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1989 J. Phys.: Condens. Matter 1 4491

(http://iopscience.iop.org/0953-8984/1/27/025)

J. Phys.: Condens. Matter 1 (1989) 4491–4496. Printed in the UK

LETTER TO THE EDITOR

Electric-field gradient calculations for $YBa_2Cu_3O_{7-x}$

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Abstract. The electric-field gradients (EFGs) at the two Cu positions of $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$ are calculated on the basis of full-potential linearised augmented-plane-wave calculations by an *ab initio* method. Good agreement with experimental EFGs is found for the Cu(1) position in both compounds, while for the Cu(2) position in the superconductor the symmetry of the EFG agrees with experiment: the magnitude of our theoretical EFG is, however, only half the experimental value. A small transfer of 0.07 electrons from $d_{x^2-y^2}$ to d_{z^2} symmetry would be sufficient to achieve agreement with experiment. Thus the underlying local-density approximation is not perfect, but remains a good starting point for describing ground-state properties.

The electronic structure of the superconductor $YBa_2Cu_3O_7$ (YBCO7) and the insulator $YBa_2Cu_3O_6$ (YBCO6) has been obtained by various band structure calculations (e.g. Krakauer *et al* 1988, Yu *et al* 1987). They are based on the density-functional theory (DFT) in combination with the local-density approximation (LDA). Discrepancies between the results of such calculations and experimental data (spectra, metal/insulator transition or magnetic ground state) have led to the argument that LDA calculations are not capable of describing these systems properly. Many spectroscopies involve *excited states* and consequently any attempt to understand spectra on the basis of ground-state calculations relies on the assumption that energy eigenvalues can be interpreted as excitation energies; this assumption, however, holds at best approximately. Therefore we ask to what extent can one rely on LDA band-structure results for such oxides; we will, however, use a ground-state property to investigate this question.

The electric-field gradient (EFG) is a ground-state property of a solid and depends on the electronic charge density in the crystal. All nuclei with nuclear-spin quantum number $I \geqslant 1$ have a non-spherical nuclear-charge distribution and thus an electric quadrupole moment Q. The nuclear (electric) quadrupole interaction (NQI), i.e. the interaction between Q and the EFG, provides valuable information on the charge distribution in solids.

Experimentally, YBCO7 and YBCO6 have been investigated by NMR and NQR spectroscopy (Mali *et al* 1987, Walstedt *et al* 1987, Kitaoka *et al* 1988, Lütgemeier 1988, Pennington *et al* 1988, Yasuoka *et al* 1988). The interpretation and the assignment of the quadrupole resonance frequencies to the two types of copper site may not be understood fully without a proper theoretical treatment.

Several years ago Blaha *et al* (1985) developed a first-principles method of computing EFGs from an all-electron band structure calculation. They used the full-potential linearised augmented-plane-wave (LAPW) method and have calculated the EFG directly from the self-consistent charge density by solving Poisson's equation without further

0953-8984/89/274491 + 06 $02.50

approximations. This method was successfully applied to the superionic conductor Li_3N (Blaha *et al* 1985), to all HCP metals up to Cd (Blaha *et al* 1988), and to Cu_2O (cuprite) (Blaha and Schwarz 1989). In all these cases the new method can explain the origin of the EFG both qualitatively and quantitatively, so that the study of the new class of ceramic superconductors is well founded.

We have performed such calculations for YBCO6 and YBCO7 in order to study the EFGs, but with these sensitive quantities we can also check the validity of the LDA.

We employ the well known full-potential LAPW method (Koelling *et al* 1975, Blaha and Schwarz 1983), in which no shape approximation on either the potential or the electronic charge density is made. The computational details are summarised below.

The following atomic sphere radii are used: 2.74, 2.9, 1.9 and 1.55 au for Y, Ba, Cu and O, respectively. In YBCO6 the Cu(1) radius was reduced to 1.80 au; a limit of 1000 plane waves and a maximum of $l = 12$ in the wavefunctions is used. The potential is expanded in crystal harmonics up to $L = 4$; the semi-core states Y 4s, Y 4p, Ba 5s and Cu 3p are treated in an additional band calculation using 9 k-points in the irreducible wedge of the Brillouin zone (IBZ); for the valence states 50 k-points are used in the IBZ for YBCO7; in the tetragonal YBCO6 the equivalent mesh consists of 30 k-points for the valence and 6 for the semi-core states. The calculations have been performed on an Apollo Workstation DN-10030.

