Evidence for polaronic states in metallic $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ and $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ from ultrafast phonon Raman spectroscopy

D. Mihailovic\textsuperscript{a,b,*}, T. Mertelj\textsuperscript{a}, B. Podobnik\textsuperscript{a}, J. Demsar\textsuperscript{a}, P. Canfield\textsuperscript{c}, Z. Fisk\textsuperscript{c}, C. Chen\textsuperscript{b}

\textsuperscript{a}J. Stefan Institute, Jamova 39, 61 111 Ljubljana, Slovenia
\textsuperscript{b}Clarendon Laboratory, University of Oxford, Parks Road, Oxford OX1 3PU, UK.
\textsuperscript{c}Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

Abstract

There is now an abundance of experimental evidence for the existence of polaronic states in insulating precursors of cuprate superconductors. We present new data using a non-equilibrium Raman technique studying the temperature dependence of photoinduced carrier relaxation which points to the existence of polaronic states in the metallic phase, i.e. in the normal state of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ and $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. From the symmetry of the phonons coupled to them, we deduce a predominantly $\Lambda_2$ symmetry for the $\text{Cu}_2\text{O}_2$ plane electronic states in the CT gap. As a result, it is argued that both itinerant and localized (and polaronic) states are present at the same time in the normal phase of high-$T_c$ cuprate superconductors and it is suggested that a number of apparently conflicting experimental results can be understood using this hypothesis.

1. Introduction

Eight years after the discovery of superconductivity in the cuprates, the question of the role of phonons and more generally the electron–phonon interaction (EPI) to the superconductivity mechanism has theoretically still not been satisfactorily answered. There is, however, by now an abundance of experimental evidence, both microscopic and phenomenological, which points to the relevance of lattice dynamics in superconductivity. Indeed phenomenological arguments involving lattice properties give us a clue about the role of the $c$-axis structure related to the origin of different $T_c$s in these materials [1]. In the insulating phase the EPI manifests itself through the polaronic features like the mid-infrared (MIR) absorption, overtones in absorption and Raman spectra amongst others.

*Corresponding author.

On the experimental side, the idea of the existence of localized states in the "metallic" phase of the materials came originally to us from two experiments: the first is the $\epsilon(\omega)$ in the infrared where the polaronic MIR feature is essentially insensitive to the I-M transition [2]. And the second, more recent is from photoconductivity [3], where the data show a gap full of localized states in the range 0–1.8 eV in $\text{YBa}_2\text{Cu}_3\text{O}_{6.9} (\delta \sim 0.6)$. At the I-M transition the change in behaviour is mainly in the DC transport, where there appears to be a percolation or Anderson transition involving only states near $L_s$ while the intra-gap states remain unchanged.

2. Experimental results

The present experiments are designed to probe the way that carriers cascade through the electronic states in the range 0–2.33 eV in the process of energy relaxation after
they are photoexcited by 1.5 ps, 2.33 eV laser pulses. The main idea behind the experiment is that, in the process of energy relaxation, phonons are emitted and by the use of Stokes/anti-Stokes (S/A) phonon Raman spectroscopy the non-equilibrium occupation numbers of these phonons can be measured. The temperature dependence of this phonon shake-off will tell us the nature of the states through which the carriers relax. The details of the experimental technique have been described previously [4]. The results are summarized in Fig. 1 for YBa$_2$Cu$_3$O$_{6.9}$ and La$_{1.85}$Sr$_{0.15}$CuO$_4$ samples. The unshakable experimental observation is that the relaxation shows strong temperature dependence which appears activated with an activation energy $E_a = 30 \sim 80$ meV, depending on the phonon mode being measured and on the material, but not on doping level.

3. Discussion

The carrier relaxation dynamics for intra-band relaxation is well known from semiconductor physics [5]. At short times after photoexcitation ($t \sim 100$ fs) the electronic energy $kT_e$ is essentially the carrier energy relative to the bottom of the band. In the case where the bandwidth $W \gg kT_e$, where $T_e$ is the lattice temperature, the carrier relaxation is essentially temperature independent. However, if $W \sim kT_e$ phonon reabsorption becomes important and in this case we find strongly lattice-temperependent carrier relaxation and phonon shake-off. From the data in Fig. 1, clearly in YBa$_2$Cu$_3$O$_{6.9}$ and La$_{1.85}$Sr$_{0.15}$CuO$_4$ we are in the regime where the bandwidth of the electronic states occupied by relaxing carriers $\sim kT$. These states could be either polaronic (in an extended band or in self-trapped localized states) or localized due to disorder. Although it is reasonable to assume that some states will always be localized by disorder, the non-equilibrium Raman relaxation experiments on insulating YBa$_2$Cu$_3$O$_{6.9}$ YBa$_2$Cu$_3$O$_{6.3}$ and La$_2$CuO$_4$ [6] show the carrier activation energies to be almost independent of doping. This suggests an intrinsic self-trapping mechanism for the localization and certainly a narrow bandwidth, $W \sim kT$.

The electronic structure which rather clearly emerges from the present data together with photoconductivity experiments [3] is shown schematically in Fig. 2. A narrow polaronic band (which is seen as the narrow flat band or Van Hove singularity in photoemission [7]) together with the O$_{2p}$-Cu$_{3d}$ hybridized band are both near $E_F$, with the anisotropy of the polaronic narrow band just below $E_F$ (i.e. its presence along the $Y$ direction) reflecting the symmetry of the phonon modes giving rise

![Fig. 1. The temperature dependence of the non-equilibrium phonon occupation number for the apical O ion, A$_p$-symmetry c-axis vibration arising from carrier relaxation in La$_2$CuO$_4$ and La$_{1.85}$Sr$_{0.15}$CuO$_4$ (top). Similar behaviour is seen in YBa$_2$Cu$_3$O$_{6.9}$ (bottom). The fits to the data suggest an activated $T$-dependence above 100 K. A variable range hopping (VRH) carrier relaxation model can also be fitted to the data (bottom panel). For intra-band relaxation we would expect a temperature-independent shake-off.](image1)

![Fig. 2. A schematic representation of the relaxation process scenario and the electronic structure in the "optimally doped" cuprates. The CT gap is filled with localized states. Polaronic features just below $E_F$, and extended $O_{2p}$ states hybridized with in-plane Cu$_{3d}$ are shown hatched. The excitation is with 2.33 eV photons across the gap.](image2)
to the localization. This picture of the electronic structure is consistent also with the interpretation of the optical conductivity, $\sigma(o)$, with a low-frequency Drude-like component due to the planar band and a MIR polaronic component due to the polarons. These data apparently also further confirm the hypothesis that high-$T_c$ superconductivity is a result of the interplay between the polarons and itinerant carriers in high-$T_c$ cuprates.

Acknowledgements

We wish to acknowledge the following grants: US-Slovene DF-020, the EC ULTRAFAST network and the “Ultrafast superconductors” EC project.

References