Anomalous optical properties of the mixed-valent lithium cuprate LiCu$_2$O$_2$

R. V. Pisarev,[1,*] A. S. Moskvin,[2] A. M. Kalashnikova,[1,3] A. A. Bush,[4] and Th. Rasing[3]

[1]*A. F. Ioffe Physico-Technical Institute of RAS, 194223, St. Petersburg, Russia*
[2]*Ural State University, 620083, Ekaterinburg, Russia*
[3]*IMM, Radboud University Nijmegen, 6525 ED Nijmegen, The Netherlands*
[4]*Moscow State Technical University of Radioengineering, Electronics and Automation, 117454, Moscow, Russia*
(Received 29 August 2006; published 31 October 2006)

We show that the optical properties of LiCu^{1+}Cu^{2+}O$_2$ in the spectral range of 0.6–5.8 eV radically differ from those of all other known Cu^{1+}, Cu^{2+}, and mixed-valent oxide cuprates. An extremely strong, sharp, and highly anisotropic optical feature with $\varepsilon_2^{xx}=26$ is observed at 3.27 eV which we assign to an excitonlike transition in the O^{2-}-Cu^{1+}-O^{2-} dumbbells. Our findings thoroughly disagree with reported *ab initio* calculations and can be explained by an exciton-type model that includes strong electron-hole correlations and a crystal-field splitting of the Cu^{1+} states. The excitonic effects in LiCu$_2$O$_2$ appear strongly enhanced due to the shortening of the dumbbell lattice spacing which is the shortest one among known cuprates. Our experimental data along with the model reveal a previously unknown regularity in the electronic structure of cuprates.

The discovery of high-temperature superconductivity and colossal magnetoresistance has triggered a vast amount of experimental and theoretical research of strongly correlated transition-metal oxides. Optical studies of the low-energy electron-hole excitations in the vicinity of band gaps are of primary importance for constructing appropriate Hubbard models and obtaining adequate descriptions of the electronic, magnetic, and optical properties. Despite extensive studies during the last two decades many basic problems of transition-metal oxides still remain a matter of great dispute and controversy.[1–4]

Among numerous transition-metal oxides copper-based compounds hold a distinguished position. They reveal the largest crystallographic and chemical diversity due to the remarkable ability of copper ions to occupy crystallographic positions with different symmetries and coordination properties, and the possible coexistence of copper ions in Cu^{1+} $(3d)^{10}$ and Cu^{2+} $(3d)^{9}$ oxidation states in the same compound. The Cu^{1+} ions, as a rule, occupy the linear coordinated O^{2-}-Cu^{1+}-O^{2-} dumbbell positions whereas the corner- or edge-sharing Cu^{2+}O$_4$ plaquettes form the basic elements of the crystalline and electronic structure for the overwhelming majority of the Cu^{2+}-based cuprates. This diversity finds vivid manifestation in the electric, magnetic, and optical properties of cuprates that strongly vary, depending on chemical composition, copper valency, and crystal structure.

In this paper we report the observation of an extremely strong, narrow, and highly anisotropic optical feature near 3.27 eV in the absorption spectra of the mixed-valent cuprate LiCu^{1+}Cu^{2+}O$_2$. These optical properties are very different from those of all other known Cu^{1+}, Cu^{2+}, mixed-valent cuprates, and transition-metal oxides. We explain this anomaly on the basis of an exciton model not previously applied to such type of cuprates. Our data and conclusions seriously disagree with *ab initio* calculations[5] and recently reported reflectivity data and their interpretation.[6]

LiCu$_2$O$_2$ crystallizes in the orthorhombic space group *Pnma*.[7,8] The edge-sharing CuO$_4$ squares for Cu^{2+} and the O-Cu-O dumbbells for Cu^{1+} form the basic elements of its crystalline structure schematically shown in Fig. 1. Such structure makes LiCu$_2$O$_2$ interesting as a spin-ladder system and as an ensemble of frustrated single-spin chains. Details of its magnetic structure are presently the subject of strong controversy.[9,10]

The optical complex dielectric function $\varepsilon=\varepsilon_1-i\varepsilon_2$ of LiCu$_2$O$_2$ was studied from 20 to 300 K using a spectroscopic ellipsometer in the range from 0.6 to 5.8 eV, as described elsewhere.[11] Polished samples were prepared from flux grown x-ray oriented single crystals. The spectra were found stable and reproducible over a six month period within a few percents.

