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BAND STRUCTURE OF RUTHENATE SUPERCONDUCTORS

JOHN D. DOW[1] AND ARKADIY A. ZOLOTOVSKY[2]

[1] *Department of Physics, Arizona State University,*
Tempe 85253, USA

[2] *Lashkaryov Institute of Semiconductor Physics,*
45, Prosp. Nauky, Kiev 03028, Ukraine
arkadiy_z@voliacable.com

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Abstract: We investigate the band structure of ruthenates using the first-principles method of density functional theory (DFT). We calculated the band structure and density of states at the Fermi level for superconductors Ba_2YRuO_6 and Sr_2YRuO_6. Our calculations show that the maximum critical superconducting transition temperature $T_c = 93$K can be obtained for Ba_2YRuO_6.

Keywords: band structure, superconductors, transition temperature

1. Introduction

Sr_2YRuO_6 has an onset critical temperature for superconductivity of $T_c =$ 49K when doped with Cu on Ru sites. As little as 1% of Cu dopant can produce superconductivity, and, by most accounts, this material, which becomes a superconductor at a temperature of 49K, is a genuine high-temperature superconductor. Its sister material, Cu-doped Ba_2YRuO_6, also exhibits superconductivity (at 93K) and thus it is an indisputable high-temperature superconductor (see Figure 1). For both Sr_2YRuO_6 and Ba_2YRuO_6, the onset of T_c is not tantamount to the onset of complete superconductivity, since Ru^{3+} ions, unlike Cu^{2+} ions, have vacant d-orbitals. These materials are of interest by the absence of cuprate planes, which makes them a counterexample to the assertion that the cuprate planes are necessary for high-temperature superconductivity.

In this paper, we calculate the band structures of Sr_2YRuO_6 and Ba_2YRuO_6 and demonstrate that these band structures are consistent with superconductivity [1].

2. Band-structure calculations

We calculated the band structures of high-temperature superconductors (HTSCs), using the BandLab code obtained from Bell Laboratories; BandLab was designed for Windows and performs electronic structure calculations of crystalline solids.

The bands were calculated using the method outlined by Pickett [2] and by Hohenberg-Kohn DFT [3]. A summary of the method and its applications was presented by Devreese and Van Camp [4], therefore the method is only outlined here.

Starting with the N-electron problem in the field of ionic potentials:

$$V_{\mathrm{ion}}(r) = \sum_m v_{\mathrm{ion}}(r - R_m) \tag{1}$$

with the ions fixed at positions R_m, we have the Hamiltonian:

$$H = \sum_i p_i^2/2m + \int n(r) V_{\mathrm{ion}}(r) dr + \frac{1}{2} \iint n(r) v(r - r') n(r') dr dr' \tag{2}$$

where, $n(r)$ is the electronic density at r, and $v(r - r')$ is the Coulomb interaction. Hohenberg and Kohn established that there is a one-to-one correspondence between the ionic potential V_{ion} (to within an arbitrary constant) and the ground state density n, therefore the many-body problem can be considered as a functional of the density rather than as a functional of the potential [3].

Hohenberg and Kohn [3] established that for variations δn of the energy density which conserve the particle number N, the ground-state energy functional $E[n]$ is minimized by the ground-state density, with corrections of order δn^2. The resulting variational principle allows one to accurately obtain numerical results.

Kohn and Sham [5] recast the energy functional into the form:

$$E[n] = T_0[n] + \int V_{\mathrm{ion}}(r) n(r) dr + \frac{1}{2} \iint n(r) v(r - r') n(r') dr dr' + E_{\mathrm{xc}}[n] \tag{3}$$

where $T_0[n]$ is the kinetic energy of the system of non-interacting electrons with the same density $n(r)$, and $E_{\mathrm{xc}}[n]$ is the exchange-correlation energy. If one has adequate approximations for $T_0[n]$ and $E_{\mathrm{xc}}[n]$, the energy can be obtained directly from Equation (3) by minimizing the energy with respect to $n(r)$.

Within the Kohn-Sham formalism [5], the value of $T_0[n]$ can be determined from the relations:

$$[p^2/2m + V_{\mathrm{eff}}(r;n)]\psi_i(r) = E_i \psi_i \tag{4}$$

$$V_{\mathrm{eff}}(r;n) = V_{\mathrm{ion}}(r) + \int v(r - r') n(r') dr' + v_{\mathrm{xc}}(r;n) \tag{5}$$

$$n(r) = \sum_i^{\mathrm{occ}} |\psi_i(r)|^2 \tag{6}$$

where

$$v_{\mathrm{xc}}(r;n) = \delta E_{\mathrm{xc}}[n] / \delta n(r) \tag{7}$$

The energy functional is minimized (by iteration to self-consistency) by the density functional described by Equations (4)–(6).

