Gradient-corrected density-functional studies of $CaCuO_2$

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A search for an antiferromagnetic ground state in $CaCuO_2$, using gradient-corrected local-spin-density functionals, is reported. It is found that, as with the local-spin-density approximation, a paramagnetic metallic ground state is predicted, in disagreement with experiment. The gradient corrections do, however, bring this material closer to an antiferromagnetic instability.

INTRODUCTION

Since the discovery of the high-critical-temperature (T_c) cuprate superconductors,[1] there has been considerable debate regarding the character of the normal state,[2] and, in particular, the normal state's relationship to the insulating antiferromagnetic (AF) phases such as undoped La_2CuO_4, which are often associated with these materials. Initially, it was commonly held that the metallic phases might be closely related to the insulating phases, with impuritylike charge carriers. The failure[2-5] of local-spin-density-approximation (LSDA) electronic-structure calculations to describe the insulating phases to which, it was thought, the high-T_c superconductors were related, lent credibility to a variety of theories of the metallic and superconducting materials involving unconventional non-Fermi-liquid states arising from strong correlations and/or two-dimensionality. Although recent measurements of large-area Fermi surfaces in good agreement with the predictions of band theory have greatly restricted the range of models of the high-T_c materials, it is still unclear what, if any, role magnetic fluctuations and other correlation-induced effects (which may or may not be closely related to the AF phases) play in the metallic and superconducting states of these materials. Thus, study of the AF phases and the transition from these to the metallic phases remains of considerable interest.

Recently, Svane and Gunnarsson have reported a series of electronic-structure calculations using a self-interaction-corrected density-functional theory which yielded ground states in good agreement with experiment for the $3d$ transition-metal monoxides, including CuO.[6] These calculations, unlike the LSDA calculations, also yield an insulating AF ground state for La_2CuO_4.

The wide variety of known layered cuprate materials and their often complex crystal structures complicate the process of understanding the salient features of the electronic structure leading to AF insulating behavior. The simplest compound is $XCuO_2$, which consists of CuO_2 layers separated by alkaline-earth ions. This material has been synthesized by Siegrist *et al.*[7] (in the reported material X=Ca with some replacement by Sr needed for stability), and subsequently shown to be an AF insulator with properties similar to the other insulating AF layered cuprates such as La_2CuO_4.[8] Like La_2CuO_4, $CaCuO_2$ is predicted (incorrectly) to be a paramagnetic metal within the LSDA.[3,9]

Calculations incorporating gradient corrections (GC) to the LSDA have been performed on some magnetic transition metal systems, showing that, at least in these systems, GC's favor magnetic states.[10-12] In addition, full-potential calculations for ferromagnetic iron have shown that GC's to the LSDA introduce a significant increase in the anisotropy of the exchange-correlation (XC) potential.[12] This anisotropy arises from an extra repulsion in the vicinity of the unoccupied minority spin (e_g) d lobes. Heuristic studies for $CaCuO_2$ have shown that incorporating an additional anisotropic term in the potential, which splits the minority spin Cu($d_{x^2-y^2}$) orbitals from the other Cu d states, can yield qualitatively correct AF insulating ground states.[3,9] These results suggest that GC's may stabilize a magnetic ground state in the insulating layered cuprates.

In this paper, a search for AF insulating ground states for $CaCuO_2$ with GC-LSDA is reported. Calculations were performed within the LSDA, with the Becke-exchange-only GC,[13] with the Langreth-Mehl (LM) GC functional,[14] and with the recent GC functional of Perdew (PW).[15]

METHOD

The calculations reported here were performed without shape approximations, using an extension[16] of the general-potential linearized augmented-plane-wave (LAPW) method.[17] This approach has been described in detail elsewhere.[16,17] Therefore, only a brief discussion of the parameters specific to the present calculation is given here. In this method, the LAPW basis is extended by the addition of local orbitals to facilitate the treatment of extended-core states and to relax the linearization for narrow bands. In the present study, a well-converged basis of approximately 1000 LAPW's was used with the addition of local orbitals to include the O $2s$, Ca $3s$, and Ca $3p$ states with the higher-lying valence states in a single energy window and to relax the linearization of the Cu $3d$ derived bands. The calculations were performed using the experimental structure[7] with an eight-atom unit cell corresponding to the observed magnetic symmetry.[8] Muffin-tin sphere radii of 2.50, 1.95, and 1.65 au were