Figure 2 shows the ε_1 and ε_2 room temperature spectra of LiCu$_2$O$_2$ for light polarizations along the x and z axes. The true crystal symmetry is orthorhombic and one might expect an optical anisotropy in the xy plane. However, only a small anisotropy of the order of several percents was observed. We attribute the cancellation of this anisotropy to the well-developed 90° twinning inherent in single crystals of LiCu$_2$O$_2$.[10]
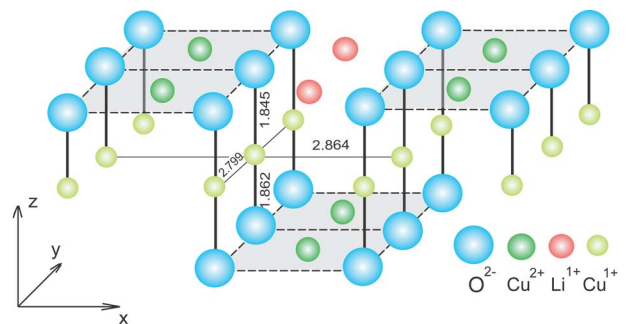
An extremely strong and narrow absorption band

FIG. 1. (Color online) Schematic crystal structure of LiCu$_2$O$_2$. Cu^{1+} ions occupy the dumbbell positions (thick solid lines) along the z axis and form the pure Cu^{1+} two-dimensional (2D) xy plane. Cu^{2+} ions occupy the edge-sharing plaquettes (gray planes). The distances are in Å according to Ref. 7.
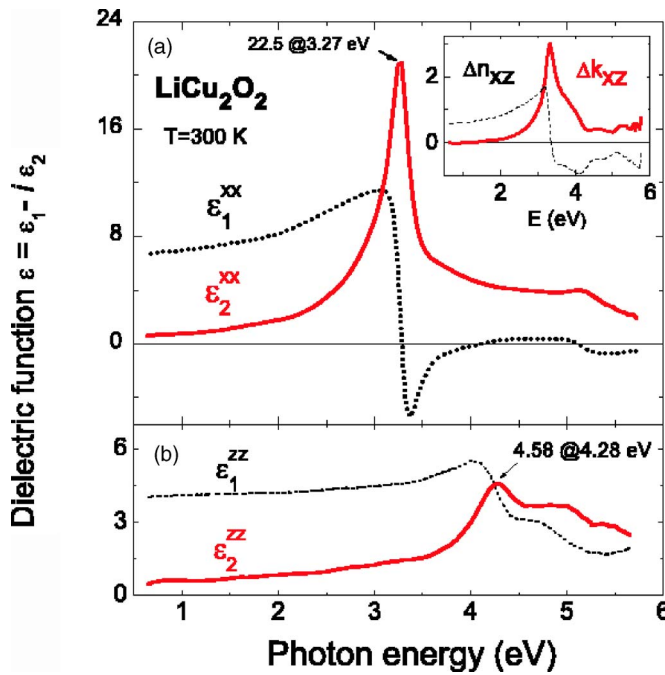
FIG. 2. (Color online) Room temperature spectra of the real ε_1 (dashed lines) and imaginary ε_2 (solid lines) parts of the dielectric functions for the light polarized (a) perpendicular and (b) parallel to the dumbbell axis z. Inset: Linear birefringence and dichroism spectra.

