjuje. Iz energijskih pojasa i elektronske gustoće stanja računom je dobiveno objašnjenje zašto supstitucija Ho,Er,Tm i Yb mogu održavati visoku temperaturu supravodljivog prijelaza, a supstitucijom Pr se to ne postiže.