BAND STRUCTURE OF RUTHENATE SUPERCONDUCTORS

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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 Ba₂YRuO₆ and Sr₂YRuO₆. Our calculations show that the maximum critical superconducting transition temperature $T_c = 93K$ can be obtained for Ba₂YRuO₆.

Keywords: band structure, superconductors, transition temperature

1. Introduction

Sr₂YRuO₆ 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 Ba₂YRuO₆, also exhibits superconductivity (at 93K) and thus it is an indisputable high-temperature superconductor (see Figure 1). For both Sr₂YRuO₆ and Ba₂YRuO₆, the onset of $T_c$ is not tantamount to the onset of complete superconductivity, since Ru³⁺ ions, unlike Cu²⁺ 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 Sr₂YRuO₆ and Ba₂YRuO₆ 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:

$$V_{\text{ion}}(r) = \sum_m v_{\text{ion}}(r-R_m)$$

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

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

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 $V_{\text{ion}}$ (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 $\delta n$ 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 $\delta n^2$. The resulting variational principle allows one to accurately obtain numerical results.

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

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

where $T_0[n]$ is the kinetic energy of the system of non-interacting electrons with the same density $n(r)$, and $E_{\text{xc}}[n]$ is the exchange-correlation energy. If one has adequate approximations for $T_0[n]$ and $E_{\text{xc}}[n]$, 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:

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

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

$$n(r) = \sum_{\text{occ}}|\psi_i(r)|^2$$

where

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

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 $V_{\text{eff}}$. 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:

$$\left(\frac{p^2}{2m}\right)\psi_i(r, E_i) + \int M(r, r', E_i)\psi_i(r', E_i)dr' = E_i\psi_i(r)$$ \hspace{1cm} (8)

This equation bears a formal resemblance to the Kohn-Sham eigenvalue equation (4). The local Hermitian effective potential $V_{\text{eff}}$ 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 $V_{\text{eff}}$. 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 $V_{\text{eff}}$ 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:

$$E_{\text{xc}}[n] = \int \varepsilon_{\text{xc}}(n(r))n(r)dr$$ \hspace{1cm} (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$_2$YRuO$_6$ and Ba$_2$YRuO$_6$

**High-$T_c$ superconductors**

The crystal structure of Ba$_2$YRuO$_6$ 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.
Figure 1. Crystal structure of \( \text{Ba}_2\text{YRuO}_6 \)

Figure 2. Results of the calculations of the band structure and density of states for \( \text{Ba}_2\text{YCuO}_6 \)
Figure 3. Results of the calculations of the band structure and density of states for Ba$_2$YRuO$_6$ at $T_c = 93$K

Figure 4. Results of the calculations of the band structure and density of states for Sr$_2$YCuO$_6$
Figure 5. Results of the calculations of the band structure and density of states for Sr$_2$YRuO$_6$ at $T_c = 49$ K.

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:

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

(10)

where $\theta$ is the Debye energy, $\Delta$ 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$_2$YRuO$_6$ and Ba$_2$YRuO$_6$ are superconductors, whereas Sr$_2$YCuo$_6$ and Ba$_2$YCuo$_6$ 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$_2$YRuO$_6$ and $T_c = 43$K for Sr$_2$YRuO$_6$.

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References
