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MULTIPHONON HOPPING TRANSPORT IN Bi_2CuO_4 SINGLE CRYSTAL

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The d.c. electrical conductivity along c- and a, b-axes for the Bi_2CuO_4 single crystal has been studied as a function of temperature for the first time. We have observed that the variable range hopping mechanism cannot dominate the charge transport process in Bi_2CuO_4, unlike the rare earth cuprate La_2CuO_4. On the contrary, we have observed that the temperature dependence of the d.c. conductivity σ can be described by $\sigma \sim T^p$, where the exponent p is dependent on measurement axes and on the temperature range. We have interpreted the results in the framework of the multiphonon assisted hopping theory with a weak electron–phonon coupling. © 1998 Elsevier Science Ltd. All rights reserved

Copper oxide compounds with copper ions coordinated with four oxygens in a square-planar configuration have recently been a subject of considerable attention, since this structure is common to the majority of copper oxide based high temperature superconductors. Bi_2CuO_4 is such a square planar compound. Its structure and magnetic properties have been investigated extensively in recent years [1]. This oxide has a tetragonal crystal structure ($c = 5.81$ A and $a = 8.51$ A) with $P4/ncc$ space group. Isolated CuO_4 square planar units are stacked one over the other in a staggered fashion along the c-axis, forming one dimensional chains of copper ions. The copper atoms are not bridged by any intervening oxygen ions, unlike the rare earth oxocuprates (e.g. La_2CuO_4) which have bridging Cu–O–Cu or Cu–O–O–Cu units made up of edge sharing CuO_n units arranged in planar arrays. In the magnetic sense Bi_2CuO_4 is a compensated antiferromagnet with a Neel temperature of ~45 K. The electronic properties of Bi_2CuO_4 have been studied by X-ray photoelectron spectroscopy, X-ray Auger electron spectroscopy, electron energy loss spectroscopy, etc. [2]. These studies reveal that Bi_2CuO_4 is a charge transfer insulator with a forbidden gap of about 2 eV. However, a little information is available on the electrical transport properties of this compound. On the other hand, there is an extensive report on the electrical transport properties of rare earth cuprates such as La_2CuO_4 [3]. The variable range hopping (VRH) mechanism has been observed to dominate the charge transport process in the rare earth cuprates. In this letter, we have investigated the d.c. electrical conductivity of the Bi_2CuO_4 single crystal. We have observed that the electrical conductivity for this rare earth free oxocuprate is nonactivated and cannot be interpreted in terms of the VRH theory unlike rare earth cuprates. On the contrary, we have observed that the conductivity data are proportional to T^p, where the exponent p is dependent on the c- and a, b-axes and also on the temperature range of measurements. We have shown that this behavior of the electrical properties of Bi_2CuO_4 can be interpreted in terms of the multiphonon hopping of charge carriers with a weak electron–phonon coupling.

The Bi_2CuO_4 single crystal used in the present study was grown from the melt by a floating zone technique associated with an image furnace [4]. The d.c. conductivity along the c- and a, b-axes was measured with a Keithley electrometer (model 617) using gold as an electrode material. For measurements at low temperatures the sample cell was inserted in a cryogenic unit, while measurements at high temperatures were taken by placing the sample cell in a furnace. The absence of barrier layers at the contacts was confirmed from the linear I–V characteristics before measurements.

The temperature dependence of the d.c. conductivity measured along c-axis is shown in Fig. 1 as a function of

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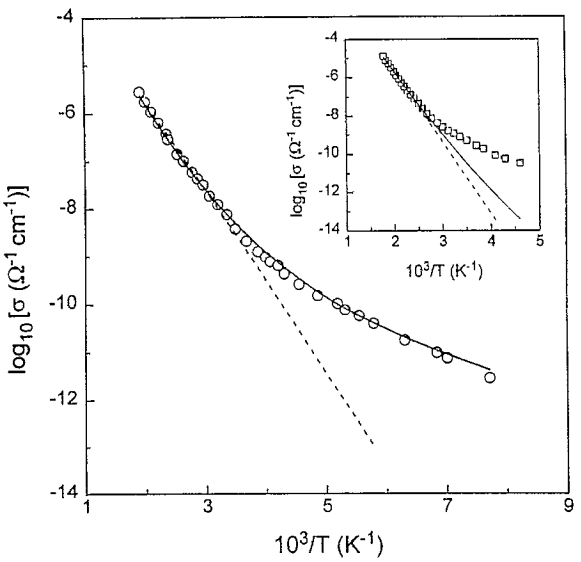

