Microwave and millimeter wave spectroscopy in the slightly hole-doped ladders of Sr$_{14}$Cu$_{24}$O$_{41}$

H. Kitano$^1$, R. Inoue$^1$, T. Hanaguri$^2$, A. Maeda$^{1,3}$, N. Motoyama$^2$, M. Takaba$^2$, K. Kojima$^2$, H. Eisaki$^2$ and S. Uchida$^2$

$^1$ Department of Basic Science, The University of Tokyo - Meguro-ku, Tokyo 153-8902, Japan
$^2$ Department of Advanced Materials Science, The University of Tokyo - Bunkyo-ku, Tokyo 113-8656, Japan
$^3$ CREST, Japan Science and Technology Corporation (JST) - Kawaguchi 332-0012, Japan

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Abstract. – We have measured the temperature- and frequency dependence of the microwave and millimeter wave conductivity $\sigma_1(T, \omega)$ along both the ladder ($c$-axis) and the leg ($a$-axis) directions in Sr$_{14}$Cu$_{24}$O$_{41}$. Below a temperature $T^* (\sim 170 \text{ K})$, we observed a stronger frequency dependence in $\sigma_1^c(T, \omega)$ than that in $\sigma_1^a(T, \omega)$, forming a small resonance peak developed between 30 GHz and 100 GHz. We also observed nonlinear dc conduction along the $c$-axis at rather low electric fields below $T^*$. These results suggest some collective excitation contributes to the $c$-axis charge dynamics of the slightly hole-doped ladders of Sr$_{14}$Cu$_{24}$O$_{41}$ below $T^*$.

Following a theoretical predictionenv and the experimental discoveryenv of superconductivity in the two-leg ladder systems, the study of Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ compoundsenv with both Cu$_2$O$_3$ ladders and CuO$_2$ chains has attracted the attention of many physicists. Self-doped holes already exist in this compound, since the average valence of Cu is +2.25. An early optical measurement revealed that the isovalent substitution of Ca for Sr made the self-doped holes redistribute from the CuO$_2$ chains to the Cu$_2$O$_3$ ladders, which effectively enables the hole doping on the two-leg laddersenv. They also suggested that the low-energy charge excitation ($\lesssim 1 \text{ eV}$) was mainly dominated by holes on the Cu$_2$O$_3$ ladders rather than on the CuO$_2$ chains, because the Cu3d-O2p transfer integral of the ladders was larger than that of the chains due to the difference of the angle of the Cu-O-Cu bonds. Thus, systematic study of the low-energy charge dynamics of Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ compounds is expected to reveal rich physics from the holes on the two-leg ladders, which may also provide useful information for understanding high-$T_c$ superconductivity in cuprates.

It is particularly important to study the charge dynamics of the parent material Sr$_{14}$Cu$_{24}$O$_{41}$ (estimated to have 0.07 holes per ladder Cu siteenv), because it provides a starting point to
consider strong correlations of holes doped on the two-leg ladders. This compound shows semiconductor-like behavior in the dc resistivity \( \rho_{dc} \) below room temperature [5]. Although it was already established that a charge-ordered state exists as a dimerization between two \( \text{Cu}^{2+} \) ions in the chain layers below room temperature [6–8], some studies on the low-energy charge dynamics of this compound [5, 7] have suggested the possibility of a charge ordering in the ladder layers below a temperature lower than room temperature. In particular, an NMR/NQR measurement [7] has suggested that the charge dynamics of holes on the ladders which was manifested in the quadrupole relaxation at ladder Cu sites below 150 K can be explained not by a hopping process of localized holes but by a different type of hole motion. Thus, in such a possible charge-ordered state of the slightly hole-doped ladders, some collective charge excitation related to the strong correlated nature of the holes is expected.

