RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 49, NUMBER 6 1 FEBRUARY 1994-II

Elastic softening in superconducting $La_{2-x}Sr_xCuO_4$

Tae Song Kwon and Jong Chul Park
Korea Research Institute of Standards and Science, Taejon 305-606, Korea

Kyun Nahm
Department of Physics, Yonsei University, Wonju, Kangwon-do 222-701, Korea

Hyun Sik Noh and Chul Koo Kim
Department of Physics and Institute for Mathematical Sciences, Yonsei University, Seoul 120-749, Korea
(Received 30 September 1993; revised manuscript received 29 November 1993)

A theoretical model for the elastic softening observed in $La_{2-x}Sr_xCuO_4$ is presented. It is shown that the electronic redistribution mechanisms between the strain-split itinerant p bands and also between the strain-shifted energy pockets can satisfactorily account for the elastic softening of c_{66} and $(c_{11}-c_{12})/2$. The result suggests that the Fermi level shifts from the M point to the Γ point as a consequence of the tetragonal-to-orthorhombic structural transition. Implications of the present result on the superconducting mechanism are discussed.

Among many experimental and theoretical aspects of $La_{2-x}Sr_xCuO_4$ (LSCO), elastic properties received relatively little attention comparing to electronic, magnetic, and optical properties. However, since Axe *et al.* showed that the disappearance of the orthorhombicity of the crystal could destroy the superconductivity, elastic properties drew considerable interest.[1] Especially, Migliori *et al.* carried out ultrasonic measurements on the high-temperature tetragonal (HTT) phase $La_{1.86}Sr_{0.14}CuO_4$ and reported a giant elastic softening only on c_{66} among several elastic constants.[2] More recently, Nohara *et al.* measured the elastic constants of the midtemperature orthorhombic (MTO) phase $La_{1.86}Sr_{0.14}CuO_4$ and observed that only $(c_{11}-c_{12})/2$ softens with decreasing temperature below 50 K.[3] This type of selective softening has been observed in various types of materials, such as $A-15$ and Th_3P_4 type superconductors, $LaAg_xIn_{1-x}$ and heavily doped semiconductors.[4–7] It is known that this elastic softening yields valuable information on the nature of the Fermi level. Therefore, it is expected that proper understanding of the physical origin of these softening effects in LSCO will lead to more detailed information on the Fermi level and, consequently, to the superconducting mechanism.

In this paper, we present a theoretical model for the above elastic softening effect and, in the process, show that the model strongly supports that the oxygen p holes play the dominant role as the itinerant carriers. The softening in LSCO is known to depend on the doping level sensitively.[2] This dependence clearly suggests that the elastic softening originates from the electronic origin, in which the reduction of the free energy is achieved through redistribution of electrons. There exist two different and, yet, conceptually similar softening mechanisms.[4–7] The first mechanism in which the electrons redistribute between the strain-split degenerate energy levels is usually called the band Jahn-Teller effect.[8] In the second mechanism, the electrons redistribute between the strain-shifted energy pockets which are located at the equivalent $\vec{k}$ points of the Brillouin zone.[6,7] Here, we consider the two mechanisms in turn whether they are applicable to LSCO and can explain the elastic softening satisfactorily.

A crucial point for applicability of the band Jahn-Teller effect to the present case is the existence of degenerate or nearly degenerate electronic levels at the Fermi surface. For the pure tetragonal La_2CuO_4, several calculations showed that the Fermi level lies on a doubly degenerate p band near the M point.[9,10] Here, we assume that the band structure does not change upon Sr doping and only the position of the Fermi level is shifted. With this assumption, the doped holes will occupy the $O(2p)$ bands near the M point.[9] Since we are interested in the perturbation of the electronic levels due to the strain, we need the eigenfunctions of the p bands at the M point. For this purpose, a simple tight-binding approximation can be employed. In this method, the tight-binding parameters are fitted to the band structure of the first-principles calculations and, in turn, from these parameters, most of the prominent features of the original calculation can be reproduced. This type of calculation has been carried out in Ref. 9 and we simply use their results. In this approximation, the energy level on which the Fermi level lies is given by

$$E_M = E_p + 2\,[V_{pp\sigma} - V_{pp\pi}]\,,$$

and

$$|\,\Psi_1\rangle = \frac{1}{\sqrt{2}}\,[\,|\,x_1\rangle - |\,y_2\rangle]\,, \qquad (1)$$
$$|\,\Psi_2\rangle = \frac{1}{\sqrt{2}}\,[\,|\,x_2\rangle - |\,y_1\rangle]\,,$$

where E_p is the energy of the atomic p level, and $V_{pp\sigma}$ and $V_{pp\pi}$ are the usual Slater-Koster parameters. The