Fig. 1. The logarithmic conductivity shown as a function of $1/T$ for measurements along c-axis. The solid and broken curves are best fits to the Emin's small polaron model for $\nu_0 = 6 \times 10^{-13}\ s^{-1}$ and $10^{-12}\ s^{-1}$, respectively. Inset: the same for measurements along a, b-axes. The solid and broken lines are best fits to the same model for $\nu_0 = 2 \times 10^{-13}\ s^{-1}$ and $10^{-12}\ s^{-1}$, respectively.

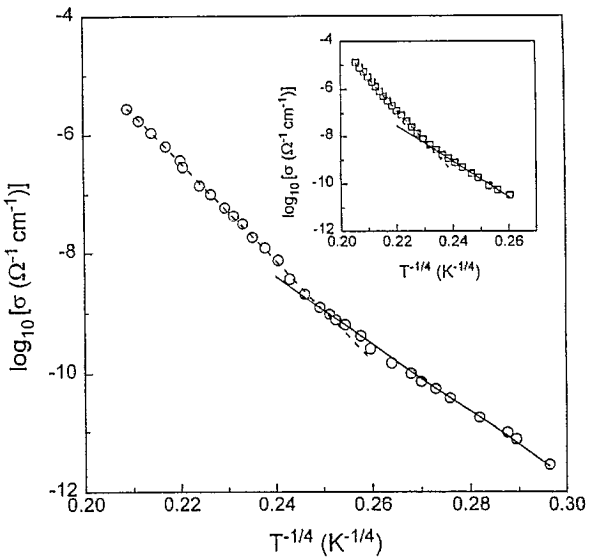

Fig. 2. The logarithmic conductivity shown as a function of $T^{-1/4}$ for measurement along c-axis. The solid and broken lines are least square straight line fits to the data at low and high temperatures, respectively. The inset shows same for measurements along a, b-axes.

reciprocal temperature. The same measured along a, b-axes is also shown in the inset. It is clear that the conductivity is anisotropic being higher along the c-axis than that along the a, b-axes and that the conductivity in all cases is nonactivated. The activation energy decreases continuously with a decrease of temperature. At the highest temperature of measurements an approximate estimate of the activation energy of the order of 0.37 eV was made along c-axis. This value is much less than the energy gap (~2 eV) obtained from the electron spectroscopy [2]. These results suggest that the band conduction is absent and that the conduction occurs by the hopping of charge carriers within localised states [5]. The most accepted charge transport mechanism accounting for a decrease of the activation energy with the decreasing temperature is the so-called VRH theory proposed by Mott and others [6–9]. The VRH theory was employed to interpret adequately the charge transport mechanism in amorphous semiconductors [7] and in insulating rare earth cuprates [3]. According to the VRH theory the d.c. conductivity can be described by $\sigma = \sigma_0 \exp[-(T_0/T)^{\gamma}]$, where $\gamma = 1/4$, $1/3$ and $1/2$ for three, two and one dimensional systems, respectively. We have examined the conductivity data for Bi_2CuO_4 measured along c and a, b axes in terms of the VRH theory for $\gamma = 1/4$, $1/3$ and $1/2$. In all cases the plot of $\log_{10}\sigma$ vs $T^{-\gamma}$ could not be described by a single straight line in the entire temperature range of measurements in disagreement with the VRH theory. However, in all cases the plot could be fitted by two approximate straight lines: one at high temperatures and other at relatively low temperatures. Such a plot is shown in Fig. 2 for $\gamma = 1/4$. It may be mentioned that the VRH theory of Efros and Shklovski [9], which takes the correlation of carriers into account, predicts a $T^{-1/2}$ dependence of the logarithmic conductivity. However, we have not observed such a temperature dependence. Assuming that the Mott's VRH theory [6] is applicable, we have obtained $T_0 = 2.2 \times 10^8$ K and $\sigma_0 = 1.3 \times 10^4\ S\ cm^{-1}$ at low temperatures (solid line in Fig. 2) and $T_0 = 1.3 \times 10^9$ K and $\sigma_0 = 4 \times 10^{11}\ S\ cm^{-1}$ at high temperatures (broken line in Fig. 2) for measurements along c-axis, while for measurements along a, b axes we have obtained $T_0 = 8.2 \times 10^8$ K and $\sigma_0 = 4 \times 10^8\ S\ cm^{-1}$ at low temperatures (solid line in the inset of Fig. 2) and $T_0 = 1.3 \times 10^{10}$ K and $\sigma_0 = 4 \times 10^{23}\ S\ cm^{-1}$ at high temperatures (broken line in the inset of Fig. 2). These values of T_0 are higher by several orders of magnitude than the values of T_0 (10^5–10^6 K) obtained for undoped and doped La_2CuO_4 [3]. Using a value for the localization length $\alpha^{-1} = 10$ Å, values for the density of states at the Fermi level $N(E_F)$ of 2×10^{16}–$5 \times 10^{17}\ eV^{-1}\ cm^{-3}$ were estimated from $N(E_F) = 16\alpha^3/kT_0$ obtained from Mott [6]. These values of $N(E_F)$ are lower than the lower limit (10^{18}–$10^{20}\ eV^{-1}\ cm^{-3}$) observed for amorphous semiconductors [7] and are much lower than that (10^{19}–$10^{20}\ eV^{-1}\ cm^{-3}$) obtained for La_2CuO_4 [3]. The