Within density functional theory, the one-electron eigenvalues and eigenfunctions have no physical meaning and are not physically realizable. They are the true excitation energies and eigenfunctions of the system of non-interacting electrons, which has the same density as the interacting material of interest; they arise from the "external" potential V_{eff}. This system is not physically realizable, but has an interesting connection to the excitations: when well-defined quasiparticles exist (*i.e.*, their widths are much less than their energies), they are described by a non-Hermitian problem:

$$(p^2/2m)\psi_i(r,E_i)+\int M(r,r',E_i)\psi_i(r',E_i)dr' = E_i\psi_i(r) \tag{8}$$

This equation bears a formal resemblance to the Kohn-Sham eigenvalue equation (4). The local Hermitian effective potential V_{eff} is replaced by a non-local, complex, energy-dependent "mass operator" or self-energy, M. In many solids, angle-resolved photoemission studies have shown that the bands from Equation (4) bear a close resemblance to the single-particle excitations in the region of the fundamental band gap. The self-energy is well represented by a local, real, energy-independent, effective potential V_{eff}. Conversely, when the excitations do not correspond directly to the calculated bands, one can conclude that the non-locality or energy-dependence of the self-energy is necessary for the comprehension of excitations. If the correspondence between calculated bands is lacking, the local Hermitian effective potential V_{eff} is replaced by a non-local one, and the observed excitation itself does not invalidate the formalism for obtaining the ground-state properties.

The exchange-correlation functional $E_{\text{xc}}[n]$ remains unknown. The majority of calculations invokes the highly successful local-density approximation:

$$E_{\text{xc}}[n]=\int \varepsilon_{\text{xc}}(n(r))n(r)dr \tag{9}$$

where $\varepsilon(n)$ is the exchange-correlation energy density of the homogeneous interacting electron gas of density n, which is known. Reviews containing discussions of applications of density functional theory and the generalization to spin-polarized systems are given, for example, in the book by Devreese and Van Camp [4].

3. Band structures of Sr_2YRuO_6 and Ba_2YRuO_6 high-T_c superconductors

The crystal structure of Ba_2YRuO_6 is shown in Figure 1.

Ab initio calculations were carried out for several ruthenates and cuprates in the framework of an approach based on density functional theory. The results of the calculations are presented in Figures 2–5 for the band structure and density of states in ruthenates. Through a comprehensive study of the density of states, a dependence of the value of T_c on the density of states at the Fermi level was revealed.

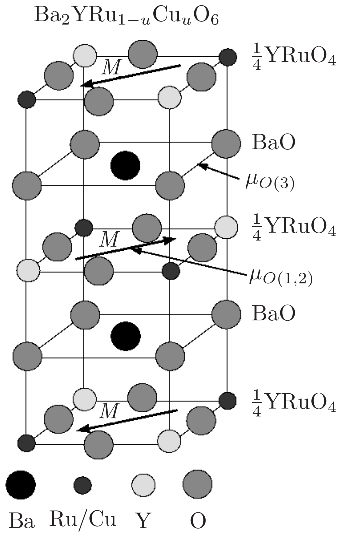
Ba$_2$YRu$_{1-u}$Cu$_u$O$_6$
$\frac{1}{4}$YRuO$_4$
M
BaO
$\mu_{O(3)}$
$\frac{1}{4}$YRuO$_4$
M
$\mu_{O(1,2)}$
BaO
$\frac{1}{4}$YRuO$_4$
M
Ba
Ru/Cu
Y
O