In this paper, we describe the charge dynamics along both the ladder (c-axis) and leg (a-axis) directions of \( \text{Sr}_{14}\text{Cu}_{24}\text{O}_{41} \) in the microwave and millimeter wave regions [9]. We observed that a small and narrow conductivity peak developed between 30 GHz and 100 GHz below a temperature \( T^* \approx 170 \text{ K} \) in the c-axis conductivity \( \sigma_c(T, \omega) \), while we did not observe any sign of it in the a-axis conductivity \( \sigma_a(T, \omega) \). The resonance-like conductivity peak in the low-energy region around 50 GHz (\( \sim 0.2 \text{ meV} \)) was observed up to moderately high temperatures (\( \lesssim T^* \approx 10 \text{ meV} \)). Thus, it is difficult to explain this conductivity structure in terms of any single particle excitations. Rather it is reminiscent of a pinned collective mode in the density wave systems such as charge-density waves (CDW) and spin-density waves (SDW), or that in the Wigner crystals. We also measured the c-axis dc conductivity \( \sigma_{dc}^c \) as a function of electric field, and found a clear nonlinearity even at low electric fields below \( T^* \), which is also similar to observations in the sliding CDW and SDW states, or that in the Wigner crystals. These results suggest that some collective excitation contributes to the peak feature in \( \sigma_c^c(\omega) \) and the nonlinear conduction in \( \sigma_{dc}^c(E) \) below \( T^* \).

Measurements were made on 9 pieces of \( \text{Sr}_{14}\text{Cu}_{24}\text{O}_{41} \) single crystals in 3 batches. They were grown by the traveling-solvent-floating-zone (TSFZ) method. Typical transport and magnetic properties of these crystals are described elsewhere [10]. All samples were cut into rectangular shapes with various dimensions [11] and microwave and millimeter wave responses were measured by the standard cavity perturbation technique [12]. To study the frequency dependence of \( \sigma_1 \), we measured the responses at 6 frequencies between 30 GHz and 100 GHz with several Cu (OFC) cylindrical cavity resonators operated in the \( \text{TE}_{011} \) or \( \text{TE}_{013} \) modes. For measurements of the c(a)-axis microwave properties, using a sapphire plate fixed on the endplate of the cavity resonator, the crystal with the longer dimension along the c(a)-axis was placed at a position into the cavity, so that the \( \theta \) component of the microwave electric field \( E_\theta \) was parallel to the c(a)-axis of the crystal [13]. To avoid too large a perturbation by the insertion of the crystal into the cavity resonator, smaller crystals were used at higher frequencies, so that a filling factor \( \gamma \), which was proportional to the volume ratio of the sample to the cavity, was less than \( 1 \times 10^{-4} \). In addition, we confirmed that the experimental results were almost independent of sample size within experimental error, by measuring two or three crystals with different dimensions at each frequency (described below).

As is well known, in the depolarization regime (DPR), the real and imaginary parts of the complex frequency shift \( \Delta f/f - i \Delta (1/2Q) \), (the difference between the presence and absence of a crystal in the cavity), are directly related to the complex dielectric constant \( \epsilon_1 + i\epsilon_2 \), as [12]
Fig. 1 – The temperature dependence of the real and imaginary parts of the complex frequency shift \( \Delta f/f \) (dashed lines) and \( \Delta(1/2Q) \) (solid lines), respectively, along the c-axis (upper panels) and a-axis (lower panels). They are normalized by the geometrical factor \( \gamma/n^2 \).

\[
\begin{align*}
\frac{\Delta f}{f} &= \frac{\gamma}{n^2} \left( \frac{\epsilon_1 - 1 + \frac{1}{n}}{\left( \frac{\epsilon_1 - 1 + \frac{1}{n}}{\epsilon_1} + \epsilon_2^2 \right)} \right) + C, \\
\Delta \left( \frac{1}{2Q} \right) &= \frac{\gamma}{n^2} \frac{\epsilon_2}{\left( \frac{\epsilon_1 - 1 + \frac{1}{n}}{\epsilon_1} + \epsilon_2^2 \right)^2},
\end{align*}
\]

where \( n \) is the depolarization factor of the sample which can be estimated by an ellipsoidal approximation (typically \( \sim 0.1 \) for the measured samples) \([14]\), and \( C \) is an offset of \( \Delta f/f \) which should be determined experimentally.