preexponential factor σ_0 provides unphysically large values (10^{70}–10^{100} eV^{-1} cm^{-3}) for $N(E_F)$. The VRH mechanism thus may not dominate the charge transport process in Bi_2CuO_4, unlike rare earth cuprates such as La_2CuO_4 [3].

It has been suggested [7, 10–13] that when kT is much higher than the energy of phonons, the multiphonon assisted hopping of charge carriers may dominate the charge transport process. For the multiphonon hopping process, there may be two cases depending on the strength of the electron–phonon coupling. We first consider the weak coupling case. The d.c. hopping conductivity at a temperature T can, in general, be written as [11]

$$\sigma = n_c e^2 R^2 \Gamma / 6kT, \tag{1}$$

where n_c is the number density of carriers, R is the hopping distance and Γ is the hopping rate. Different authors [10–13] have calculated the hopping rate for the multiphonon assisted hopping of carriers with a weak electron–phonon coupling that can be written as

$$\Gamma = C \exp(-\gamma p) \exp(-2\alpha R)[kT/h\nu_0]^p, \tag{2}$$

where $C \sim \nu_0$, $p = \Delta/h\nu_0$ and $\gamma = \ln(\Delta/E_M) - 1$. ν_0 is the frequency of the acoustical phonon which is most effectively coupled to localized electrons. Δ is the energy difference between two sites. The parameter E_M or γ is a measure of the electron–phonon coupling strength which should satisfy the condition $E_M/h\nu_0 \ll 1$ for weak electron–phonon coupling [12]. The localization length α^{-1} must be much larger than the lattice constant for weak electron–phonon coupling. Since the large radius localized electrons couple only to long wavelength phonons [10], ν_0 must be smaller than the maximum phonon frequency. The multiphonon process involves absorption and emission of p phonons, so the value of p is an integral number. However, if Δ or ν_0 is distributed around a certain value, p may have a finite distribution and its mean value will be nonintegral. It can be noted that as n_c in equation (1) must be given by $N(E_F)kT$, the d.c. conductivity, σ, obtained from equations (1) and (2) for the weak coupling is proportional to T^p. To examine the d.c. conductivity data for Bi_2CuO_4 presented in Fig. 1 in light of the above theory, we have plotted the conductivity data in Fig. 3 as a function of logarithmic temperature. The data measured along c and a, b-axes can be fitted by two straight lines and thus the d.c. conductivity is proportional to T^p. The values of $p = 8.4$ and 10.9 were estimated at low and high temperatures for measurements along c-axis, while for measurements along a, b-axes, $p = 10.5$ and 16.8 were estimated at low and high temperatures, respectively. These results suggest that the number of phonons involved in the hopping process is higher at high