Figure 1. Crystal structure of Ba_2YRuO_6

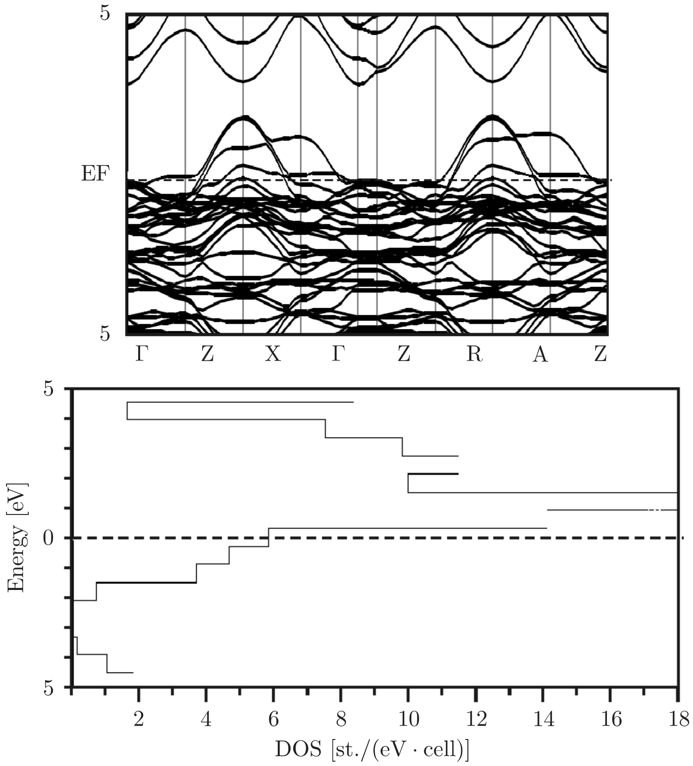

Figure 2. Results of the calculations of the band structure and density of states for Ba_2YCuO_6

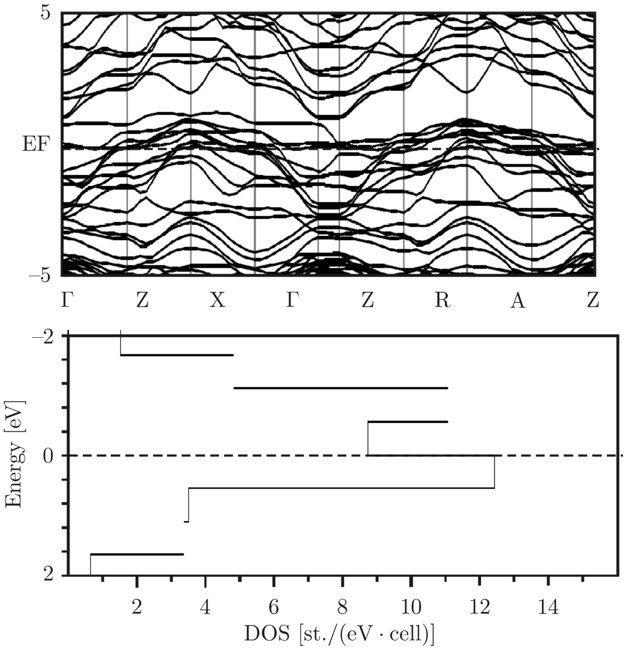

Figure 3. Results of the calculations of the band structure and density of states for Ba_2YRuO_6 at $T_c = 93$K

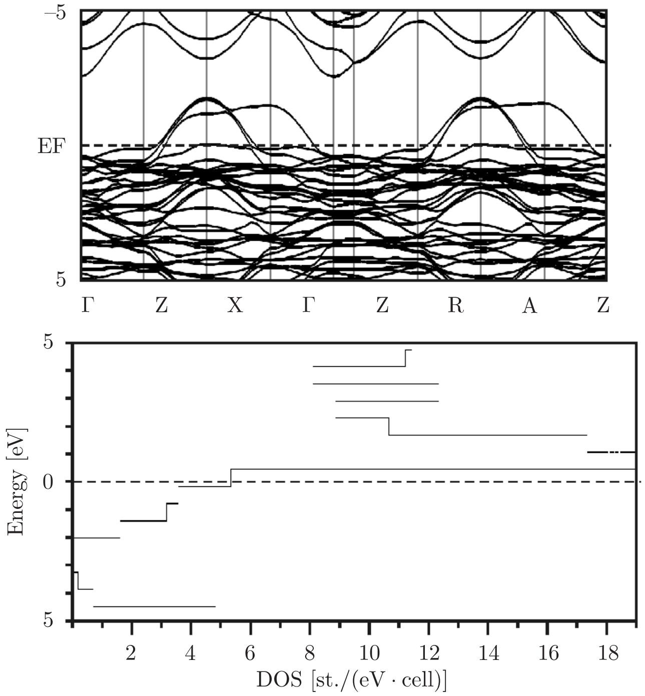

Figure 4. Results of the calculations of the band structure and density of states for Sr_2YCuO_6