FIG. 3. (Color online) (a) Low temperature (T=26 K) spectra of the real ε_1 (open circles) and imaginary ε_2 (solid circles) parts of the dielectric functions for the light polarized along the x axis and their fit with the set of Lorentz oscillators (lines); (b) the positions of the main Lorentz oscillators in the ε_2^{xx} spectra. Inset: Optical conductivity spectra at T=26 and 300 K (solid and open circles).

($\varepsilon_2^{xx}=22.5\pm1.0$, optical conductivity $\sigma^{xx}=9.2\times10^3\ \Omega^{-1}\ cm^{-1}$, absorption coefficient $\alpha^x\simeq1\times10^6\ cm^{-1}$) at a photon energy of $E=3.27\pm0.01$ eV ($\delta=0.26$ eV) is observed for the light polarized along the x axis. These observations are in disagreement with recent data where an almost twice as low peak value was reported at $E=3.1$ eV.[6] We attribute these discrepancies to a higher accuracy and reliability of the ellipsometric data in comparison to the reflectivity data. For the z-polarized light the 3.27 eV feature vanishes completely and several overlapping broad and less intense absorption bands are observed at higher energy. The most intensive one with $\varepsilon_2^{zz}=4.58$ is centered at $E=4.28$ eV. The linear birefringence $\Delta n_{xz}=n_x-n_z$ and dichroism $\Delta k_{xz}=k_x-k_z$ are extremely large; see the inset to Fig. 2. We note that no data for z-polarized light were reported in Ref. 6.

Figure 3(a) shows the dielectric functions at $T=26$ K for the light polarized along the x axis. The optical conductivity spectra at room and low temperatures are displayed in the inset to Fig. 3. They show that the position of the 3.27 eV band is temperature independent. The peak intensity grows from $\sigma^{xx}=9.2\times10^3\ \Omega^{-1}\ cm^{-1}$ at T=300 K up to $\sigma^{xx}=11.4\times10^3\ \Omega^{-1}\ cm^{-1}$ at T=26 K, however the integrated spectral weight remains constant within experimental errors.

The optical spectra of LiCu$_2$O$_2$ are anomalous in several aspects. First, they fully disagree with the band structure calculations that predict LiCu$_2$O$_2$ to be a charge-transfer insulator with a band gap of 0.69 eV.[5] Second, they radically differ from spectra of other cuprates where the copper ions occupy crystallographically analogous positions, namely, Cu^{1+} ions in dumbbells and Cu^{2+} ions in planar-square or octahedral positions. A very strong and narrow ε_2^{xx} band at
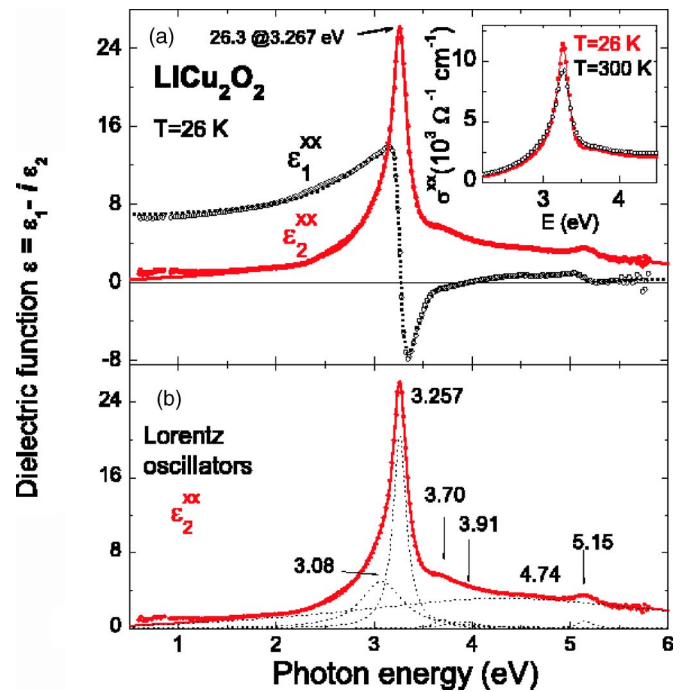
3.27 eV with a peak value $\varepsilon_2^{xx}=22-26$ is 2 to 3 times higher than in any other known cuprate or transition-metal oxide. Such a high ε_2^{xx} value even results in negative ε_1^{xx} values in this spectral region, a situation more typical to metals but not to insulators. This confirms the dominant contribution of the 3.27 eV transition to ε_2^{xx} over all other transitions.

