

Critical Covalence and Superconductivity in $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_4$

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The variations of superconductive properties with x of the n -type $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_4$ ($\text{Ln} = \text{La}_{0.5}\text{Nd}_{0.5}$, Nd, or Gd) systems have been investigated. As the size of Ln^{3+} decreases, (i) the solubility limit x of Ce decreases, (ii) the value of x at which a transition from antiferromagnetic semiconductor to superconductor occurs increases, and (iii) the width Δx of the superconductive region decreases. The decreasing solubility of Ce with decreasing size of Ln^{3+} is due to decreasing tensile strain in the CuO_2 sheets. The progressive shift of the semiconductor to superconductor transition to higher x values with decreasing size of Ln^{3+} is explained on the basis of increasing electrostatic Madelung energy E_M caused by decreasing Cu–O bond length. A larger E_M means a larger charge transfer gap Δ and a smaller covalent-mixing parameter λ and bandwidth W ; so a decreasing size of Ln^{3+} necessitates a higher level of Ce-doping in order to achieve a critical covalence essential for superconductivity to occur. © 1992

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Introduction

The copper-oxide superconductors have intergrowth structures consisting of superconductively active CuO_2 sheets alternating with other inactive layers along the c -axis. Stabilization of intergrowth structures requires bond length matching across the intergrowth interface (I). Oxidation/reduction of the CuO_2 sheets above/below the formal oxidation state Cu^{2+} is one of the necessary conditions to suppress long-range antiferromagnetic order and induce superconductivity. Superconductivity occurs in a narrow mixed-valent composition ($W \approx U$) between an antiferromagnetic semiconductor ($W < U$) and a normal metallic ($W > U$) region ($I-3$); i.e. superconductivity occurs in a narrow-band regime where the band-

width W is approximately equal to the intraatomic correlation energy U .

The width of the $\sigma_{x^2-y^2}$ conduction band is determined by the strength of the nearly 180° Cu–O–Cu interactions within a CuO_2 sheet. In the tight-binding approximation, the bandwidth is given as

$$W \approx 2zb_\sigma = 8b_\sigma \quad (1)$$

where $z = 4$ is the number of nearest neighbor oxygen atoms to a Cu atom in a CuO_2 sheet and b_σ is the electron-transfer energy (resonance) integral. b_σ is related to the covalent-mixing parameters as

$$b_\sigma \approx \varepsilon_\sigma(\lambda_\sigma^2 + \lambda_s^2), \quad (2)$$

where ε_σ is the one-electron energy and λ_σ and λ_s are the covalent mixing parameters for the Cu- $3d_{x^2-y^2}$ and O- $2p_{\sigma x}$, $2p_{\sigma y}$, or O- $2s$

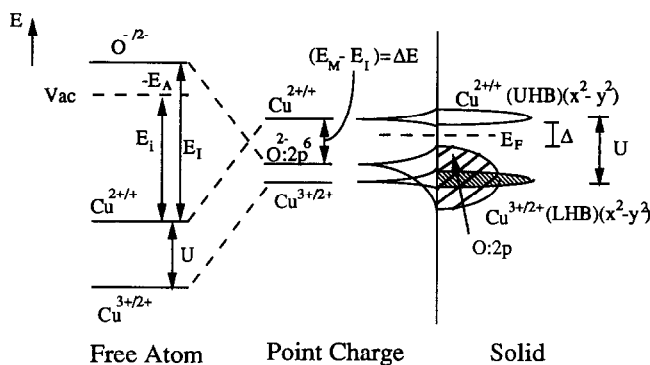


FIG. 1. Derivation of energy bands of CuO_2 sheets on an ionic model (Refs. (3) and (4)). UHB and LHB refer, respectively, to upper and lower Hubbard bands.