Bloch wave function $|x_i\rangle$ and $|y_i\rangle$ are given by

$$|x_i\rangle = \frac{1}{\sqrt{N}} \sum_n \exp(i\vec{k}\cdot\vec{r}_{ni})\ \phi_{x_i}(\vec{r}-\vec{r}_{ni}) , \qquad (2)$$
$$|y_i\rangle = \frac{1}{\sqrt{N}} \sum_n \exp(i\vec{k}\cdot\vec{r}_{ni})\ \phi_{y_i}(\vec{r}-\vec{r}_{ni}) ,$$

where i $(=1,2)$ represents the sites of oxygen in the two-dimensional unit cell and n the lattice site. ϕ_{x_i} and ϕ_{y_i} represent the p_x and p_y orbitals on the site i, respectively. The M point of the two-dimensional square lattice has the same symmetry of C_{4v} as the Γ point. It can be shown straightforwardly that $|x_1\rangle - |y_2\rangle$ belongs to the Γ_2 representation and $|x_2\rangle - |y_1\rangle$ to the Γ_3 representation, respectively. Now the ultrasonic strain Hamiltonian $H_\epsilon (= \sum_{ij} V_{ij} e_{ij})$ for the measurement of the elastic constants can be expanded in the irreducible strain components of the C_{4v} group as follows,

$$\begin{aligned} &\Gamma_1 = e_{xx} + e_{yy} ,\ e_{zz} , \\ &\Gamma_3 = e_{xx} - e_{yy} , \\ &\Gamma_4 = e_{xy} , \\ &\Gamma_5 = e_{yz} ,\ e_{zx} . \end{aligned} \qquad (3)$$

Most of the matrix elements for the strain perturbation between the degenerate $O(2p)$ levels, $\langle \phi_k | H_\epsilon^j | \phi_i \rangle$ are zero due to the matrix element theorem which stipulates that the nonzero terms satisfy the relation $\Gamma_i \times \Gamma_j = \Gamma_k$.[11] Using the direct product table for C_{4v},[12] we readily obtain the electron-strain interaction Hamiltonian H_ϵ at the Fermi level:

$$H' = \begin{pmatrix} G_1(e_{xx}+e_{yy}) + G_2 e_{zz} & G_3 e_{xy} \\ G_3 e_{xy} & G_1(e_{xx}+e_{yy}) + G_2 e_{zz} \end{pmatrix}, \qquad (4)$$

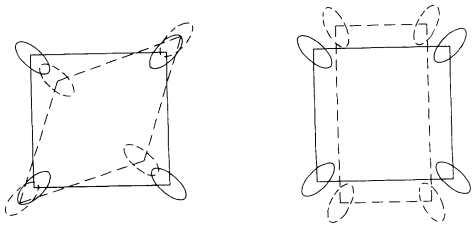
where G_1, G_2, and G_3 are the corresponding deformation potential constants. From the above equation, we observe that e_{xx}, e_{yy} and e_{zz} shift the energy levels uniformly, whereas e_{xy} removes the degeneracy. Other strain components, e_{yz} and e_{zx} do not appear in the equation and, thus, do not have any effect on the Fermi levels. Therefore, only the e_{xy} component causes the elastic softening by splitting the degenerate levels at the M point. The elastic free energy for a tetragonal structure is given by

$$\begin{aligned} F = &\tfrac{1}{2}c_{11}(e_{xx}^2 + e_{yy}^2) + \tfrac{1}{2}c_{33}e_{zz}^2 + c_{12}e_{xx}e_{yy} \\ &+ c_{13}(e_{xx}e_{zz} + e_{yy}e_{zz}) \\ &+ \tfrac{1}{2}c_{44}(e_{yz}^2 + e_{xz}^2) + \tfrac{1}{2}c_{66}e_{xy}^2 . \end{aligned} \qquad (5)$$

This equation shows that the corresponding elastic constant to the e_{xy} strain component is c_{66}. Thus, only c_{66} will soften as the result of the ultrasonic perturbation when the Fermi level is at the M point and described by Eqs. (1) and (2). This fact explains the reason why, for LSCO, only c_{66} softens while other elastic constants including c_{44} show the normal behavior. Therefore, we conclude that the elastic anomaly of LSCO can be explained consistently using the electronic redistribution mechanism between the strain-split $O(2p)$ levels at the M point.