Let us now dwell on the near-band-gap electronic transitions in insulating cuprates. The optical response of even monovalent cuprates crucially depends on the crystal structure. Indeed, the charge transfer (CT) gap in insulating cuprates with the one-dimensional (1D) or 2D arrangement of the *corner-sharing* Cu^{2+}O$_4$ square plaquettes is determined by the superposition of (i) a weak CT excitation from the O $2p\pi$ nonbonding (NB) band to the upper Hubbard band (UHB) and (ii) a strong excitation from the lower Hubbard band (LHB) to the UHB with the energy near 2 eV.[12,13] A distinctive feature of the *edge-sharing* Cu^{2+}O$_4$ square plaquettes usually forming CuO$_2$ chains is a strong suppression of the hole transfer from one plaquette to its nearest neighbors for the in-plane states, due to the nearly 90° Cu-O-Cu bond angle along the chain. As a result, a suppression of the LHB-UHB transitions takes place. The in-plane charge excitations are localized in the plaquettes and with respect to electronic properties the CuO$_4^{2-}$ centers in these compounds can be considered to be approximately isolated as in the 0D systems.[14]

This point of view is fairly well confirmed in optical and electron energy loss spectra for the monovalent chain cuprate Li$_2$Cu^{2+}O$_2$ in which the CuO$_2$ chains formed by the edge-

TABLE I. Crystallographic and optical data for dumbbell cuprates.

| Material | Crystal structure | Bond length (Å) | | Main band | | References |
		Cu^{1+}-O^{2-}	Cu^{1+}-Cu^{1+}	Position (eV)	ε_2	
$LiCu_2O_2$	1D orthorhombic	1.862	2.864 (*x* axis)	3.27	26.3 (25 K)	this work
		1.845	2.779 (*y* axis)		22.5 (300 K)	
$CrCuO_2$	2D delafossite	1.85	2.975	~3.5	8.6	Ref. 16
Cu_2O	3D cubic	1.85	3.02	~3.5	12.0	Ref. 19
$YCuO_2$	2D delafossite	1.835	3.524	4.2	9.3	Ref. 16
$YBa_2Cu_3O_6$	2D tetragonal	1.8	3.856	4.2	8.0	Refs. 16 and 18

sharing CuO_4 square plaquettes closely resemble those of the mixed-valent $LiCu_2O_2$.[9] The Li_2CuO_2 reveals no significant optical absorption features in a wide spectral range up to 4–5 eV. A rather strong absorption band peaked at 4.4 eV (Ref. 14) [4.25 eV (Ref. 15)] is unambiguously assigned to a strong one-center in-plane $b_{1g} \rightarrow e_u(\sigma)$ CT hole transition in CuO_4 square plaquettes.[14] Hence the broadband in the spectral range of 4–5 eV seen in our spectra (Figs. 2 and 3), rather than the huge resonance at 3.27 eV, may be attributed to an electronic excitation from the O $2p\sigma$ NB band to the UHB.