YBCO7 (YBCO6) is orthorhombic (tetragonal) with space group Pmmm (P4/mmm) and is paramagnetic (antiferromagnetic). The structural parameters are taken from Beno *et al* (1987) for YBCO7 and from Hewat *et al* (1987) for YBCO6 (using the data at 100 °C). Both compounds, YBCO7 and YBCO6, are studied by non-spin-polarised calculations.

We calculate the full potential numerically by solving Poisson's equation according to a method proposed by Weinert (1981). From this full potential, which has no shape approximations and which is obtained from all electrons and the nuclear charges, the EFG can be obtained directly from the $L = 2$, $M = 0$ and the $L = 2$, $M = 2$ components of the potential expansion inside the spheres (Blaha *et al* 1989):

$$\begin{aligned} V_{xx} &= (5/4\pi)^{1/2} \lim_{r\to 0} [(\sqrt{3}V_{22}(r) - V_{20}(r))/r^2] \\ V_{yy} &= (5/4\pi)^{1/2} \lim_{r\to 0} [(-\sqrt{3}V_{22}(r) - V_{20}(r))]/r^2] \\ V_{zz} &= (5/4\pi)^{1/2} \lim_{r\to 0} (2V_{20}(r)/r^2). \end{aligned} \tag{1}$$

The x, y and z axis point in the crystallographic a, b and c directions. We denote the largest of the components V_{xx}, V_{yy} and V_{zz} by EFG. The asymmetry parameter η is given by $\eta = |V_2| - |V_1|/|V_3|$, where for this definition the components are ordered according to $|V_1| < |V_2| < |V_3|$. Since in the band calculation all polarisation effects are included self-consistently, we do not need additional Sternheimer factors or other (arbitrary) corrections.

The band structures and densities of states of YBCO6 and YBCO7 have been published several times, so we do not present our results here. In general they agree well with those of other authors (Krakauer *et al* 1988, Yu *et al* 1987).

In table 1 the electric-field gradients and asymmetry parameters for YBCO7 and YBCO6 are compared with experimental data. Here we present the results for the two copper positions (the EFGs at the yttrium, barium and oxygen sites will be published in a full paper). Most experiments determine only the magnitude of the EFG and the asymmetry

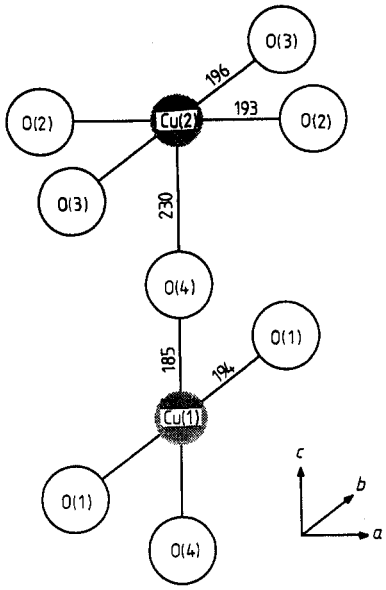

Figure 1. The nearest-neighbour coordination of Cu(1) and Cu(2) in YBCO7 is shown (the distances are given in pm).

Table 1. Electric-field gradients and asymmetry parameters for Cu(1) and Cu(2) in YBCO7 and YBCO6 in 10^{21} V m^{-2}. The experimental data are taken from Pennington *et al* (1988) and Kitaoka *et al* (1988) for YBCO7 and from Yasuoka *et al* (1988) and Lütgemeier (1988) for YBCO6. The nuclear quadrupole moment of 0.211 b is used for ^{63}Cu (Sternheimer 1986).

		YBCO7					YBCO6	
		V_{xx}	V_{yy}	V_{zz}	EFG	η	EFG	η
Cu(1)	Theory	−6.7	+7.4	−0.7	+7.4	0.8	−10.9	0.0
	Experiment	∓7.4	±7.5	∓0.0	±7.5	0.9–1.0	∓11.8	0.0
Cu(2)	Theory	+3.0	+2.6	−5.6	−5.6	0.1	−3.6	0.0
	Experiment	±6.2	±6.2	∓12.3	∓12.3	0.0	—	—

parameter, but for YBCO7 Pennington *et al* (1988) made measurements on single crystals and thus could also determine the orientation of the EFG.

