Infrared reflectivity of untwinned YBa$_2$(Cu$_{1-x}$Zn$_x$)$_3$O$_{7-\delta}$ single crystals

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The ab-plane reflectivity of untwinned YBa$_2$(Cu$_{1-x}$Zn$_x$)$_3$O$_{7-\delta}$ single crystals is measured between 250 and 20 000 cm^{-1} at room temperature. Through Zn substitution, the optical conductivity along $\mathbf{E}\|b$ shows a broad peak at about 2000 cm^{-1} suggesting localization of the chain band carrier. The conductivity along $\mathbf{E}\|a$ shows no mid-infrared absorption and slightly decreases from the far- to mid-infrared region through Zn substitution. Analysis of the conductivity along $\mathbf{E}\|a$ shows that the main effect of Zn substitution is to increase the impurity scattering rate. A small amount of carrier reduction and suppression of effective mass enhancement at low frequency are also observed. The suppression of the effective mass enhancement is discussed by the antiferromagnetic spin-fluctuation theory of Fermi liquid.

There have been many studies on the effect of Zn substitution on the electronic structure in high-T_c cuprates. Most of these studies use twinned crystals for the measurements, which assume that the substitution changes the electronic structure only in the CuO$_2$ planes, not in the CuO chains. This assumption is based on the many structural studies which conclude that Zn substitutes primarily the plane copper site Cu(2).[1,2] However, the relation between electronic structure and crystal structure has not been clarified yet, and to confirm the assumption, measurements using untwinned crystals are indispensable.

The most prominent change of electronic properties through Zn substitution is the strong suppression of T_c, which has promoted much discussion. Transport and microwave measurements show that an increase in the elastic scattering rate is caused by the substitution.[3-5] T_c reduction can be explained by this increase in scattering if the gap has nodes.[3] This mechanism is also supported by a ^{63}Cu(2) NMR experiment, which shows a very small exchange coupling J_{eff} between the induced local moment and the Cu holes that could not explain the suppression of T_c within Abrikosov-Gorkov pair breaking.[6] On the other hand, Mahajan et $al.$ deduce a large exchange coupling J_{eff} from their ^{89}Y NMR measurement of oxygen-deficient Zn-substituted samples, and suggest that the moment causes a suppression of T_c, which might not require superconductivity with nodes.[7] Ishida et $al.$ find Korringa behavior below T_c for the Zn-substituted samples, which is consistent with d-wave pairing. However, they also find local suppression of the antiferromagnetic spin fluctuation in Cu spins adjacent to Zn impurities, which can be also responsible for the T_c suppression mechanism.[8]

This paper reports measurements of the ab-plane reflectivity of twinned and untwinned YBa$_2$(Cu$_{1-x}$Zn$_x$)$_3$O$_{7-\delta}$ single crystals. Through Zn substitution, the conductivity along $\mathbf{E}\|b$ shows a broad peak at about 2000 cm^{-1}, suggesting localization of the carriers in the chains. For the conductivity along $\mathbf{E}\|a$, Zn substitution increases the impurity scattering rate. From a one-component analysis, suppression of the effective mass

enhancement at low frequency is also observed. This can be related to the suppression of antiferromagnetic spin fluctuations and is discussed according to the antiferromagnetic spin-fluctuation theory of Fermi liquids within a memory function formalism.

