

# SEMIEMPIRICAL AND FIRST PRINCIPLES STUDY OF THE CRYSTAL FIELD ACTING ON THE 4*f* ELECTRONS IN RARE EARTH CUPRATES\*

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*(Received July 10, 2002)*

A theoretical investigation of the rare earth ( $\text{RE}^{3+}$ ) localized 4*f* energy spectrum at regular sites of  $\text{RE Ba}_2\text{Cu}_3\text{O}_{6+x}$  ( $x = 0, 1$ ), and  $\text{RE}_2\text{CuO}_4$  cuprates was performed. To predict the  $k = 4$  and 6 crystal field (CF) parameters  $B_{kq}$ , we employed the semiempirical superposition model (SM) used earlier for quantitative estimates of the CF interaction acting on 4*f* states in RE cuprates. The SM model does not apply for the  $k = 2$  CF parameters where the long range electrostatic contribution dominates. Therefore, to calculate the  $k = 2$  CF parameters, we used the parameter-free first-principles method based on the density functional theory.

PACS numbers: 74.72.Jt, 71.70.Ch, 71.70.Mb

## 1. Introduction

The rare-earth (RE) ions in high  $T_c$  superconductors enter typically sites adjacent to the  $\text{CuO}_2$  planes where spin and charge carriers relevant to superconductivity are located. In contrast to conventional superconductors the presence of magnetic 4*f* electrons has only a negligible impact to the superconducting properties. The coexistence of the RE magnetism and superconductivity is particularly interesting in view of recent experimental evidence that in-plane electrons from hybridized O-2*p* and Cu-3*d* states mediate relatively strong RE-RE exchange interaction [1]. This finding indicates that

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\* Presented at the International Conference on Strongly Correlated Electron Systems, (SCES 02), Cracow, Poland, July 10–13, 2002.

spin-breaking theory of Abrikosov and Gorkov does not apply and that a non-conventional type of superconducting state is present. Thus the insight gained by the study of the RE magnetism is believed to be also helpful in understanding mechanism of high  $T_c$  superconductivity. The present work is focused on the phenomenological and first principles calculations of the crystal field (CF) interaction perturbing localized and strongly correlated states of the  $4f$  electrons in cuprate superconductors. Concrete calculations are performed for  $\text{REBa}_2\text{Cu}_3\text{O}_7$  ( $\text{RE} = \text{Pr}-\text{Yb}$ ) and  $\text{RE}_2\text{CuO}_4$  ( $\text{RE} = \text{Pr}, \text{Nd}, \text{Sm}$ ) systems providing ample experimental data on the CF interaction [2,3].

## 2. Theoretical method

An interaction with the CF produced by the neighboring core charges and valence electronic charge density is the strongest perturbation of the free ion  $4f$  shell state of trivalent RE ions in cuprates. The interaction Hamiltonian can be written as  $\mathcal{H}_{\text{CF}} = \sum B_{kq}[C_q^{(k)} + C_{-q}^{(k)}]$  where  $C_q^{(k)}$  transform as tensor operators under simultaneous rotation of the coordinates of all the  $4f$  electrons [1].  $B_{kq}$  are the so-called CF parameters. For a prediction of the  $k = 4$  and  $6$  CF parameters the standard superposition model (SM) was found to be very efficient in cuprates [1,3]. The SM does not apply for the second order parameters where the long range electrostatic contribution appears to dominate what causes a breakdown of one of the postulates of the SM model. Therefore to calculate second order CF parameters  $B_{20}$  and  $B_{22}$  we use first principles method recently applied to  $\text{SmBa}_2\text{Cu}_3\text{O}_6$  [4] and rare earth borocarbides [5]. Within this method the electronic structure and related distribution of the ground state charge density are obtained from the first principle calculations based on the density functional theory (DFT). Exchange and correlation effects are treated within the local spin density approximation (LSDA) [6]. The calculations described are performed using the full potential linearized augmented plane wave method (LAPW) implemented in the WIEN97 computer code [7]. The RE- $4f$  states are treated as atomic-like core states in the spherical part of the crystal potential (open-core treatment, see *e.g.* [8]). Within the DFT the parameters  $B_{2q}$  of the CF Hamiltonian, originating from the effective potential inside the crystal, are written as  $B_{2q} \propto \int |R_{4f}(r)|^2 V_q^2(r) r^2 dr$  where the non-spherical component  $V_q^2(r)$  reflects besides the nuclear potentials and Hartree part of the inter-electronic interaction also the exchange correlation term which accounts for many particle effects [4,5,8]. The wave function  $R_{4f}$  describes the radial shape of the localized  $4f$  charge density of  $\text{RE}^{3+}$  ion in studied compounds. It is well known that the use of self-consistent LSDA “open core”  $R_{4f}$  leads to poor description of the CF interaction. The reason is that the so-called “self interaction” (SIC) potential felt by a localized  $4f$  electron is not correctly