Monovalent O^{2-}-Cu^{1+}-O^{2-} dumbbell cuprates include the model 3D cubic semiconductor Cu_2O with a broad intensive band at 3.5 eV,[16] and a wide class of hexagonal cuprates with the delafossite structure.[17] One example is $YCuO_2$, which shows sharp features in the range of 3.6–4.2 eV with maximum values of $\varepsilon_2 \simeq 9$ assigned to transitions within the dumbbell complexes.[16]

The mixed-valent Cu^{1+} and Cu^{2+} compounds are rarely found. A well-known example is the parent-superconductor oxide $YBa_2Cu_3O_6$ with a tetragonal O^{2-}-Cu^{1+}-O^{2-} dumbbell lattice and the CuO_2 planes formed by the *corner-sharing* $Cu^{2+}O_4$ plaquettes. This material shows strong optical features at 1.7 and 4.1 eV (Ref. 16) attributed to the LHB-UHB transition within the CuO_2 planes and the intra-atomic $3d$-$4p$ transition within the O^{2-}-Cu^{1+}-O^{2-} dumbbells, respectively.[18]

This brief review of the optical spectra of cuprates allows us to exclude any relation between the 3.27 eV anomaly in $LiCu_2O_2$ and the charge-transfer transitions in the $Cu^{2+}O_2$ chains. On the other hand, some of the Cu^{1+} dumbbell cuprates show spectral features resembling the 3.27 eV anomaly in $LiCu_2O_2$, implying its relation with the O^{2-}-Cu^{1+}-O^{2-} dumbbells. To elucidate the origin of this anomalous optical response in $LiCu_2O_2$, we must look closer at the relationship between the crystallographic structure of the dumbbell systems and their optical properties. The specific Cu^{1+}-O^{2-} and Cu^{1+}-Cu^{1+} bond lengths and their effects on the crystal-field should be of primary importance. In Table I such data are collected for several cuprates, clearly showing that $LiCu_2O_2$ is an extreme case: it has the shortest Cu^{1+}-Cu^{1+} and the longest Cu^{1+}-O^{2-} bond lengths while the main peak lies at the lowest photon energy and has the highest peak intensity among known cuprates.

Strictly speaking, a reasonable comparison of the dumbbell optical features can be made only for $LiCu_2O_2$ and

$YBa_2Cu_3O_6$ as both systems have the similar tetragonal ordering of the dumbbell units. The variation of the Cu^{1+}-O^{2-} bond length between these materials is only 3.7%. It is hard to imagine that such a small change could be responsible for a huge shift of the dumbbell peak from 4.2 eV in $YBa_2Cu_3O_6$ to 3.27 eV in $LiCu_2O_2$, along with the enormous increase of its intensity. In contrast, the Cu^{1+}-Cu^{1+} bond length between the neighboring dumbbells in $LiCu_2O_2$ is about 1 Å less than in $YBa_2Cu_3O_6$, making the crystal-field effect a much more likely cause for the shift by about 1 eV of the main band.

Band structure calculations for $YBa_2Cu_3O_6$ do assign the prominent band at 4.2 eV mainly to a $3d$-$4p$ transition in the Cu^{1+} ion of the O^{2-}-Cu^{1+}-O^{2-} dumbbells.[18] These fail to correctly describe strongly correlated electronic systems. In particular, from these models one cannot conclude whether the low-lying electron-hole excitations are comprised of free charge carriers or excitons. Our data point to a strong exciton effect for the 3.27 eV feature in $LiCu_2O_2$. Using a simple model, we show below that this is a direct result of the intra-atomic electrostatic interaction between the Cu $4p$ electron and the Cu $3d$ hole, with an additional effect of the low-symmetry crystal field.