The crystals were grown in air in a Pt crucible by self-flux growth, and annealed at 500 °C with flowing oxygen for 100 h. Crystal quality and bulk superconductivity were checked with a dc superconducting quantum interference device (SQUID), a polarized light microscope, and an x-ray precession camera. The Zn content was determined by electron-probe microanalysis (EPMA). Contamination of the crucible material (Pt) is less than 0.7% per copper atom for both Zn undoped and doped crystals. The ab-plane resistivity measurements show that $\rho_{ab}(100$ K$) = 50$ $\mu\Omega$ cm and $T_{c0} = 92.3$ K for $x = 0$ and $\rho_{ab}(100$ K$) = 180$ $\mu\Omega$ cm and $T_{c0} = 53.0$ K for $x = 0.028$ samples. Experimental details have been described in a previous paper.[3] Untwinned crystals up to 1 mm $\times$ 0.6 mm $\times$ 0.05 mm were accidentally obtained in the same crucibles. Since they were grown in the same crucibles, we assumed that the crystals have the same resistive properties as the twinned ones. Room temperature reflectivity was measured in a frequency range between 250 cm^{-1} and 20 000 cm^{-1} using a rapid scan interferometer combined with a microscope with an incident angle of $\theta \approx 15°$.[9] Although the deviation from normal incidence is negligible for unpolarized measurements, it is not negligible for polarized measurements. S-polarized reflectivity was measured and corrected self-consistently using the dielectric function obtained by Kramers-Kronig transformation of the measured reflectivity. The deviation of the polarized reflectivity from the normal incidence was about 0.5-1.0 %.

Figure 1(a) shows the ab-plane reflectivity of twinned YBa$_2$(Cu$_{1-x}$Zn$_x$)$_3$O$_{7-\delta}$ single crystals. The spectra for $x = 0$ agree well with earlier results of YBa$_2$Cu$_3$O$_{7-\delta}$.[10] Although the reflectivity at high frequency does not change through Zn substitution, it reduces below 10 000 cm^{-1}. These changes are different from those in an oxygen-depleted case, and indicate that the electric structure is modified only near the Fermi level. In the oxygen-
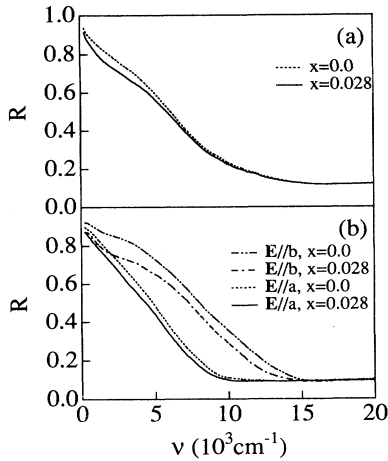
FIG. 1. (a) Reflectivity spectra of twinned $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ single crystals. (b) Reflectivity spectra of untwinned $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ single crystals.

FIG. 2. (a) Optical conductivity of twinned $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ single crystals obtained from the Kramers-Kronig transformation of the reflectivity spectra. (b) Optical conductivity of untwinned $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ single crystals.

depleted case, high-frequency reflectivity is affected due to the appearance of a Cu-O charge transfer gap at 1.7 eV. Reflectivity spectra for the untwinned crystals are shown in Fig. 1(b). The substitution mainly affects reflectivity with $E\|b$. This result suggests that the major part of the change in the optical spectrum is related to chain conductivity.