To obtain the conductivity spectra, \( \sigma_1(\omega) \), from cavity perturbation measurements at several frequencies, it is important to estimate carefully the error involved in the geometrical factor \( \gamma/n^2 \) of Eq. (1). Our method was as follows. The main source of the error is in the estimation of \( n \). In the DPR, \( C \) is given by \( -\gamma/n + \Delta z \), where \( \Delta z \) is a change related to the mechanical reproducibility in opening and closing the cavity for inserting the crystal. We found that \( |\Delta z| \) could be smaller than \( 1 \times 10^{-4} \) in our cavity resonators by improving the mechanical reproducibility. On the other hand, the constant \( C \) could be determined by equating \( \Delta f/f - C \) and \( \Delta(1/2Q) \) at the so-called “depolarization peak (DP)” in the DPR, since \( \epsilon_2 = \epsilon_1 - 1 + 1/n \) at the DP \([12]\). The determined values of \( |C| \) (typically \( \sim 1 \times 10^{-3} \)) were found to be much larger than \( |\Delta z| \). Thus, it was suggested that \( C \) was dominated by \( -\gamma/n \) not by \( \Delta z \). This enables us to estimate \( n \) from \( C \). We estimated \( n \) by this procedure,
and confirmed that it showed a good agreement with the value estimated by an ellipsoidal approximation within the error range of ±20%, which corresponded to an error range of ±40% for estimation of a geometrical factor $\gamma/n^2$ in $\Delta(1/2Q)$. By measuring two or three crystals with different sizes at each frequency, we also found that the magnitude of the DP in $\Delta(1/2Q)$ was almost proportional to $\gamma/n^2$ within the error range of ±50%. Thus, we concluded that the errors involved in $\gamma/n^2$ were less than ±50% in our measurements.

The conductivity as a function of electric field was measured not only by the usual four-probe dc method but also by the pulse method using a boxcar averager and a digital oscilloscope, in order to check the Joule-heating effect. By using rectangular-shaped pulses with a width of 100 µsec and a repetition period of 10 msec, we confirmed that the Joule-heating in the pulse measurement was negligibly small below 300 K.

Figure 1 shows the typical temperature dependence of the real and imaginary parts of the complex frequency shift $|\Delta f/f|$ (dashed lines) and $\Delta(1/2Q)$ (solid lines), respectively, along the $c$-axis (upper panels) and the $a$-axis (lower panels) at several frequencies. All of the data were normalized by $\gamma/n^2$. At all frequencies and along both directions, we observed the DPs in $\Delta(1/2Q)$ at around 200 K [15]. By measuring other compounds such as the undoped compound $La_6Ca_8Cu_{24}O_{41}$ and the Ca substituted compounds $Sr_{14-x}Ca_xCu_{24}O_{41}$ ($x=1,3,12$) at 50 GHz, we found that the DPs in $\Delta(1/2Q)$ were observed only for the compounds with the slightly hole-doped ladders ($x=0,1,3$), and that the peak position was systematically shifted from $\sim-200$ K to $\sim$40 K with increasing $x$ from 0 to 3. These results suggested that the behavior of $\Delta(1/2Q)$ was strongly dependent on the hole concentration on the ladders.

In addition, as shown in Fig. 1, we found two features related to the behavior of $\sigma_c^T$ and $\epsilon_1^T$. One feature is that the magnitude of $\Delta(1/2Q)$ for $E_{\omega} \parallel c$ at 50 GHz below $\sim$150 K was much larger than at other frequencies, suggesting that the behavior of $\sigma_c^T$ was strongly dependent on frequency at around 50 GHz below $\sim$150 K, as shown in Fig. 2. We emphasize that the frequency-dependent $\sigma_c^T$ is intrinsic based on the following reasons. (1) The measurements for $E_{\omega} \parallel c$ on the same crystal showed an anomaly only at $\sim$50 GHz, and this anomaly was independent of the crystal batch. (2) $\Delta(1/2Q)$ for $E_{\omega} \parallel a$ did not show any anomaly at $\sim$50 GHz, suggesting that this anomaly was not attributed to the specific property of the 50 GHz cavity resonator. (3) This anomaly at $\sim$50 GHz along the $c$-axis was common to the compounds with the slightly hole-doped ladders ($x=0,1,3$).

The other feature is that $\Delta f/f$ for $E_{\omega} \parallel c$ slightly decreased with decreasing temperature below $\sim$150 K at all frequencies, while for $E_{\omega} \parallel a$ it did not show any decrease with decreasing temperature. We found that this behavior was related to an anomalous increase of $\epsilon_1^T$ below $\sim$150 K, as will be shown in Fig. 3.