used for the Ca, Cu, and O ions, respectively (note, however, that this is a general potential method and thus has no shape approximations to the charge densities or potentials). The Brillouin-zone integrations were performed using a set of 20 special **k** points[18] in the irreducible wedge. Improving the sampling beyond this has only a minimal effect on the induced moments.[9] The LSDA calculations were performed using the von Barth–Hedin (vBH) local XC function.[19] Further, this function was used for the local part of the Becke and LM functionals. For the local part of the PW functional a fit, by Perdew and co-workers, to the Ceperley-Alder data was used.[20] Since this local XC function and the vBH function are quite similar, we do not expect this difference in the local XC function to be significant.

In searching for an AF ground state, it is necessary to rule out the possible existence of a magnetic state which may be missed in self-consistent iterations to a nonmagnetic solution. In order to do this it is common to stabilize a solution near the one sought, using external applied fields, and to reduce gradually the applied field while iterating to self-consistency. For example, in seeking a ferromagnetic solution, one may apply a uniform external magnetic field to induce a solution near the expected ground state and then reduce the field while iterating to self-consistency. If it is found that the induced magnetism varies smoothly with field going to zero at zero field it may be concluded that there is no ferromagnetic solution for the system under consideration. In $CaCuO_2$, external anisotropic fields induce states in qualitative agreement with the experimental ground state.[3,9] Accordingly, anisotropic fields were applied to the Cu spheres in seeking out an AF ground state. In particular, fields, $v^{\rm ext}$, of the following form (which we denote $L4$) were used:

$$v_\sigma^{\rm ext}(r)=\pm v_0\{Y_{4,4}(\mathbf{r})+Y_{4,-4}(\mathbf{r})\}/\sqrt{2}\ , \qquad (1)$$

where **r** is the position in a Cu sphere (the field is zero outside the Cu spheres) and v_0 is the field strength. The signs are such that the fields are in an AF array with the experimental symmetry, with the spin-up and spin-down components at a given point being opposite (that is, the field is magnetic in character). As mentioned, the addition of this $L4$ field induces qualitatively correct (but unstable) insulating AF solutions for $CaCuO_2$ within the LSDA.

RESULTS AND DISCUSSION

The principal result of this study is given in Fig. 1 where the variation of the induced Cu moments with applied $L4$ field strength is given for self-consistent calculations with the vBH, Becke, LM, and PW XC functionals. In all cases, the variation of the induced moment with field strength is smooth going to zero as the applied $L4$ field goes to zero. The largest moments for a given field are obtained with the LM and PW XC functionals. The curves for these two functionals are nearly coincident. The Becke GC is found to have a considerably smaller effect on the induced moment than the LM and PW GC's. This is in contrast to results for ferromagnetic iron, where it is found that the Becke and LM functionals yield similar stabilizations of the magnetic state.[12]

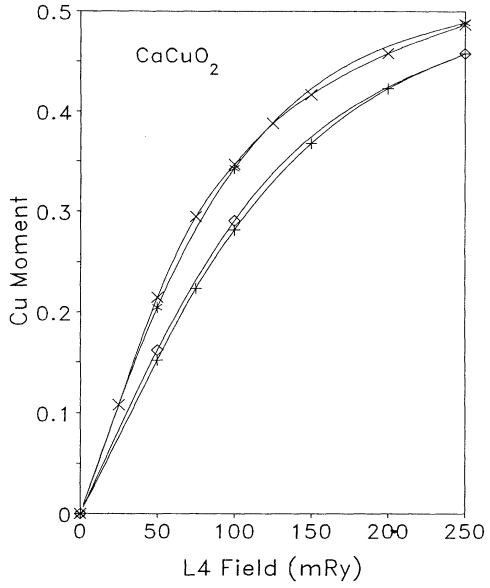

FIG. 1. Induced Cu spin moment (μ_B) as a function of applied $L4$ field, v_0, for $CaCuO_2$. The plus, diamond, star, and × symbols denote calculated points using the vBH, Becke, LM, and PW XC functionals, respectively. The solid curves are spline interpolations through the calculated points.