hybridizations, respectively. With an ionic model, the covalent mixing parameters are given as

$$\lambda = b^{\text{ca}}/\Delta E \quad (3)$$

where b^{ca} is the anion-cation resonance integral that depends on the overlap integral between $\text{O}-2p_{\sigma}$ and $\text{Cu}-3d_{x^2-y^2}$ orbitals and ΔE is the energy separation between $\text{Cu}^{2+/+}$ and $\text{O}:2p^6$ levels. ΔE is related to the electrostatic Madelung energy E_M gained by allowing the point charges, Cu^{2+} and O^{2-} , to order themselves in a crystalline lattice and the total energy E_1 required to transfer an electron from a Cu^+ ion to an O^- ion at infinite separation (2-4) as

$$\Delta E = E_M - E_1. \quad (4)$$

ΔE is often referred to as the charge-transfer gap Δ between the top of the $\text{O}:2p$ band and the bottom of the $\text{Cu}-3d_{x^2-y^2}$ upper Hubbard band (UHB) in copper oxides. These relationships are illustrated schematically in Fig. 1, proposed by Goodenough *et al.* (2-4).

The covalence in the CuO_2 sheets and hence the $\sigma_{x^2-y^2}$ conduction bandwidth W can be increased either by an increase in b^{ca} or by a decrease in $\Delta E = E_M - E_1$. Generally in an ionic model, the variations in b^{ca} with bond length changes will be smaller

than those in ΔE . Therefore, the changes in covalence in the CuO_2 sheets and bandwidth W are predominantly determined by changes in $\Delta E = E_M - E_1$. A transition from antiferromagnetic semiconductor to superconductor region requires a critical bandwidth $W \approx U$ and hence a critical covalence λ_c in the CuO_2 sheets; i.e., it requires a decrease in $E_M - E_1$ (see Eqns. 3 and 4) to a critical limit $E_M \approx E_1$. The sensitivity of the antiferromagnetic semiconductor-to-superconductor transition to changes in $E_M - E_1$, introduced by variations in $\text{Cu}-\text{O}$ bond lengths, is demonstrated by investigating the superconductive properties of the n -type $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_4$ ($\text{Ln} = \text{La}_{0.5}\text{Nd}_{0.5}$, Nd , or Gd) systems.

Experimental

$\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_4$ ($\text{Ln} = \text{La}_{0.5}\text{Nd}_{0.5}$, Nd , or Gd) were obtained by firing required quantities of the component oxides first at 950°C for 24 h, and then at 1050°C for 48 h with two intermittent grindings and pelletizations. The resulting $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_{4+\delta}$ were then annealed in N_2 at 890°C for about 18 h to drive off the excess δ oxygen and quenched to room temperature in N_2 . Formation of single phase products was confirmed by X-ray powder diffraction. The ox-

xygen content was determined by iodometric titration (5). The superconductive properties were determined with a SQUID magnetometer with a field of 10 Oe.

Results and Discussion

All the $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_4$ ($\text{Ln} = \text{La}_{0.5}\text{Nd}_{0.5}$, Nd, or Gd) samples were found from X-ray powder diffraction to be single phase materials crystallizing in the T' structure of Nd_2CuO_4 (6). The solubility limit x of Ce in $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_4$ decreases from $x = 0.23$ for $\text{Ln} = \text{La}_{0.5}\text{Nd}_{0.5}$ to $x = 0.20$ for $\text{Ln} = \text{Nd}$, and to $x = 0.15$ for $\text{Ln} = \text{Gd}$. Stabilization of T' structure requires a bond length matching between the $(\text{Ln})_2\text{O}_2$ fluorite and CuO_2 perovskite layers. The larger the size of Ln^{3+} , the greater is the bond length mismatch between the $(\text{Ln})_2\text{O}_2$ fluorite and CuO_2 perovskite layers and so the greater is the tensile strain in the CuO_2 sheets. The greater the tensile strain, the easier it is to stretch the Cu–O bonds by the addition of antibonding electrons into the CuO_2 sheets. Therefore, as the size of Ln^{3+} increases from $\text{Ln} = \text{Gd}$ to $\text{Ln} = \text{La}_{0.5}\text{Nd}_{0.5}$, the extent to which the Cu–O bonds can be stretched by the substitution of Ce^{4+} for Ln^{3+} increases; i.e., the solubility of Ce increases with increasing size of Ln^{3+} and the a parameter.