The MTO phase of LSCO emerges as a result of a second-order phase transition accompanied by cooperative tilting of the CuO_6 octahedra about either the [110] or [1$\bar{1}$0] axis of the HTT phase. Nohara *et al.* measured the elastic properties of the MTO phase using the crystalline coordinates defined in the HTT phase.[3] They found that, among c_{11}, c_{33}, $(c_{11}-c_{12})/2$, c_{66} and c_{44}, only $(c_{11}-c_{12})/2$ exhibited the softening effect above T_C. Below T_C, it showed a hardening trend. Since they used the tetragonal crystalline coordinates to measure the elastic constants of the MTO phase, the above theoretical analysis used for the HTT phase can also be applied to the MTO case. Because the distortion from the tetragonal structure is not large, it is expected that the main character of the wave functions does not change drastically, although the relative positions of the energy levels at various points of the Brillouin zone may shift, thus changing the position of the Fermi levels. For $(c_{11}-c_{12})/2$, the corresponding strain is given by $e_{xx}-e_{yy}$.[3] We see that $e_{xx}-e_{yy}$ does not appear in Eq. (4). Thus, $(c_{11}-c_{12})/2$ is not affected by the M point electronic redistribution mechanism. Therefore, we should look for another degenerate state near the Fermi surface, which is the Γ_5 state according to Ref. 9. At the Γ point, the Bloch wave functions have the simple atomic orbital character, thus making the analysis simple. The direct product table[12] shows that $\Gamma_5 \times \Gamma_5$ contains $\Gamma_1 + \Gamma_3 + \Gamma_4$. Since $e_{xx}-e_{yy}$ belongs to the Γ_3 representation, we observe that the electronic redistribution between the strain-split Γ_5 levels can cause the elastic softening for $(c_{11}-c_{12})/2$. We believe that this fact explains the $(c_{11}-c_{12})/2$ softening observed by Nohara *et al.* Indeed, Nohara *et al.* showed that the formula for the electronic redistribution[4] can satisfactorily fit the observed data in their Fig. 1. It implies that the Fermi level of the superconducting MTO phase LSCO is located at the Γ point whereas the nonsuperconducting HTT phase LSCO has its Fermi level located at the M point. We believe that this Fermi level shift may be directly related to the fact that the disappearance of the orthorhombicity suppresses the superconductivity.

Next, we examine whether the redistribution mechanism between the energy pockets also contribute to the elastic softening of LSCO. For this mechanism to be applicable, it is necessary that the Fermi surface has energy pockets at equivalent $\vec{k}$ points of the Brillouin zone. With the simplified band picture discussed above, LSCO has



(a) (b)

FIG. 1. Illustration of the effect of the strain on the hole pockets at the four M points: (a) the diagonal strain, e_{xy} and (b) the orthorhombic strain, $e_{xx}-e_{yy}$.

four hole pockets at the four M points. When the e_{xy} strain which measures c_{66} is applied, two of the M points will move closer to the zone center whereas the remaining two move away as shown in Fig. 1(a). Thus, we expect that there will be redistribution of electrons between the strain-shifted hole pockets. This electronic redistribution will cause the elastic softening for c_{66}. However, with the e_{yz} and e_{zx} strain which correspond to c_{44}, the M-point energy pockets move approximately in the same fashion. Therefore, c_{44} is not expected to soften. Next, we consider $e_{xx}-e_{yy}$ which corresponds to $(c_{11}-c_{12})/2$. As shown in Fig. 1(b), the four M-point pockets remain equivalent under the tetragonal or orthorhombic strain, and, thus, $(c_{11}-c_{12})/2$ is not affected. Therefore, we observe that the redistribution mechanism between the energy pocket also explains satisfactorily the selective softening of c_{66} in the HTT phase LSCO. Here, we observe that this redistribution scheme between the M-point pockets cannot explain the $(c_{11}-c_{12})/2$ softening of the MTO phase LSCO, because the M-point pockets remain equivalent under the orthorhombic strain as shown in Fig. 1(b). Therefore, it is again necessary to assume that the position of the Fermi surface is shifted from the M point. When the Fermi surface is assumed to be moved to the Γ point, then the analysis becomes identical to the band Jahn-Teller case, since there is no other equivalent point to the Γ point.