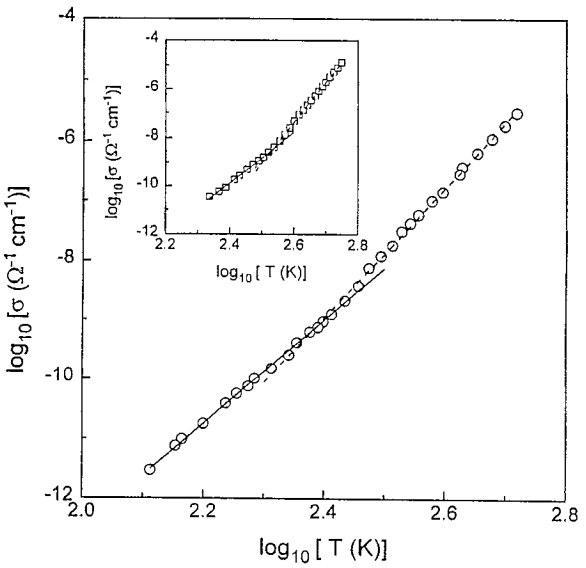

Fig. 3. The logarithmic conductivity shown as a function of logarithmic temperature for measurement along c-axis. The solid and broken lines are least square straight line fits to the data at low and high temperatures, respectively. The inset shows same for measurements along a, b-axes.

temperatures. Also smaller number of phonons is involved for hopping along c-axis than that along a, b-axes. To confirm the validity of the multiphonon hopping theory with a weak electron–phonon coupling for Bi_2CuO_4, the electron–phonon coupling parameter γ was estimated by fitting the experimental data to equations (1) and (2). In the calculation, we have used $n_c \cong 10^{20}$ cm^{-3}, $R = (n_c)^{-1/3} \cong 21.5$ Å and $\nu_0 = 10^{12}$ s^{-1}. The carrier density n_c was determined from the electron spin resonance experiment [14], while the phonon frequency ν_0 was obtained from the neutron scattering experiment [4]. We have obtained from equation (1) the hopping rate Γ of ~ 1–10^2 s^{-1} (depending on temperature) at low temperatures and Γ of $\sim 10^4$–10^5 s^{-1} at higher temperatures. Although values of the hopping rate obtained at high temperatures seem large for the multiphonon hopping with a weak coupling, values of the hopping rate obtained at lower temperatures are reasonable for the weak coupling region [11]. Assuming a reasonable value of $\alpha^{-1} = 20$ Å (larger than the lattice constants), we have obtained values of the coupling parameter γ in the range 3.1–3.5 in the entire temperature range of measurements for hopping along c- and a, b-axes. These estimated values of γ are reasonable for weak coupling regime [7, 12] and yield $E_M/h\nu_0 = 0.06$–0.30 depending on temperature. These values of $E_M/h\nu_0$ clearly satisfy the condition for the weak electron–phonon coupling [12].

On the other hand, for the multiphonon assisted hopping process if the electron–phonon coupling is strong ($E_M/h\nu_0 \gg 1$), small polarons are formed [15]. The small polaron hopping theory [11, 15, 16] can predict a decrease of the activation energy with the decreasing temperature as observed in Fig. 1. We have examined our data of Fig. 1 in terms of the small polaron theory [16] which considers a strong interaction of electrons with both the optical and acoustical phonons. The solid curves in Fig. 1 are the best fits of this theory to the data obtained for an average phonon frequency $\nu_0 = 6 \times 10^{13}\ s^{-1}$ which is higher by an order than that obtained from experiment [4]. For the experimental value of $\nu_0 = 10^{12}\ s^{-1}$, we have obtained broken curves in Fig. 1 as best fits. Obviously, the fits are worst in this case. Thus the small polaron theory is not suitable to describe the electrical conduction in Bi_2CuO_4.

In summary, we have measured the d.c. conductivity of the Bi_2CuO_4 single crystal along *c*- and *a*, *b*-axes and examined the results in the framework of the single phonon assisted hopping (VRH) as well as the multiphonon assisted hopping theories with both strong and weak electron–phonon coupling. We have observed that the multiphonon assisted hopping with a weak electron–phonon coupling is the dominant charge transport mechanism for Bi_2CuO_4.

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