RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 46, NUMBER 9 1 SEPTEMBER 1992-I

Electric-field gradients in $YBa_2Cu_3O_7$: Discrepancy between experimental and local-density-approximation charge distributions

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(Received 14 May 1992)

Local-density-approximation (LDA) -based calculations of electric-field gradients (EFG's) for $YBa_2Cu_3O_7$ using an extended linearized-augmented-plane-wave method are reported. This extended method controls errors that might arise from extended core states on the Y ions or linearization of the narrow $3p$ states. The calculated EFG's agree well with experiment except for the plane Cu site. For this site a large discrepancy is found, which is attributed to an inadequate description of anisotropic effects within the LDA.

INTRODUCTION

Since the discovery of the cuprate high critical temperature (T_c) superconductors by Bednorz and Muller,[1] there has been an ongoing debate regarding to what extent the electronic structure of these materials can be described by conventional local-density-approximation (LDA) calculations. A variety of experimental probes have demonstrated that the metallic materials have Fermi surfaces in reasonable agreement with predictions of LDA-based calculations.[2] LDA-based total-energy calculations have yielded structural parameters, phonon frequencies, and instabilities in good agreement with experiment.[3,4] Measured positron wave-function effects are also in good agreement with calculations based on LDA electronic structures.[5] These results demonstrate at a minimum that the LDA provides a reasonable description of charge densities and density responses. These and other successes have made the LDA an important tool in achieving an understanding of the complex high-T_c superconductors.

On the other hand, many of the high-T_c superconductors have antiferromagnetic (AF) insulating sister compounds (often referred to as undoped materials), and these materials are not well described by local-spin-density approximation (LSDA) calculations.[6] For example, pure La_2CuO_4 is predicted by LSDA calculations to be a paramagnetic metal even though the material is an AF insulator in reality. It is perhaps initially surprising therefore that LDA calculations for this material yield structural parameters and phonon frequencies in good agreement with experiment. This can be understood by considering the effect of corrections to the LSDA, which are needed to describe the insulating materials. Recently, Svane and co-workers[7] and Anisimov, Zaanen, and Anderson[8] have performed calculations incorporating different orbital-dependent corrections, both of which correctly predict insulating AF behavior for undoped high-T_c materials. An important effect of these orbital-dependent terms is to alter the occupations of the individual Cu d orbitals, favoring more anisotropic solutions.[9] However, the largest contribution to the phonon frequencies in these materials is due to ionic interactions, which depend on spherical averages of the density.[10] Positrons, which sample the interstitial preferentially, are also most sensitive to the spherical component of the charge density in these materials.

Electric-field gradients (EFG's) at the nuclei can be measured using a variety of experimental techniques and provide a very sensitive probe of the anisotropies of charge densities. They may be expected to be a particularly good probe of the occupations of the different Cu d orbitals in the high-T_c cuprates because the spherically symmetric component of the charge density does not contribute to the EFG and because the largest contributions usually come from the charge distribution in the interior of an ion. It is, however, difficult to obtain reliable predictions of EFG's with which to compare because they can be very sensitive to small changes in the charge distribution, especially near the nucleus, and accordingly highly accurate calculations are needed.

Blaha, Schwarz, and Herzig used the full potential linearized-augmented-plane-wave (LAPW) method for this purpose demonstrating the feasibility of obtaining reliable EFG's in solids from first-principles LDA-based calculations.[11] More recently, two independent LDA-based calculations of EFG's for the high-T_c superconductor, $YBa_2Cu_3O_7$ have been performed using this approach. These calculations yielded similar results except for the Y site, which is not experimentally accessible.[12,13] Calculations have also been reported for $YBa_2Cu_4O_8$, which is a related high-T_c superconductor.[14]

In all the cases the calculated EFG's are found to be in good agreement with experimental measurements[15,16] except for the plane-Cu [Cu(2)] site. For the plane-Cu site of $YBa_2Cu_3O_7$, the principal component of the experi-

mental EFG is more than twice the calculated value. For $YBa_2Cu_4O_8$ the discrepancy is even larger with the experimental value being more than three times the calculated value. It is most remarkable that the EFG for the plane-Cu(2) site disagrees so strongly with experiment, even while results for the chain-Cu(1) site, which is treated exactly as the Cu(2) site, are in good agreement with experiment. Schwarz and co-workers[12] note that in $YBa_2Cu_3O_7$ transferring 0.07 electrons from the $d_{x^2-y^2}$ into the d_{z^2} orbital would increase the anisotropy sufficiently to reproduce the experimental value, and they suggest that the discrepancy may well be an LDA error consistent with the known deficiencies of the LSDA in describing the AF sister phases. Yu *et al.*,[13] however, note that the Sternheimer antishielding factor (the contribution arising from polarization of the upper core states) for the Cu 3*p* states is quite different for the chain and plane Cu. Thus it is possible that a treatment of the Cu 3*p* core state that is adequate for the chain Cu EFG may not be adequate for the plane Cu. Based on this, they suggest that the discrepancy could result from an inaccurate treatment of the response of the Cu 3*p* shell. Presumably, if there is such an inadequacy in the treatment of the Cu 3*p* states, it is a computational problem and not an LDA error, since LDA errors, if significant, would be in the direction of overly extended and polarizable core states yielding a discrepancy opposite to that found.[17] Yu *et al.* suggest the neglect of spin orbit for the 3*p* states in their calculation and that of Schwarz and co-workers, and/or problems with the linearization of this narrow band as possible sources of the discrepancy.