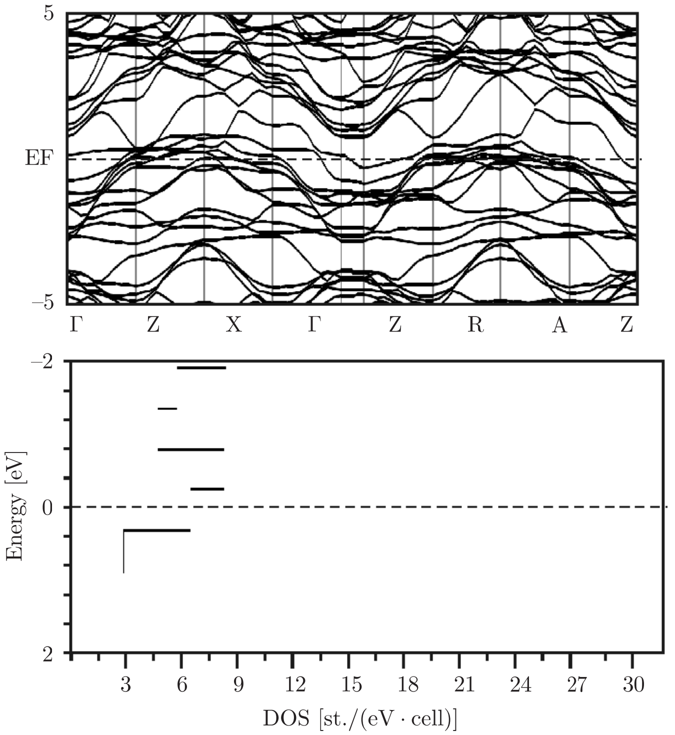

Figure 5. Results of the calculations of the band structure and density of states for Sr_2YRuO_6 at $T_c = 49K$

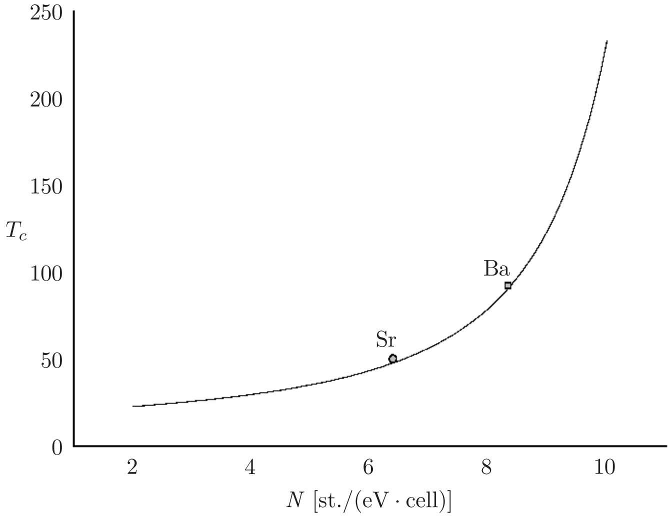

Figure 6. Dependence of T_c on the density of states at the Fermi surface $N(E_f)$ for ruthenate superconductors

In Figure 6, we present the dependence of the value of T_c on the density of states $N(E_f)$ at the Fermi surface. For the calculations of T_c, we applied the Bardeen-Cooper-Schrieffer model:

$$T_c = 1.14 \frac{\theta}{k_B} \exp\left(-\frac{1}{N(E_f)V}\right) \tag{10}$$

where θ is the Debye energy, V is the attractive pairing potential acting between electrons, and $N(E_f)$ is the density of states at the Fermi surface.

The calculations of band structures and densities of states showed that Sr_2YRuO_6 and Ba_2YRuO_6 are superconductors, whereas Sr_2YCuO_6 and Ba_2YCuO_6 are not. An analysis was performed to establish the ability of Cu and Ru to capture electron pairs. Results indicate that Cu is not able to capture electron pairs, since there are no vacancies in the d-orbitals of Cu. In contrast, in Ru there were vacancies in the d-orbitals and thus electron pairs were captured. Therefore, the consideration presented above allows us to conclude that Ru is responsible for the high-temperature superconductivity.

4. Summary

Ab initio calculations were performed for a number of ruthenates in the framework of density functional theory. The results indicate that the maximum critical superconducting transition temperature is $T_c = 93$K for Ba_2YRuO_6 and $T_c = 43$K for Sr_2YRuO_6.

Acknowledgements

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