Figures 2 and 3 show the temperature dependence of $\sigma_1(T)$ and $\epsilon_1(T)$ along both directions at several frequencies. They were obtained from $\Delta(1/2Q)$ and $\Delta f/f$ by solving Eq. (1) inversely for $\epsilon_1$ and $\epsilon_2(=4\pi\sigma_1/\omega)$. Because Eq. (1) is valid only for the DPR, it is important to know the region where the concept of the DPR can be applied. In fact, if we apply Eq. (1) to the regions above 200 K (the higher temperature regions above the DP), $\sigma_1^T$ above 200 K is found to show apparent metallic temperature dependence which is definitely different from that of $\sigma_{dc}^T$. We found that this disagreement was due to a breakdown of the application of Eq. (1). Therefore, we only discuss the behavior of $\sigma_1(T)$ and $\epsilon_1(T)$ up to 200 K below.

As shown in Fig. 2, we found that the temperature dependence of $\sigma_1^T(T)$ was strongly frequency-dependent below a temperature $T^{*}(\sim$170 K), while the frequency dependence of $\sigma_1^T$ above $T^*$ and $\sigma_1^T(T)$ below 200 K was negligibly small within the experimental errors. In particular, the magnitude of $\sigma_1^T$ at 50 and 60 GHz was larger than those of $\sigma_1^T$ at 35 and 98 GHz by one order of magnitude at the lowest temperature. This is well above the possible error in the estimation of $\gamma/n^2$. Thus, as was already discussed, it appears that the strongly
frequency-dependent \( \sigma_c^1(T) \) was intrinsic in the \( c \)-axis charge dynamics below \( T^* \), and its frequency dependence implies a resonance-like conductivity peak developed below \( T^* \).

The peculiar feature in the \( c \)-axis charge dynamics below \( T^* \) was also observed in the temperature dependence of \( \epsilon_c^1(T) \), as shown in Fig. 3. As shown in the inset of Fig. 3, \( \epsilon_c^1(T) \) continued to decrease with decreasing temperature. On the other hand, \( \epsilon_c^1(T) \) showed a minimum at \( \sim 150 \text{ K} \) and increased with further decreasing temperature at all frequencies. Comparing with a recent optical study \[17\], this increase in \( \epsilon_c^1(T) \) suggests some softening of a phonon mode which was manifested in the far infrared reflectivity as a sharp edge near \( 38 \text{ cm}^{-1} \) below \( T^* \). On the other hand, the frequency dependence of \( \epsilon_c^1(\omega) \) appeared to be considerably smaller than that of \( \epsilon_c^1(\omega) \) both above and below \( \sim 150 \text{ K} \) within the experimental errors. This is apparently inconsistent with the strongly frequency dependent \( \sigma_c^1(\omega) \). However, since the contribution of the observed peak of \( \sigma_c^1(\omega) \) to \( \epsilon_c^1(\omega) \) was expected to be very small (roughly \( \sim \pm 10 \)), this behavior does not contradict the observed \( \sigma_c^1(\omega) \). In order to compare \( \sigma_c^1(\omega) \) and \( \epsilon_c^1(\omega) \) quantitatively, improvement in the measurement resolution is needed.

The existence of a resonance-like peak in \( \sigma_c^1(\omega) \) was illustrated more clearly in the conductivity spectra at \( 10 \text{ K} \), as shown in Fig. 4. It is evident that a relatively small and narrow conductivity peak was developed in \( \sigma_c^1(\omega) \) between \( 30 \text{ GHz} \) and \( 100 \text{ GHz} \), while the spectrum of \( \sigma_a^1(\omega) \) was almost flat. We found that the spectra of \( \sigma_c^1(\omega) \) could be approximately fit to a usual Lorentzian lineshape, although the peak frequency and the width of the conductivity peak were slightly dependent on the batch of crystals. It is quite important to note that this conductivity peak could be observed in the very low energy region (\( \sim 0.2 \text{ meV} \)) up to moderately high temperatures (\( \lesssim T^*\sim 10 \text{ meV} \)). If this feature of \( \sigma_c^1(\omega) \) in Fig. 4 was attributed to some gap feature in the single particle excitation spectrum, it will be completely broadened and will be no longer observed at \( 10 \text{ K} \) (\( \lesssim 1 \text{ meV} \)) due to thermal fluctuations. In addition, although the inhomogeneity in the crystals may account for the presence of any structures in
Fig. 4 – The conductivity spectra of $\sigma_1^c(\omega)$ for the crystals from 3 different batches (open marks) and $\sigma_1^a(\omega)$ (solid diamonds) at 10 K. Solid curves were obtained by fitting to a Lorentzian. Inset: $\sigma_{dc}$ as a function of electric field at several temperatures. They are normalized by the value in the low-field limit, $\sigma_0$.

