

Comparative study of the electronic structure of pure and Ti-doped Sr_2RuO_4 superconductor

Jacques Soullard ^{a,*}, Ilya G. Kaplan ^{b,*}

^a Instituto de Física, UNAM, P.O. Box 20-364, 01000 Mexico DF, Mexico

^b Instituto de Investigaciones en Materiales, UNAM, P.O. Box 70-360, 04510 Mexico DF, Mexico

Available online 28 March 2007

Abstract

The electronic structure of undoped and Ti-doped Sr_2RuO_4 ceramics is studied by means of the embedded cluster method at the Hartree–Fock (HF) level and at the Møller–Plesset2 (MP2) electron correlation level. The drastic effect of the Ti impurity on the spin density in the impure crystal was revealed, the total spin density is practically concentrated on the Ru neighboring ions.

© 2007 Elsevier B.V. All rights reserved.

PACS: 74.25.Jb; 74.70.Pq; 74.62.Dh

Keywords: Sr_2RuO_4 ; Unconventional superconductivity; Electronic structure

1. Introduction

At present, it is accepted that the unconventional superconductivity (UCSC) in Sr_2RuO_4 [1] is provided by the spin-triplet Cooper pairing that corresponds to the chiral p-wave symmetry [2,3]. The theoretical arguments [2] in favour of ³P symmetry of the Cooper pairs were based on the similarity of its Fermi-liquid properties to those of liquid ³He and ferromagnetic related compound SrRuO_3 . The direct evidence for the triplet pairing has come from the NMR Knight shift measurements [4].

Latterly, the impurity ion substitution became a powerful tool to study the nature of superconductivity. As revealed in Ref. [5], the substitution of Ru atoms by non-magnetic Ti atoms induces local magnetic moments around the impurity and destroy the superconductivity at a very small Ti concentration, a characteristic feature of UCSC.

In this report, we present the results of a comparative calculations of the electronic structure of pure and Ti-doped Sr_2RuO_4 crystal by the electron correlated version of the

embedded cluster method [6]. This method was recently applied successfully to study the mechanism of T_c suppression by Zn and Ni impurities in high T_c cuprates [7].

2. Methodology

The *ab initio* calculations are carried out using the HF method and the MP2 perturbation theory as implemented in the Gaussian03 program. The core electrons of Ru and Sr atoms were described by the Los Alamos National Laboratory pseudopotential LANL2 with its proper DZ basis set. On oxygen atoms where all electrons are taken into account, the doubly split valence basis set 6-31G is supplemented by a shell of d polarization functions. To calculate the charge distribution we use the natural bond orbital (NBO) analysis provided by the program.

3. Results and discussion

3.1. Cluster $\text{Sr}_2\text{Ru}_4\text{O}_{20}$

The charge and spin distributions calculated at the UHF level is presented in Table 1 for the undoped and Ti-doped $\text{Sr}_2\text{Ru}_4\text{O}_{20}$ clusters in the state with spin $S = 1$ embedded in

* Corresponding authors.

E-mail addresses: soullard@fisica.unam.mx (J. Soullard), kaplan@iim.unam.mx (I.G. Kaplan).

Table 1
Charge and spin distribution at the HF level ($S = 1$)

	Spin density	NBO charge	Valence orbital population
<i>(a) Sr₂Ru₄O₂₀</i>			
Ru	+0.26	+1.40	5s ^{0.27} 4d ^{5.83}
Sr	+0.30	+1.46	5s ^{0.41}
O1	+0.14	-1.16	2s ^{1.78} 2p ^{5.37}
O2	-0.03	-1.39	2s ^{1.88} 2p ^{5.50}
<i>(b) Sr₂Ru₂Ti₂O₂₀</i>			
Ti	+0.05	+1.22	4s ^{0.27} 3d ^{2.01}
Ru	+1.06	+1.42	5s ^{0.25} 4d ^{5.91}
Sr	+0.02	+1.74	5s ^{0.16}
O1	-0.05	-1.20	2s ^{1.76} 2p ^{5.43}
O2	-0.01	-1.43	2s ^{1.85} 2p ^{5.57}

the Madelung field of pure crystal. The calculation of NBO charges takes into account an electronic density in excited (Rydberg) states which is not included in the valence orbital population shown in Table 1. This electronic density is small in the case of oxygen ions but is about 0.2e–0.5e in the case of cations.

For the charge distribution with Ti impurity, we note a strong reduction of Sr electronic charge (–0.28e) and an increase of 2p orbital population on O1 and O2. However, the main effect of the Ti impurity is a strong modification of the bonding in its vicinity.

The spin distribution in the pure material shows a positive uniform spin density on Ru, Sr and O1. There is a drastic effect of the Ti impurity on the spin density in the impure crystal, this density disappears on Sr and O1 and strongly increases on Ru (with respect to the pure case). The total spin density is practically concentrated on the Ru neighboring ions. This result is in agreement with the experimental findings of Ref. [5]. With respect to the crystal case, this can induce a strong modification of its magnetic behavior due to Ti impurities.

3.2. Cluster Ru₅O₁₆

The results for the undoped and Ti-doped Ru₅O₁₆ clusters are presented in Table 2. At the HF level, there is an electron transfer of 0.1e per Ti to the 2p orbitals of O1. It comes mainly from the 4s and 3d orbitals on the Ti

Table 2
Charge distribution at the HF and MP2 level ($S = 0$)

	NBO charge	Valence orbital population
<i>(a) Ru₅O₁₆</i>		
HF	Ru _{central}	+2.53
	Ru _{lateral}	+2.69
	O1	-1.26
MP2	Ru _{central}	+1.86
	Ru _{lateral}	+2.18
	O1	-0.95
<i>(b) Ru₄TiO₁₆</i>		
HF	Ti	+2.65
	Ru _{lateral}	+2.67
	O1	-1.36
MP2	Ti	+2.05
	Ru _{lateral}	+2.67
	O1	-1.11

impurity, the Ru valence orbital population is practically not modified.

Comparing HF and MP2, the impurity effect increases. In Ti-doped crystal, the Ru orbital population decreases and that of the of O1 increases. There is also a net increase of the Rydberg population likely related to conduction bands in metals.

Acknowledgements

The authors are pleased to acknowledge Manfred, Sigr-ist for valuable suggestions and comments. The study was partly supported by Grants, CONACyT(Mexico)46770 and UNAM IN107305.

References

- [1] Y. Maeno et al., Nature 372 (1994) 532.
- [2] T.M. Rice, M. Sgrist, J. Phys.: Condens. Matter 7 (1995) L643.
- [3] A.P. Mackenzie, Y. Maeno, Rev. Mod. Phys. 75 (2003) 657.
- [4] K. Ishida et al., Nature 396 (1998) 658.
- [5] M. Minakata, Y. Maeno, Phys. Rev. B 63 (2001) 180504(R).
- [6] I.G. Kaplan, J. Soullard, J. Hernández-Cobos, R. Pandey, J. Phys.: Condens. Matter. 11 (1999) 1049.
- [7] I.G. Kaplan, J. Soullard, J. Hernandez-Cobos, Phys. Rev. B 65 (2002) 214509.