treated within the LSDA [8]. Therefore, the present study uses the value of the  $R_{4f}$  resulting from the SIC corrected LSDA atomic calculations with occupation numbers of the valence electrons of the RE (6s, 5d, 6p) fixed to their values obtained in the self consistent LSDA calculations in a given RE cuprate. This approach [9] was found to give the 4f charge density which is very close to that obtained from more rigorous DFT band calculation which includes SIC for the 4f states directly [8].

### 3. Results and discussion

We present the calculated CF parameters  $B_{20}$ ,  $B_{22}$  for  $\text{REBa}_2\text{Cu}_3\text{O}_7$  and  $B_{20}$  for  $\text{RE}_2\text{CuO}_4$  in Fig. 1. These data compare favourably with available experimental values. Those for  $B_{20}$  and  $B_{22}$  in  $\text{REBa}_2\text{Cu}_3\text{O}_7$  range from  $92 \text{ cm}^{-1}$  to  $591 \text{ cm}^{-1}$  and  $13$  to  $212 \text{ cm}^{-1}$ , respectively [1–3]. The  $B_{20}$  in  $\text{RE}_2\text{CuO}_4$  range from  $-129$  to  $-567 \text{ cm}^{-1}$  [1–3]. Another check of our method is provided by similar calculations for  $\text{ErBa}_2\text{Cu}_3\text{O}_6$ . In this case we found  $B_{20} = 36.5 \text{ cm}^{-1}$  which should be compared to  $B_{20} = 156 \text{ cm}^{-1}$  obtained for  $\text{ErBa}_2\text{Cu}_3\text{O}_7$ . Thus our method reproduces correctly not only the positive sign of  $B_{20}$  but also the experimental finding that the second order CF parameter  $B_{20}$  is larger for  $x = 1$  than for  $x = 0$  in the case of  $\text{REBa}_2\text{Cu}_3\text{O}_{6+x}$  cuprates [2–4]. The sign of the  $B_{20}$  in regular sites, positive

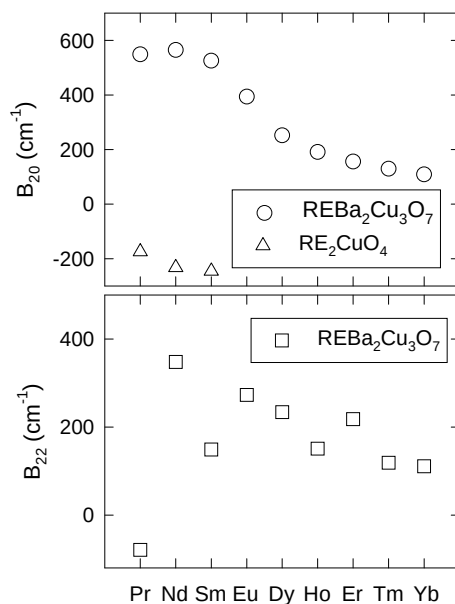


Fig. 1. The CF parameters calculated using first principles DFT method.

in  $\text{REBa}_2\text{Cu}_3\text{O}_{6+x}$  and negative in  $\text{RE}_2\text{CuO}_4$ , is governed by the shape of the crystal potential, which has positive maximum in  $\text{REBa}_2\text{Cu}_3\text{O}_{6+x}$ , and two negative minima in  $\text{RE}_2\text{CuO}_4$ . These minima (maximum) are located in the neighborhood of the maximum of the  $4f$  radial charge density situated roughly 50 pm from the RE nucleus.

In summary we calculated the second order CF interaction for RE-cuprates using first principles DFT method. We demonstrated that our approach can be used to estimate the CF parameters, which are in good agreement with the experiment. The work concerning theoretical estimates of CF interaction for RE ions occupying Ba sites ( $C_{4v}$  symmetry) in  $\text{REBa}_2\text{Cu}_3\text{O}_6$  and La sites in  $\text{La}_2\text{CuO}_4$  systems (T-structure) is in progress.

The work was supported by GACR (Pr. 202/00/1602 and 202/02/0739), GAUK (Pr. 145/2000/B FYZ) and the research programs MSM113200002 and AVOZ1-010-914.

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