$\sigma_1(\omega)$ in this region, it seems to be quite difficult that such an effect accounts for the difference between $\sigma_1^c(\omega)$ and $\sigma_1^a(\omega)$. Thus, the most possible candidate may be a collective excitation similar to a pinned phason mode in the CDW and SDW states for quasi-one dimensional materials [18, 19], or that in the Wigner crystal observed for the two dimensional hole system of GaAs/Al$_{1-x}$Ga$_x$As heterojunction [20]. Furthermore, the possibility of the collective excitation in $\sigma_1^c$ below $T^*$ is also supported by a nonlinear conduction in the electric field dependence of $\sigma_{dc}$, as shown in the inset of Fig. 4. We observed a clear nonlinear conduction at rather low fields below $T^*$. This is also similar to observations in sliding CDW and SDW states [18, 19], or in the Wigner crystal state [20]. The detailed study of the nonlinear conduction in Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ compounds will be discussed in a different paper [21].

Unfortunately, however, we can not specify the origin of the possible collective excitation at present. We only speculate that such collective mode corresponds to the dynamics of a possible charge-ordered state on the ladders. For the density wave systems, it is well known that the pinning frequency $\omega_0$ of the pinned collective mode is related to the electric threshold field for the onset of the nonlinear conduction, $E_0$, by

$$eE_0 \approx m^* \omega_0^2 \lambda,$$

where, $m^*$ is the effective mass. $\lambda$ is the distance necessary to induce translational motion of the collective mode by the electric field. For the present collective mode, our results in Fig. 4 suggested that $\omega_0/2\pi \sim 50$ GHz, and the detailed study of the nonlinear conduction [21] suggested that $E_0$ was presumably between 0.1 and 1 V/cm. Thus, if $\lambda$ is assumed to be similar to the Cu-Cu distance along the c-axis on the ladders ($\sim 3.95$ Å), we can estimate that $m^* \approx m_e$ ($m_e$ is a free electron mass) from Eq. (2), suggesting a possible charge-ordered state without a lattice distortion or with a negligibly small lattice distortion. Since no enhancement in $m^*$ strongly suggests the importance of the electron-electron interaction, it is speculated...
that the strongly correlated nature of doped-holes on the ladders is essential.

On the other hand, we found that the spectral weight (SW) of the observed conductivity peak was significantly small. In fact, by using $n_h \sim 0.07$ as the hole density per ladder-Cu site, the SW determined by a fit to a usual Lorentzian (solid curves in Fig. 4) was found to be smaller by at least six orders of magnitude than the SW expected for the above effective mass ($m^* \approx m$). A similar reduced SW of the collective mode was also reported in the pinned SDW mode in the Bechgaard salts [3], which remains a serious puzzle. Since the electronic correlation is extremely important both in the SDW systems and the present ladder systems, the reduced SW may be a common important issue for the motion of the collective mode in strongly correlated systems.

In conclusion, by detailed investigation of $\sigma_1(T, \omega)$ and $\epsilon_1(T, \omega)$ along both the c- and a-axes, we concluded that some collective excitation probably contributed to the c-axis charge dynamics in the slightly hole-doped ladders of Sr$_{14}$Cu$_{24}$O$_{41}$ below $\sim$170 K. Although we cannot specify the origin of the collective mode at present, we speculate that it is closely related to a possible charge-ordered state of the very small amount of holes doped on ladders, and may be characteristic of strongly correlated materials.

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