A recent EFG calculation for TiO_2 by Blaha *et al.*[18] suggests yet another explanation. Full-potential LAPW calculations in which the high-lying core states were treated in a separate energy window (as in the calculations for $YBa_2Cu_3O_7$) yielded a very poor EFG on the Ti site, which was found to depend strongly on computational parameters affecting the treatment of Ti *p* states, and the source of this problem was traced to the extended (so-called semicore) Ti 3*p* state. This is reminiscent of the situation in $YBa_2Cu_3O_7$, where the Y ion has an extended 4*p* state, which could not be treated fully satisfactorily in the LAPW EFG calculations. In fact, qualitatively different results are found for the Y EFG in the calculations of Schwarz and co-workers[12] and those of Yu *et al.*[13] However, since there is no Y isotope with an electric quadrupole, the EFG on the Y site has not been measured, and so LDA predictions of it are of limited value. What makes the treatment of the Y 4*p* state of interest is the fact that in TiO_2 the standard treatment of the Ti semicore state was found to result in substantial errors in the O EFG. In $YBa_2Cu_3O_7$ the Y ions are sandwiched between the two copper-oxygen planes and so errors in the plane-O and plane-Cu EFG's arising from the treatment of the Y semicore state cannot be ruled out *a priori*.

All known cuprate high-T_c superconductors have doped copper-oxygen planes. Thus it is particularly important to know how accurately the LDA describes the electronic structure of these planes. As discussed above the LSDA does not provide a good description of the spin density of the AF insulating materials. This result, however, does not necessarily mean that there are corresponding errors in the metallic (and superconducting) materials. If the discrepancy between calculated and experimental EFG's for the Cu(2) site is due to a LDA error (as opposed to a computational artifact arising from the treatment of Y and/or Cu semicore states) then this would be evidence for a qualitatively similar, though smaller, error in the LDA charge density for the metallic phases. Here well-converged EFG calculations are reported for $YBa_2Cu_3O_7$ in which ambiguities present in the LAPW treatment of extended semicore states are removed using a local orbital extension of the basis.[19] Besides removing ambiguities due to extended core tails, this approach is more accurate than the standard LAPW method for narrow bands because the local orbitals make the method quadratic rather than linear. This technique has been tested in EFG calculations for TiO_2, and found to yield reliable results.[18]

METHOD

The calculations reported below were performed using a local orbital extension[19] of the general potential LAPW method.[20] Local orbitals were used to treat the Y 4*s* and 4*p*, Ba 5*s* and 5*p*, Cu 3*p* and O 2*s* states with the valence states in a single energy window. These and the valence states were treated in a scalar relativistic approximation with the exception of one calculation (see below). Spin orbit was included for all lower-lying core states, which were treated in a spherical approximation. Additional local orbitals were used to relax the linearization of the Cu 3*d* bands (relaxing the linearization of both the 3*p* and 3*d* states could be important if the small 3*p*-3*d* hybridization affects the EFG as could be the case under the scenario of Yu *et al.*[13]). Highly converged basis sets corresponding to LAPW's up to a plane-wave cutoff of 17.6 Ry were used.[21] This choice of cutoff yields approximately 1525 basis functions (the exact number is k dependent). The Brillouin-zone sampling in the self-consistent calculations was performed using 72 special k points[22] in the irreducible wedge of the orthorhombic zone. Calculations with a smaller number of k points (16) yielded similar results [see Tables I and II for Cu(2) EFG's with the two samplings]. Two additional calculations using the smaller set of k points were used to test the conjecture of Yu *et al.* that spin-orbit effects on the Cu 3*p* state could modify the Cu(1) EFG and to verify that the contribution from the Cu 3*s* state is indeed negligible. The first of these calculations was performed as above but with spin-orbit effects included self-consistently in a second variational step.[23] The second of these tests was performed as above (without spin orbit) but including the Cu 3*s* states in the valence window through the local orbital extension, thereby allowing a contribution from the polarization of these states as well. All calculations were performed using the LDA exchange correlation functional of Hedin and Lundqvist[24] as in previous studies. The structural parameters are as in the earlier LDA calculation of Krakauer, Pickett, and Cohen.[25]

RESULTS AND DISCUSSION

The calculated EFG's are given in Table I along with the results of previous calculations and experimental values. They are in good agreement with previous calculations with the exception of the Y and Ba ions, which have extended semicore states. The differences for these ions are no doubt due to the improved treatment of these semicore states in the present calculation. For the Ba site we obtain essentially the same anisotropy parameter, η, as for earlier calculation ions but somewhat larger EFG's. These larger EFG's are in very good agreement with recent experiments.[26,27] As expected the differences for the Y ions are largest, although these cannot be measured.