Figure 4 illustrates the step-by-step formation of the $4p$ electron-$3d$ hole pair energy spectrum starting from the strong correlation limit. The $4p$ electron and the $3d$ hole
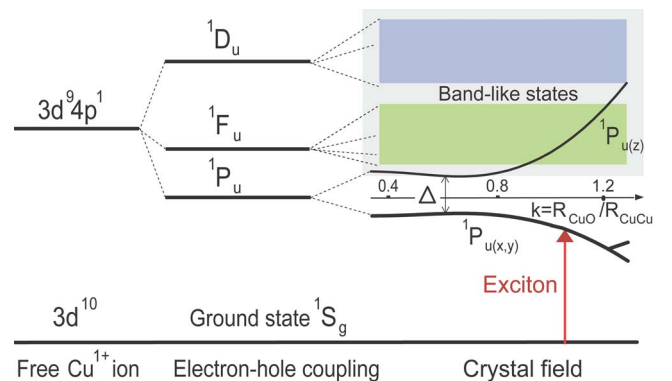

FIG. 4. (Color online) $4p$-$3d$ electron-hole energy spectrum: strong correlation limit and tetragonal crystal-field effects for ^1P_u term calculated using the point charge model. The crystal-field splitting of this term as a function of the inverse dumbbell-lattice spacing $k = R_{CuO}/R_{CuCu}$ is shown. At large k values the $^1P_{u(x,y)}$ term is split off by the orthorhombic field.

form a two-particle configuration with three terms ^1P_u, ^1D_u, and ^1F_u. The ^1P_u term has the lowest energy[20] and provides the only dipole-allowed intra-atomic $(3d^{10})^1S_g \rightarrow (3d^94p)^1P_u$ transition. The crystal field and covalency effects result in a lifting of the orbital degeneracy by a mixing of different terms and a pronounced splitting-off of the lowest $^1P_{u(x,y)}$ doublet. The latter is a clear candidate for the final state of the excitonlike transition. To include the crystal-field effect, we use a point-charge model for an idealized tetragonal dumbbell lattice and calculate the splitting of the ^1P_u term,

$$\Delta = E(^1P_{u(z)}) - E(^1P_{u(x,y)})$$
$$= \frac{3}{20}\left(\langle r^2\rangle_{3d} - \frac{1}{5}\langle r^2\rangle_{4p}\right)\sum_n q_n e^2 (3Z_n^2 - R_n^2)/R_n^5, \quad (1)$$

where n stands for Cu^{1+} or O^{2-} and Z_n and R_n indicate the projection on the z axis and the corresponding bond length, respectively. Given $q_{O^{2-}} = -2$, $q_{Cu^{1+}} = +1$, $\langle r^2\rangle_{4p} > 5\langle r^2\rangle_{3d}$, we obtain $\Delta > 0$ and a stabilization of the $^1P_{u(x,y)}$ doublet. It is important to emphasize that the contribution of the surrounding Cu^{1+} ions into Δ steeply ($\propto R_{CuCu}^{-3}$) rises with the shortening of the dumbbell-lattice spacing, whereas the oxygen contribution reveals a minimum near $k = R_{CuO}/R_{CuCu} \approx 1/\sqrt{2}$, pointing to an effect of the symmetry increase related with cubic contributions of the oxygen ions. We see that the

anomalous excitonic effect in $LiCu_2O_2$ reflects a strong Cu $4p$-$3d$ electron-hole coupling along with a strong splitting-off of the $^1P_{u(x,y)}(3d\ ^94p^1)$ doublet due to an enhanced tetragonal crystal field produced by the anomalous shortening of the dumbbell-lattice spacing R_{CuCu} in the xy plane.

In conclusion, we observed in $LiCu_2O_2$ an anomalous spectral feature at 3.27 eV with a very high peak intensity $\varepsilon_2^{xx} \simeq 26$ (T = 26 K) which we assign to coupled O^{2-}-Cu^{1+}-O^{2-} dumbbell complexes. This feature exceeds the analogous ε values in other copper oxides or transition-metal compounds by a huge factor of 2 to 3. We propose an exciton-type model, in which this feature originates from an interplay between strongly correlated copper $4p$ electrons $3d$ holes, and the crystal field splitting of the excited states. The model predicts a splitting-off of the $^1P_{u(x,y)}(3d\ ^94p^1)$ state and a stabilization of the exciton with a shortening of the dumbbell lattice spacing which for $LiCu_2O_2$ is the shortest one in the large family of cuprates. This model along with our experimental data reveals a previously unknown regularity in the electronic structure of cuprates.