We first focus on the Cu(1) position (figure 1): good agreement between theory and experiment is found, both qualitatively and quantitatively, for YBCO6 as well as YBCO7. The z component V_{zz} in YBCO7 is very small, while V_{xx} and V_{yy} are large and have similar values leading to an asymmetry parameter, η, of about 1. Due to the tetragonal symmetry in YBCO6, η is 0 and the EFG points in the c direction. We describe the increase of the EFG by about 50% from YBCO7 to YBCO6 correctly, although we have neglected magnetic effects, especially in YBCO6. This indicates that magnetism is not crucial for the Cu(1) position.

The situation is different for the Cu(2) position: in YBCO6 Lütgemeier (1988) does not find any frequency corresponding to Cu(2) and he argues that this could be caused by magnetic behaviour of these sites. In YBCO7 we find qualitative agreement with the experimental data, namely that the EFG points in the c direction while V_{xx} and V_{yy} are similar, leading to an η of about 0. While the symmetry agrees well, the magnitude of

Table 2. Partial valence-charges in electrons of Cu(1) and Cu(2) in YBCO7 and YBCO6.

		s	p	p_x	p_y	p_z	d	d_{z^2}	$d_{x^2-y^2}$	d_{yz}	d_{yz}	d_{xz}
YBCO7	Cu(1)	0.231	0.230	0.029	0.070	0.103	8.609	1.408	1.652	1.841	1.844	1.864
	Cu(2)	0.200	0.176	0.074	0.069	0.034	8.693	1.763	1.442	1.851	1.819	1.818
YBCO6	Cu(1)	0.219	0.126	0.018	0.018	0.089	8.574	1.475	1.752	1.752	1.797	1.797
	Cu(2)	0.203	0.174	0.072	0.072	0.029	8.712	1.772	1.458	1.846	1.818	1.818

the theoretical EFG is only about half the experimenal value. This serious discrepancy could be interpreted as a breakdown of the LDA, but we will present an analysis below which shows that a very small charge redistribution can reproduce the experimental EFG.

From our results we find that the EFG at the Cu sites originate from the valence electron distribution, while contributions from lower-lying core states or from the lattice are very small, a situation similar to that found in HCP metals (Blaha *et al* 1988). It is the asymmetry of the 4p and 3d valence electrons which determines the EFG and therefore the different EFG contributions can be related to the symmetry-decomposed partial charges. These *l*-like charges of the copper atoms in YBCO7 and YBCO6 and their symmetry decomposition are first discussed (table 2). Note that partial charges are a special separation of the total charge and thus depend on the choice of the sphere radii.

The charges corresponding to Cu 4p states are relatively small, since they originate mainly from the surrounding oxygen p wavefunctions (so-called off-site components). Therefore their relative magnitudes correlate with the distances to the oxygen neighbours (figure 1). For example, in YBCO7 the distance Cu(1)–O(4) is smaller than Cu(1)–O(1), so that the charge of $4p_z$ is larger than that of $4p_y$; the smallest component is $4p_x$, since the oxygen neighbours are missing in the *a* direction. In YBCO6, where no O(1) sites are present, the charges for $4p_y$ and $4p_x$ are equal, due to the tetragonal symmetry.

For the Cu 3d charges, which are the Cu on-site components, we use a different argument than above, and employ a simplified frontier-orbital picture. Cu has an almost filled d shell and thus interaction with oxygen leads to bonding and antibonding orbitals, both of which are in most cases filled. If they are not completely occupied it is the antibonding part which remains empty, and this situation leads to smaller charges and favours shorter distances, e.g. between Cu(1) and O(4). The d_{z^2} and the $d_{x^2-y^2}$ states are not completely filled. For Cu(2) there is more charge in the d_{z^2} orbital than in $d_{x^2-y^2}$, because the distances to O(2) and O(3) are shorter than the one to O(4), for Cu(1) the occupation of the d_{z^2} orbital is smaller than that of $d_{x^2-y^2}$ (in contrast to Cu(2)). The states d_{xy}, d_{xz} and d_{yz} are nearly filled (note again that the partial charges depend on the sphere radii).