In spite of the changes in the calculated EFG on the Y site, and in contrast to the situation for the O site in TiO_2, the calculated EFG on the Cu(2) site is similar to the values obtained in earlier LAPW studies. This means that the discrepancy between the EFG calculated within the LDA and experiment cannot be explained as being due to errors resulting from linearization of the Cu $3p$ "bands" or the treatment of extended semicore states. The additional calculations (see above) including spin orbit and including the Cu $3s$ state with the valence states yield essentially the same result (see Table II) demonstrating that these are not responsible for the discrepancy either. Both these effects lead to small increases in the EFG's, but these increases are much smaller than the discrepancy between the calculated LDA and experimental EFG's. This confirms the suggestion of Schwarz and co-workers[12] that the discrepancy represents a real LDA error and is not due to a computational artifact. We emphasize that the EFG's are just second derivatives of the Coulomb potential, and thus are well-defined ground-state properties determined uniquely by the charge density.

TABLE I. EFG's for $YBa_2Cu_3O_7$ in units of 10^{22} V/m^2. Experimental results (denoted Expt.) are from Refs. 15, 16, and 26 for the Cu, O, and Ba sites, respectively. The overall sign cannot be experimentally determined and has been assumed to agree with the calculations. Previous theoretical results are those of Schwarz and co-workers (Ref. 12) and Yu *et al.* (Ref. 13). LAPW+LO denotes the present calculations using 72 special k points.

Site		V_{xx}	V_{yy}	V_{zz}
Y	LAPW+LO	−0.02	0.21	−0.20
	Schwarz	−0.02	−0.32	0.34
	Yu	−0.06	0.20	−0.14
	Expt.			
Ba	LAPW+LO	−0.86	−0.06	0.92
	Schwarz	−0.67	−0.06	0.73
	Yu	−0.56	−0.06	0.62
	Expt.	−0.835	−0.035	0.87
Cu(1)	LAPW+LO	−0.54	0.69	−0.14
	Schwarz	−0.67	0.74	−0.07
	Yu	−0.55	0.61	−0.06
	Expt.	−0.74	0.75	0.00
Cu(2)	LAPW+LO	0.25	0.23	−0.49
	Schwarz	0.30	0.26	−0.56
	Yu	0.29	0.28	−0.57
	Expt.	0.62	0.62	−1.23
O(1)	LAPW+LO	−0.60	1.87	−1.27
	Schwarz	−0.61	1.83	−1.22
	Yu	−0.68	1.84	−1.17
	Expt.	−0.51	1.73	−1.21
O(2)	LAPW+LO	1.26	−0.77	−0.49
	Schwarz	1.18	−0.70	−0.48
	Yu	1.35	−0.83	−0.53
	Expt.	1.05	−0.63	−0.41
O(3)	LAPW+LO	−0.76	1.26	−0.51
	Schwarz	−0.70	1.19	−0.49
	Yu	−0.83	1.38	−0.55
	Expt.	−0.63	1.02	−0.39
O(4)	LAPW+LO	−0.49	−0.71	1.20
	Schwarz	−0.47	−0.70	1.17
	Yu	−0.54	−0.73	1.27
	Expt.	−0.40	−0.76	1.16

TABLE II. Calculated EFG for the Cu(2) site in $YBa_2Cu_3O_7$ as in Table I but with 16 special k points (denoted I), including spin orbit (denoted s.o.) and including the Cu $3s$ states in the valence window (denoted $3s$).

Calculation	V_{xx}	V_{yy}	V_{zz}
I	0.28	0.20	−0.48
s.o.	0.29	0.21	−0.50
$3s$	0.29	0.21	−0.49

CONCLUSIONS

We have performed highly converged LDA calculations of the EFG's for $YBa_2Cu_3O_7$ using a local orbital extension of the general potential LAPW method. This method removes ambiguities in the standard LAPW method, which arise from extended core states. It is found that there is a substantial discrepancy between the LDA and experimental EFG's for the plane-Cu site. Calculations including spin orbit and the lower-lying Cu $3s$ state show that these do not account for the discrepancy. Thus we conclude that the LDA yields too little anisotropy around the plane-Cu site in *metallic superconducting* $YBa_2Cu_3O_7$ and speculate that corrections to the LDA such as those used by Anisimov, Zaanen and Andersen[8] may be needed to accurately describe the occupations of the plane-Cu d orbitals in the metallic materials as well as in the undoped AF sister phases. On the other hand, good agreement with experiment is found for the chain-Cu site.

ACKNOWLEDGMENTS

We are pleased to acknowledge helpful conversations with W. E. Pickett. Work at NRL was supported in part by the Office of Naval Research. Work at TU Wien was supported by the Fonds zur Forderung der wissenschaftlichen Forschung, Project No. P8176 (Austria). Computations were performed at the Cornell National Supercomputer Facility.

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