The optical conductivity of twinned and untwinned crystals is obtained through a Kramers-Kronig transformation. In transforming the spectrum, Hagen-Rubens extrapolation is used for low frequency, and for high frequency, data by Tajima et al.[11] and Zibold et al.[12] are used for twinned and untwinned crystals, respectively. The optical conductivity of twinned crystals is shown in Fig. 2(a). Zn substitution decreases the far-infrared conductivity but increases that in the midinfrared region, indicating the appearance of midinfrared absorption by substitution. This absorption peak is more pronounced in the conductivity of untwinned crystals, which are shown in Fig. 2(b). For $x = 0$, large anisotropy is observed between $\sigma_b(\omega)$ and $\sigma_a(\omega)$, and $\sigma_b(\omega)$ shows no absorption peak which confirms the high quality of the samples.[13] For $x = 0.028$, $\sigma_b(\omega)$ shows a clear peak at about 2000 cm^{-1}, while $\sigma_a(\omega)$ shows no peaks. In general, this anisotropy between $\sigma_b(\omega)$ and $\sigma_a(\omega)$ comes from the conductivity of chains and/or anisotropy of the CuO_2-plane conductivity and/or the coupled system of planes and chains. In the following discussion, we simply assume that the conductivity of chains is dominant among them and the latter effects can be negligible, since the effect of the former seems larger than that of the latter from the crystal structure point of view and there is no way to separate them from this experiment. By this assumption, the absorption peak at about 2000 cm^{-1} is regarded as a chain contribution, which is also observed in low-quality $YBa_2Cu_3O_{7-\delta}$ and in $PrBa_2Cu_3O_7$, and is attributed to the presence of disorder along chains.[13,14] In this case, the origin of disorder may be due to a change of polaronic electron-phonon intercation by Zn substitu-
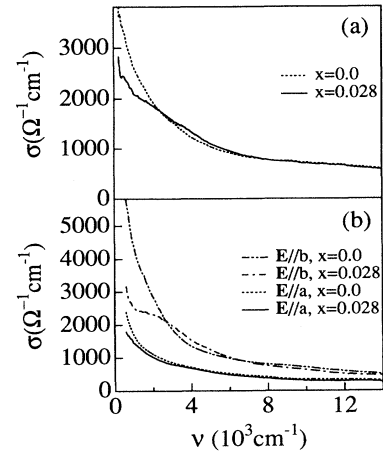
tion at Cu(2)-plane sites, a small amount of Zn substitution at Cu(1)-chain sites, or a small amount of oxygen vacancy in chains. In the first case, chain band carriers are modelately coupled to the Cu(1)-O(4) stretching mode and form polarons.[15] Through Zn substitution at Cu(2)-plane sites, polarons just above the Zn may be strongly influenced by the change of this apical O(4) vibrational mode and may be localized. In the latter two cases, the amount of Zn substitution or oxygen vacancy are very small, since a number of structual and chemical studies conclude that Zn primarily substitutes in the Cu(2)-plane site, and that the oxygen content stays constant through Zn substitution.[1–3] Interestingly, there also remains a Drude contribution in $\sigma_b(\omega)$-$\sigma_a(\omega)$. Since the above disorder may electrically cut the CuO chain into isolated segments and the Drude conductivity needs infinite chain length,[15] this Drude contribution indicates that the carriers in one chain segment can move to another chain segment by way of the CuO_2 planes. This suggests that large coupling exists between chains and planes in this system.

In Fig. 2(b), $\sigma_a(\omega)$ decreases slightly from the far- to midinfrared region through Zn substitution. This means carriers in the planes are reduced by a small amount. However, the amount of carrier reduction is smaller than that of the oxygen-deficient sample with the same T_c. By calculating the integrated spectral weight up to 5000 cm^{-1} and assuming bare electron mass, the carrier concentration is estimated to be 0.24 for $x = 0$ and 0.21 for $x = 0.028$ carriers per one CuO_2 unit, which is larger than 0.15 carriers for the oxygen-deficient case $(T_c = 56$ K).[16] So the mechanism of T_c reduction through Zn substitution cannot be explained by the reduction of carriers.

To understand the effect of Zn substitution on the CuO_2-plane conductivity, we analyzed the $\sigma_a(\omega)$ by the generalized Drude model. There has been much discussion over the one-component and the two-component pictures to describe the optical conductivity of high-T_c