The as-prepared $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_{4+\delta}$ samples had $\delta \approx 0.03$ and were semiconducting for all values of x . The excess δ oxygen atoms randomly occupy the empty c -axis positions (0.5, 0.5, 0.3513 sites in the $I4/mmm$ space group of the T' Nd_2CuO_4 structure) and perturb the periodic potential associated with the CuO_2 sheets. This seems to introduce Anderson localized states at the edges of the conduction band and give small-polaron conduction even at higher doping levels like $x = 0.20$ (7).

The N_2 -annealed samples all had $\delta \approx 0.00$ and the variations of superconductive properties with x for $\text{LaNd}_{1-x}\text{Ce}_x\text{CuO}_4$ and

$\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ are shown in Fig. 2a and b. $\text{Gd}_{2-x}\text{Ce}_x\text{CuO}_4$ samples are semiconductive for all values of $0 \leq x \leq 0.15$ as has been previously found by others (8, 9). As we go from $\text{Ln} = \text{La}_{0.5}\text{Nd}_{0.5}$ to $\text{Ln} = \text{Gd}$ in the $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_4$ system, the value of x at which the transition from antiferromagnetic semiconductor to superconductor occurs increases. For example, the transition occurs at $x = 0.10$ for $\text{Ln} = \text{La}_{0.5}\text{Nd}_{0.5}$ (Fig. 2a), and at $x = 0.14$ for $\text{Ln} = \text{Nd}$ (Fig. 2b). These results are in close agreement with that observed by Tao *et al.* (10). No superconductivity has been observed for $\text{Ln} = \text{Gd}$ up to $x = 0.15$; probably it would become superconductive if one could increase the solubility limit x of Ce in $\text{Gd}_{2-x}\text{Ce}_x\text{CuO}_4$ beyond 0.15.

As we move from $\text{Ln} = \text{La}_{0.5}\text{Nd}_{0.5}$ to $\text{Ln} = \text{Gd}$, the a parameter and the Cu–O bond length decrease. A shorter Cu–O bond means a larger electrostatic Madelung energy E_M —i.e., a larger $E_M - E_1$ and charge-transfer gap Δ —and a greater raising of the antibonding $\sigma_{x^2-y^2}$ band. In fact, a linear increase in charge-transfer gap Δ with decreasing in-plane Cu–O bond length in the T' Ln_2CuO_4 has recently been observed by Arima *et al.* (11) from optical spectroscopy. Substitution of Ce^{4+} for Ln^{3+} would stretch the Cu–O bond and lower $E_M - E_1$ and the relative position of the $\sigma_{x^2-y^2}$ band. Therefore, as the Cu–O bond length in the undoped Ln_2CuO_4 decreases from LaNdCuO_4 to Gd_2CuO_4 , a larger amount of Ce-doping is necessary to decrease $E_M - E_1$ to a critical limit $E_M \approx E_1$ that can give a critical covalence λ_c in the CuO_2 sheets and induce superconductivity. Furthermore, the increase in electronegativity of Ln^{3+} ions from $\text{Ln} = \text{La}_{0.5}\text{Nd}_{0.5}$ to $\text{Ln} = \text{Gd}$ may also decrease the covalence in the CuO_2 sheets via inductive effect—as the oxygen atoms of the CuO_2 sheets are also bonded to Ln^{3+} ions—and necessitate a higher level of Ce-doping in order for a critical covalence λ_c to be realized in the CuO_2 sheets for superconductiv-

