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Superconductivity and Lattice Parameters in $(La_{1-x}Sr_x)_2CuO_{4-\delta}$ Solid Solution System

Shinsaku KANBE, Kohji KISHIO,* Koichi KITAZAWA,* Kazuo FUEKI,*
Hidenori TAKAGI,† and Shoji TANAKA†
Department of Industrial Chemistry, Faculty of Engineering,
The University of Tokyo, Bunkyo-ku, Tokyo 113
†Department of Applied Physics, Faculty of Engineering,
The University of Tokyo, Bunkyo-ku, Tokyo 113

The superconducting critical temperature T_c increased with increase in x in $(La_{1-x}Sr_x)_2CuO_{4-\delta}$ associated with the shortening of the Cu-O bond in the basal plane and the elongation of the lattice along the c-axis in the K_2NiF_4 structure. The results are discussed in terms of two-dimensional itinerant band formation of $Cu:d_{x^2-y^2}-O:p_\sigma$ bond.

It has recently been established that the Ba-La-Cu-O (Balacuo) system becomes superconducting below about 30 K.[1-4] This material has later turned out to possess the extremely high critical field as well.[5,6]

In a previous report,[7] we described the occurrence of superconductivity in $(La_{1-x}Sr_x)_2CuO_{4-\delta}$ (LSCO) with even higher T_c, 37 K at which the sharp transition set in according to both a.c. susceptibility and resistivity measurements. LSCO exhibited a higher critical field[5] than the Balacuo system. The crystal structure of LSCO, which was responsible for the superconductivity, was identified to be the same as that in the Balacuo system, i.e., tetragonal K_2NiF_4 structure.[2,4] This structure is composed of a stack of layers of two dimensionally inter-connected octahedra with Cu ions on the center. Each of the layers is separated by the region composed mainly of La and O which seems to be electrically inactive. Therefore the variation of the lattice spacings with composition x appears to be interesting in relation with the superconducting properties, because the material may somehow exhibit the low dimensional nature in the superconductivity.

In the present paper, we report the change in T_c as well as in the lattice parameters with variation in the relative composition of Sr to La in the $(La_{1-x}Sr_x)_2CuO_{4-\delta}$ system.

The details of sample preparation and a.c. magnetic susceptibility measurements were given in a previous paper.[7] All the samples were heat-treated in air at 1000 °C and quenched. The powder X-ray diffraction peaks could be assigned as those of the tetragonal K_2NiF_4 structure for all the specimens

except for x=0, i.e., La_2CuO_4 which was orthorhombic as reported by Longo and Raccah.[8] This transition from orthorhombic to tetragonal symmetry as La ions are replaced by Sr ions is in accord with the observation by Michel and Raveau.[9] The lattice parameters were obtained by the least square fitting to minimize the deviation of the observed 2θ results from the calculated ones. The temperature at which a sharp transition started in the a.c. susceptibility was taken as the onset T_c.

The PXRD analysis indicated that the specimens were single phase of the tetragonal K_2NiF_4 structure for x=0.025 and 0.05. Presence of a small amount of perovskite phase was detected for specimens with $0.075<x<0.11$, whereas an additional unidentified phase was present in an increasing manner as x increases above x=0.125. According to Goodenough et al.,[10] specimens with x=0.5 could be obtained as a single phase when heat-treated under a high oxygen pressure. The present results, however, indicate that the solubility limit of Sr in LSCO is around x=0.125 under the heat treatment conditions in the present experiment.

Figure 1 illustrates the dependence of the lattice parameters and the T_c values on the composition x. As can be seen in the figure, the lattice parameters a_0 and c_0, and hence c_0/a_0 change monotonically with increase in x. On the other hand, the superconducting critical temperature T_c increases from 14 K for x=0.025 to the maximum 37 K for x=0.10, but sharply drops down above x=0.11. In the mixed phase region for $x > 0.15$, the T_c value remains nearly constant with the further increase in x, but the diamagnetic susceptibility signal becomes weaker in the same region. This again supports the presence of the phase boundary around x=0.125.

The above variation of T_c as well as the crystallographic data may be interpreted as follows. The electron-phonon coupling constant λ is intensified as Sr substitutes for La, resulting in the rise in T_c, but the excessive increase in λ finally induces the lattice instability at x=0.125. The exceptionally high T_c of this material suggests the attainment of a large λ which should be attributed to the special crystal structure composed of the metallic layers of the inter-connected octahedra and the apparently inactive