We note that, as shown in Fig. 1, the GC's increase the initial slope of the induced moment as a function of applied field. This initial slope can be thought of as a generalized susceptibility, which we denote χ. Perhaps, a more interesting quantity is the inverse χ^{-1} which is given in Table I. An instability to an AF state would be assured if χ^{-1} were to become zero. Thus, χ^{-1} may be used as a crude measure (the AF state may appear before χ^{-1} reaches zero) of the nearness of the system to such an instability. An examination of the values in Table I reveals that the largest reduction in χ^{-1} of approximately 32% is for the PW GC. In view of this relatively small reduction and the absence of any indications of local minima in Fig. 1, we conclude that it is unlikely that a correct description of the ground states of the AF insulating layered cuprates can be obtained by refining current GC-LSDA density functionals.

TABLE I. Generalized inverse susceptibility, χ^{-1} (see text) in Ry/μ_B, for $CaCuO_2$ with $L4$ fields, using the vBH, Becke, LM, and PW XC functionals. $\Delta(\chi^{-1})$ is the change in χ^{-1} from the LSDA result.

XC functional	χ^{-1}	$\Delta(\chi^{-1})$
vBH	0.32	
Becke	0.30	−0.02
LM	0.23	−0.09
PW	0.22	−0.10

CONCLUSION

A search for an AF state with the experimental symmetry has been performed for $CaCuO_2$ using GC-LSDA in a general potential method. It is found that the GC's do move the system towards a magnetic solutions but that the correction is too small to produce an instability of the paramagnetic ground state.

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[1]J. C. Bednorz and K. A. Muller, Z. Phys. B **64**, 180 (1986).
[2]W. E. Pickett, Rev. Mod. Phys. **61**, 433 (1989), and references therein.
[3]D. Singh, W. E. Pickett, R. E. Cohen, D. A. Papaconstantopoulos, and H. Krakauer, Physica B **163**, 470 (1990).
[4]H. Winter, Z. Szotek, and W. M. Temmerman, Z. Phys. B **79**, 241 (1990).
[5]C. Ambrosch-Draxl and K. Schwarz, Solid State Commun. **77**, 45 (1991).
[6]A. Svane and O. Gunnarsson, Phys. Rev. Lett. **65**, 1148 (1990); A. Svane (private communication).
[7]T. Siegrist, S. M. Zuharak, D. W. Murphy, and R. S. Roth, Nature **334**, 231 (1988).
[8]D. Vaknin, E. Caignol, P. K. Davies, J. E. Fisher, D. C. Johnston, and D. P. Goshorn, Phys. Rev. B **39**, 9122 (1989).
[9]D. Singh, W. E. Pickett, and H. Krakauer, Physica C **162-164**, 1431 (1989).
[10]P. Bagno, O. Jepsen, and O. Gunnarsson, Phys. Rev. B **40**, 1997 (1989).
[11]B. Barbiellini, E. G. Moroni, and T. Jarlborg, J. Phys.: Condens. Matter **2**, 7597 (1990).
[12]D. Singh, W. E. Pickett, and H. Krakauer, Phys. Rev. B **43**, 11 628 (1991).
[13]A. D. Becke, Phys. Rev. B **38**, 3098 (1988).
[14]D. C. Langreth and M. J. Mehl, Phys. Rev. Lett. **47**, 446 (1981); C. D. Hu and D. C. Langreth, Phys. Scr. **32**, 391 (1985).
[15]J. P. Perdew, in *Proceedings of the 21st Annual International Symposium on the Electronic Structure of Solids, Dresden, 1991*, edited by P. Zieshe (Nova, Commack, 1991).
[16]D. Singh, Phys. Rev. B **43**, 6388 (1991).
[17]O. K. Andersen, Phys. Rev. B **12**, 3060 (1975); D. R. Hamann, Phys. Rev. Lett. **42**, 662 (1979); E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Phys. Rev. B **24**, 864 (1981); S.-H. Wei and H. Krakauer, Phys. Rev. Lett. **55**, 1200 (1985); S.-H. Wei, H. Krakauer, and M. Weinert, Phys. Rev. B **32**, 7792 (1985).
[18]A. Baldereschi, Phys. Rev. B **7**, 5212 (1973); D. J. Chadi and M. L. Cohen, *ibid.* **8**, 5747 (1973); H. J. Monkhorst and J. D. Pack, *ibid.* **13**, 5188 (1976); **16**, 1748 (1977).
[19]L. Hedin and B. I. Lundqvist, J. Phys. C **4**, 2064 (1971); U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).
[20]D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).