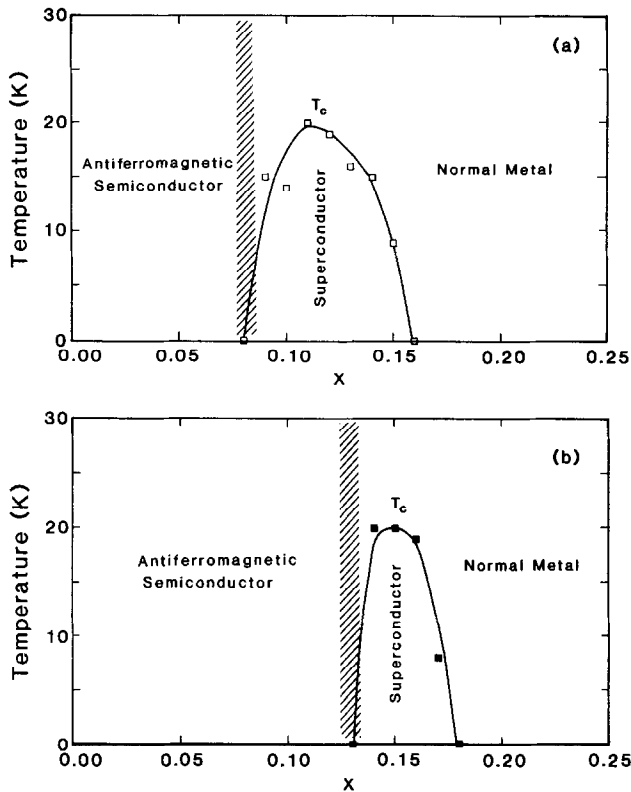


FIG. 2. Variations of T_c with x for (a) $\text{LaNd}_{1-x}\text{Ce}_x\text{CuO}_4$ and (b) $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$. The shaded area refer to two-phase regions consisting of antiferromagnetic semiconductor and superconductor phases.

ity to occur. Therefore, the antiferromagnetic semiconductor to superconductor transition in $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_4$ occurs at progressively higher values of x as the size of Ln^{3+} ions and the a parameter decrease. This model can now explain why $\text{Gd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ is not superconductive. With a shorter Cu–O bond and larger $E_M - E_I$, $\text{Gd}_{2-x}\text{Ce}_x\text{CuO}_4$ needs a Ce-doping level of >0.15 to induce superconductivity. Unfortunately, the bond length matching criterion with a smaller Gd^{3+} limits the solubility of Ce to $x = 0.15$ in this system.

As we pass from $\text{Ln} = \text{La}_{0.5}\text{Nd}_{0.5}$ to $\text{Ln} = \text{Nd}$, the width Δx of the superconductive region decreases. For example, the width Δx of the superconductive region de-

creases from $\Delta x = 0.06$ for $\text{Ln} = \text{La}_{0.5}\text{Nd}_{0.5}$ (Fig. 2a) to $\Delta x = 0.04$ for $\text{Ln} = \text{Nd}$ (Fig. 2b); if $\text{Gd}_{2-x}\text{Ce}_x\text{CuO}_4$ could be made superconductive by increasing the solubility x of Ce beyond 0.15, then superconductivity might occur only over a narrow range $\Delta x < 0.04$ in this system. The decrease in the width Δx suggests that the transition from $W < U$ (antiferromagnetic semiconductor) to $W > U$ (normal metal) via $W \approx U$ (superconductive) occurs more rapidly in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ than in $\text{LaNd}_{1-x}\text{Ce}_x\text{CuO}_4$. Also the width $\Delta x \approx 0.05$ of the superconductive region in the n -type $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_4$ is much smaller than the width $\Delta x \approx 0.20$ in the p -type $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. It appears that as the electronegativity of the counter cations

Ln^{3+} or Sr^{2+} decreases the transition from $W < U$ to $W > U$ occurs much more slowly, giving a larger width Δx for the superconductive region.

Conclusions

The solubility x of Ce in the n -type $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_4$ systems decreases with decreasing size of Ln^{3+} in order to maintain bond length matching between the $(\text{Ln,Ce})_2\text{O}_2$ fluorite and CuO_2 perovskite layers. The antiferromagnetic semiconductor to superconductor transition in copper oxides requires a critical covalence and bandwidth. We have demonstrated, for the first time, that this transition is sensitive to the electrostatic Madelung energy E_M , and can be modulated by Cu–O bond length. Our study also explains that a doping level of $x = 0.15$ in $\text{Gd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ with a shorter Cu–O bond is not sufficient to reduce E_M to the critical limit $E_M \approx E_I$ and induce superconductivity. The width Δx of the superconductive region in copper oxides appears to decrease with decreasing size and increasing electronegativity of the counter cations, Ln^{3+} .

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