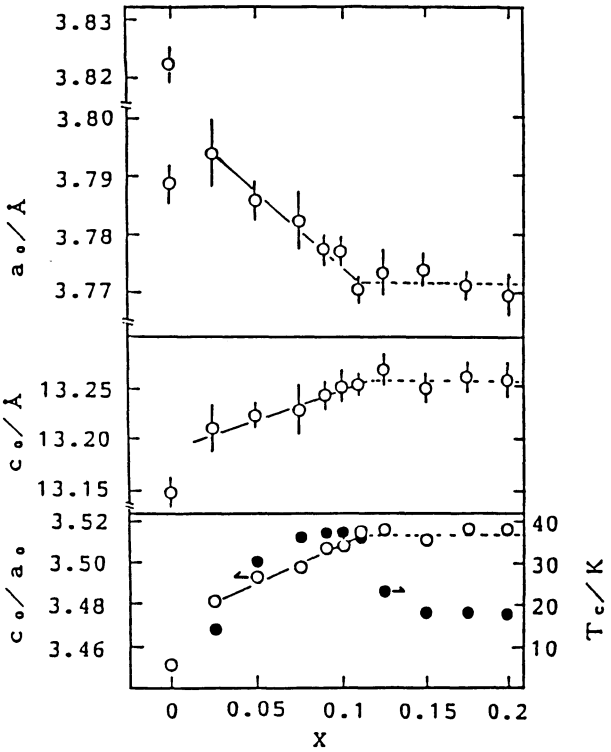

Fig. 1. Tetragonal Lattice Parameters a_0, c_0, c_0/a_0 ratio and Critical temperature T_c vs. Sr composition x in $(La_{1-x}Sr_x)_2CuO_{4-\delta}$; The two data points for a_0 at x=0 were caluculated from corresponding orthorhombic parameters.

La-O layers.

The reason that c_0/a_0 increases with x until the phase boundary is reached may be attributed to the gradual elongation of the oxygen octahedra along the c-axis with the associated shrinkage in the basal plane. It is known that the octahedra are elongated along the c-axis already in La_2CuO_4.[8] This further distortion seems to be induced by the increase in the effective negative charge of O ions which intensifies the crystal field around the Cu ions. Since the character of Sr-O bond is more ionic than La-O bond, the substitution of Sr for La seems to lead to this change in the effective charge of O ions.

It has been reported that the metallic nature of La_2CuO_4 is intensified when the lattice parameter a_0 decreases as different lanthanide ions are introduced on La sites.[11] Singh et al.[12] has proposed a density of states model for La_2CuO_4 as shown in Fig. 2a. The σ^* band composed of $Cu:d_{x^2-y^2}-O:p_\sigma$ bonds is split in two, because of the strong correlation between the electrons. In the present material $(La_{1-x}Sr_x)_2CuO_{4-\delta}$, it seems to be reasonable to modify their diagram as shown in Fig. 2b. The σ^* becomes a single band in the basal plane. Because of the two-dimensional nature of this band, the density of states is illustrated to distribute as nearly square-like. There may remain a pseudo-gap at the center of the band due to the incomplete merging of the upper and lower Hubbard bands, while the d_{z^2} levels are relatively lowered due to the stretching of the Cu-O bond along the c-axis.

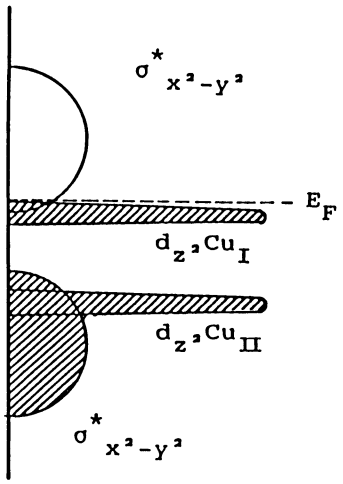

Fig. 2a. Schematic density of states model[12] for orthorhombic La_2CuO_4 in which two inequivalent Cu_I and Cu_{II} sites are involved. A correlation splitting is assumed for $\sigma^*_{x^2-y^2}$ band.

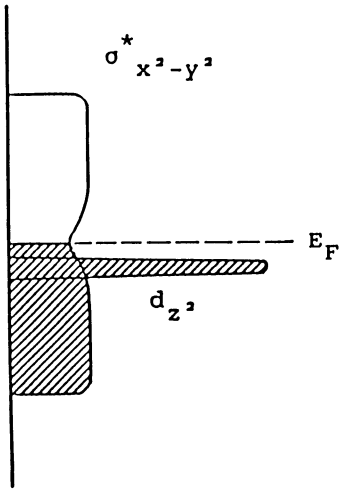

Fig. 2b. Schematic density of states model proposed for tetragonal $(La_{1-x}Sr_x)_2CuO_{4-\delta}$. An increased itinerancy of the $\sigma^*_{x^2-y^2}$ band is assumed because of the unusually short Cu-O bond distance. The extent of the appearance of the pseudo-gap depends on a_0 as well as on the oxygen deficiency.

We have experienced that a slight reduction of the specimen, which seems to introduce oxygen deficiency, leads to a semiconductive resistivity-temperature relationship. In the context of the proposed model, this can be explained in the relatively strong appearance of the pseudo-gap. But generally, the metallic nature of the specimens is intensified as Sr is incorporated on La sites, which is understood as the result of the formation of the two dimensional σ^* band. The decrease in the lattice parameter a_0 is a strong support to this picture.

Since the lattice parameter c_0 increases in the mean time, while the T_c increases, we presume that the two-dimensional σ^*, i.e., $Cu{:}d_{x^2-y^2}\text{-}O{:}p_\sigma$ itinerant band in the basal plane through the inter-connected oxygen octahedra plays the essential role in the superconductivity in this material system. A two dimensional band can give a large density of states at the Fermi level.

Furthermore, a strong electron-phonon coupling may be expected in this sort of electronic structure, because the deformation of the oxygen octahedra exerts a great influence on the energy of the electronic states near the Fermi level if the two-dimensional itinerant band formation is the case. Further investigation is currently undertaken in this context.

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