*Electronic address: pisarev@mail.ioffe.ru

[1] M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. **70**, 1039 (1998).

[2] M. A. Kastner, R. J. Birgeneau, G. Shirane, and Y. Endoh, Rev. Mod. Phys. **70**, 897 (1998).

[3] D. N. Basov and T. Timusk, Rev. Mod. Phys. **77**, 721 (2005).

[4] R. Ruckamp et al., New J. Phys. **7**, 144 (2005).

[5] D. A. Zatsepin, V. R. Galakhov, M. A. Korotin, V. V. Fedorenko, E. Z. Kurmaev, S. Bartkowski, M. Neumann, and R. Berger, Phys. Rev. B **57**, 4377 (1998).

[6] M. Papagno, D. Pacilé, G. Caimi, H. Berger, L. Degiorgi, and M. Grioni, Phys. Rev. B **73**, 115120 (2006).

[7] S. J. Hibble, J. Köhler, A. Simon, and S. Paider, J. Solid State Chem. **88**, 534 (1990).

[8] R. Berger, A. Meetsma, S. van Smaalen, and M. Sundberg, J. Less-Common Met. **175**, 119 (1991).

[9] A. A. Gippius, E. N. Morozova, A. S. Moskvin, A. V. Zalessky, A. A. Bush, M. Baenitz, H. Rosner, and S.-L. Drechsler, Phys. Rev. B **70**, 020406(R) (2004).

[10] T. Masuda, A. Zheludev, A. Bush, M. Markina, and A. Vasiliev, Phys. Rev. Lett. **92**, 177201 (2004).

[11] A. M. Kalashnikova and R. V. Pisarev, JETP Lett. **78**, 143 (2003).

[12] A. S. Moskvin, R. Neudert, M. Knupfer, J. Fink, and R. Hayn, Phys. Rev. B **65**, 180512(R) (2002).

[13] A. S. Moskvin, J. Málek, M. Knupfer, R. Neudert, J. Fink, R. Hayn, S.-L. Drechsler, N. Motoyama, H. Fisaki, and S. Uchida, Phys. Rev. Lett. **91**, 037001 (2003).

[14] S. Atzkern, M. Knupfer, M. S. Golden, J. Fink, C. Waidacher, J. Richter, K. W. Becker, N. Motoyama, H. Eisaki, and S. Uchida, Phys. Rev. B **62**, 7845 (2000).

[15] Y. Mizuno, T. Tohyama, S. Maekawa, T. Osafune, N. Motoyama, H. Eisaki, and S. Uchida, Phys. Rev. B **57**, 5326 (1998).

[16] M. K. Kelly, P. Barboux, J.-M. Tarascon, and D. E. Aspnes, Phys. Rev. B **40**, 6797 (1989).

[17] Xiliang Nie, Su-Huai Wei, and S. B. Zhang, Phys. Rev. Lett. **88**, 066405 (2002).

[18] J. Kircher, M. Alouani, M. Garriga, P. Murugaraj, J. Maier, C. Thomsen, M. Cardona, O. K. Andersen, and O. Jepsen, Phys. Rev. B **40**, 7368 (1989).

[19] Landoldt-Börnstein, *Group III, Condensed Matter* (Springer, Berlin, 1998), Vol. 41C.

[20] In terms of the radial Slater parameter $F^2(ddpp) > 0$ the energies of ^1P_u, ^1F_u, and ^1D_u terms are $-\frac{1}{5}$, $-\frac{2}{5.7}$, and $+\frac{1}{5}$, respectively. It should be noted that this order of terms is inverted as compared to that for a two-electron or a two-hole $3d4p$ configuration.