From the above analysis, we observe that the two mechanisms can equally account for the elastic softening of LSCO, although the magnitudes of the contributions may differ due to difference in the deformation potential constant. In order to determine the deformation potential constants, more elaborate experiments[6] would be required on LSCO. At present, since the two relaxation channels are equally possible, we conclude that both mechanisms jointly contribute to the elastic softening of LSCO. Since it is not clear at present, whether the dominant itinerant carrier is of p or d-like nature, we believe that it is imperative to make sure whether the softening effect can be explained also by d-like levels. We have carried out the same calculations with the d-type orbitals. However, we found that it was not possible to produce the selective softening reported in Refs. 2 and 3.

The elastic hardening at T_C is not wholly unexpected. Although exact calculation on this effect is not possible due to the lack of knowledge on the exact mechanism of the high-T_C superconductivity, theoretical calculations based on the BCS mechanism have been carried out. The results showed that the elastic hardening was expected at T_C.[13]

In conclusion, we have shown that the elastic softening for c_{66} in the HTT phase LSCO originate from the electronic redistribution between the strain-split $O(2p)$ levels and also between the strain-shifted energy pockets near the M point. The $(c_{11}-c_{12})/2$ softening of the MTO phase LSCO is believed to originate from the electronic redistribution between the strain-split levels at the Γ point. The result suggests that the Fermi level shifts as a result of the structural phase transition and has a close connection with the suppression of the superconductivity with the disappearance of the orthorhombicity.

This work was partially supported by the nondirected research program of the Korea Research Foundation, by KOSEF through the SRC program of SNU-CTP, and by the Korean Ministry of Science and Technology.

[1] J. D. Axe *et al.*, Phys. Rev. Lett. **62**, 2751 (1989); T. Suzuki and T. Fujita, Physica (Amsterdam) **159c**, 111 (1989).

[2] A. Migliori *et al.*, Phys. Rev. Lett. **64**, 2458 (1990); A. Migliori *et al.*, Phys. Rev. B **41**, 2098 (1990).

[3] M. Nohara, T. Suzuki, Y. Maeno, T. Fujita, I. Tanaka, and H. Kojima, Phys. Rev. Lett. **22**, 3447 (1993).

[4] B. Lüthi, J. Magn. Magn. Mater. **52**, 70 (1985).

[5] Y. Cho, K. Nahm, and C. K. Kim, Phys. Status Solidi B **144**, k81 (1987); C. K. Kim, K. Nahm, Y. Cho, H. Fütterer, and J. Pelzl, J. Phys. F **18**, L271 (1988).

[6] M. Niksch, B. Lüthi, and J. Kübler, Z. Phys. B **68**, 291 (1987).

[7] R. W. Keyes, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1967), Vol. 20, p. 37.

[8] J. Labbe and J. Friedel, J. Phys. (Paris) **27**, 153 (1966); **27**, 303 (1966); **27**, 708 (1966); J. Muller, Rep. Prog. Phys. **43**, 641 (1980).

[9] A. K. McMahan, R. M. Martin, and S. Satpathy, Phys. Rev. B **38**, 6650 (1988); A. K. McMahan, J. F. Annett, and R. M. Martin, *ibid.* **42**, 6268 (1990).

[10] P. Entel and J. Zielinski, Phys. Rev. B **42**, 307 (1990).

[11] M. Tinkham, *Group Theory and Quantum Mechanics* (McGraw-Hill, New York, 1964), p. 80.

[12] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (MIT Press, Cambridge, MA, 1963).

[13] M. Kataoka, J. Phys. C **19**, 2939 (1986).