We now return to the discussion of the EFG on YBCO7 at the Cu(2) position, where our theory yields -5.6×10^{21} V m^{-2}. The two main contributions to that EFG originate from the 4p and 3d valence-wavefunctions of Cu and yield 9.6 and -14.9×10^{21} V m^{-2}, respectively. In the special case of the Cu(2) position, where η is about 0, one can split the EFG into contributions from two groups of p and three groups of d functions. Since V_{22} is about 0 it is useful to define an anisotropy count (Blaha *et al* 1988):

$$\begin{aligned} \Delta n_p &= \tfrac{1}{2}(p_x + p_y) - p_z \\ \Delta n_d &= d_{xy} + d_{x^2-y^2}) - \tfrac{1}{2}(d_{xy} + d_{yz}) - d_{z^2}. \end{aligned} \tag{2}$$

The partial charges, grouped with prefactors and signs according to (2), contribute with

Table 3. EFG analysis for Cu(2) in YBCO7: part of the asymmetry count n in electrons, corresponding EFG contribution in 10^{21} V m^{-2} and the ratio M = EFG/n.

	p_x, p_y	p_z	$d_{x^2-y^2}, d_{xy}$	d_{z^2}	d_{xz}, d_{yz}
n	0.072	−0.034	3.293	−1.763	−1.818
EFG	18.1	−8.5	154.2	−83.0	−86.1
M	251	250	47	47	47

n to the asymmetry count Δn. These values n, the corresponding EFG contributions, and the ratio M = EFG/n are listed in table 3. The following simple analysis shows the sensitivity of the EFG with respect to charge distributions: it is sufficient to transfer only 0.07 electrons from the $d_{x^2-y^2}$ into the d_{z^2} orbital to obtain a Δ EFG $= -0.07 \times 2\,M = -6.6 \times 10^{21}$ V m^{-2}, which leads to an EFG of -12.2×10^{21} V m^{-2}, in agreement with the experimental value.

Band structures published by several groups differ in detail, since in practice it is impossible to exhaust all limits that control the convergence of such computations in the case of a system as complicated as YBCO. The accuracy of our results depends on the number of k-points in the BZ, on the number of plane waves in the LAPW basis, and how many LM-combinations and Fourier coefficients in the expansion of the potential and charge density are included. In comparison with published LAPW band calculations we have increased all these limits to the values specified above and found reasonable convergence for the EFG, but we must admit that there is still room for improvement. From this analysis we are sufficiently confident that our EFG results are reliable to about 10%. There are cases where the EFG is very sensitive to small changes in structural parameters, e.g. the c/a ratio in HCP Be (Blaha and Schwartz 1987). In YBCO7 this could happen with the z coordinate of the O(4) site (see figure 1) or the lattice constants a and b. In order to check this sensitivity we varied these parameters by ±3% but did not observe dramatic effects on the EFG. We found, however, that the individual changes in the p and d contributions to the EFG cancel each other.

Our LAPW calculations are not spin-polarised and thus for YBCO6 a comparison with experiment is justified only for the Cu(1) position where no pronounced moment is found, but not for Cu(2) which carries a magnetic moment.

In these highly correlated systems it is often questionable whether or not the LDA and band structure calculations are applicable at all, but the present analysis has shown that the LDA, although it does not perfectly describe the high-T_c materials, provides a good starting point for any discussion of the electronic structure in these compounds. Several many-body models are discussed, where the Cu atoms possess distinct valences and integer occupation numbers of the localised Cu 3d electrons (Weber 1988). Such models may not be able to explain the EFG at the Cu sites, since one missing d electron of the $(x^2 - y^2)$ symmetry produces an EFG which is almost five times the observed experimental value (table 3).

This project was supported by the 'Fonds zur Förderung der wissenschaftlichen Forschung', project number P7063P, and by the Hochschuljubiläumsstiftung der Stadt Wien'. The authors want to thank Dr Kitaoka for providing us with his results prior to publication and sending us a summary of experimental EFG data.

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