cuprates.[10] Here we use the one-component model because $\sigma_a(\omega)$ decreases both in the far- and midinfrared regions through Zn substitution and there is no clear way to divide it into two components for our room temperature spectra. Two-component analysis by subtracting the remaining conductivity below T_c is the subject for a future study. Figure 3 shows the renormalized scattering rate and effective mass enhancement obtained from the analysis.[17] For $x = 0$, the renormalized scattering rate increases with frequency in nearly linear fashion, which has been pointed out previously.[18,19] Through Zn substitution, it increases constantly for about 650 cm^{-1} without changing slope, and effective mass enhancement suppresses especially at low frequency. These changes are quite different from the changes in the carrier reduction case: From $YBa_2Cu_3O_7$ to $YBa_2Cu_3O_{6.6}$, the slope of $\tau^*(\omega)^{-1}$ increases with frequency without changing its intercept and the increment in $m^*(\omega)$ become larger,[16,19] suggesting an increase in the coupling between the carriers and whatever excitation which dominates the inelastic scattering of carriers. For Zn substitution, a constant increment in $\tau^*(\omega)^{-1}$ suggests an increase in elastic scattering. Assuming that $m^*(0) = 2$ and $\omega_p = 18\,500$ cm^{-1}, the increase in $\tau^*(\omega)^{-1}$ at about 650 cm^{-1} corresponds to an increase in residual resistivity of about 200 $\mu\Omega$ cm, which agrees approximately with the result of dc resistivity measurements. An increase in the scattering rate through Zn substitution is also observed from a far-infrared reflectivity measurement of twinned films by Drude fitting.[20]

Although the main effect of Zn substitution is to increase the impurity scattering rate, it cannot explain the small suppression of mass enhancement at low frequency. It suggests some kind of modification in the coupling between carrier and the excitation and/or in the excitation spectrum itself. To explain this suppression, we calculate the optical conductivity using the antiferromagnetic spin fluctuation model based on the Fermi liquid description.[21,22] In this theory, the non-Drude optical conductivity is explained by the inelastic scattering of the carriers by spin fluctuations and is described by the generalized Drude model within the memory function formula.[21,23] Monthoux and Pines explained the T_c-reduction mechanism by Zn substitution as the destruction of antiferromagnetic correlation around ξ_{Zn} near the

Zn atom.[22] Neglecting the cross term between Zn impurities, which may be valid for the dilute limit, the Zn substitution effect is approximately incorporated in terms of the dynamic spin susceptibility as

$$\chi_{Zn}(q, \omega) = \exp(-4\pi\xi_{Zn}^2 n_{Zn})\chi(q, \omega),$$

where n_{Zn} is the in-plane Zn concentration. The results of the calculation using the generalized Drude formula are shown in Fig. 4. For the calculation, we use the spin-fluctuation parameters in Ref. 22, and assume that $\xi_{Zn} = 0.5\xi$.[24] It shows that the suppression of $m^*(\omega)$ is explained qualitatively by the theory. However, the slope of $\tau^*(\omega)^{-1}$ is also suppressed through Zn substitution. If Zn also acts as an impurity and the effect is additive, $\tau^*(\omega)^{-1}$ increases with a constant amount, but the reduction of slope remains, which is also shown in Fig. 4. At this point, the theory cannot explain our experimental results well within the memory function formula and weak-coupling regime.

There seem to be some candidates to explain the discrepancy. In the calculation, Zn substitution simply reduces the carrier–spin-fluctuation coupling constant without changing its momentum and frequency dependence. However, the substitution may also change the momentum and frequency dependence of $\chi(q, \omega)$ when we use the exact formula for the substitution effect. This modification of $\chi(q, \omega)$ also changes the frequency dependence of optical conductivity, and may explain the discrepancy. The above calculation assumes a cylindrical Fermi surface and does not include a vertex correction. Since the latter effect changes the frequency dependence of optical conductivity,[22] strong-coupling calculations including these effects might explain the discrepancy. If we use the two-component picture instead of the one-component picture, we have to subtract the midinfrared absorption for the analysis. In this case, $m^*(\omega)$ and $\tau^*(\omega)^{-1}$ are lower and may give quantitatively better fitting; however, we also have to explain the origin of the midinfrared absorption which reduces through Zn substitution. On the other hand, the non-Fermi-liquid approach may provide another explanation to this problem. However, to our knowledge, there has been no prediction for optical conductivity through Zn substitution from this approach.

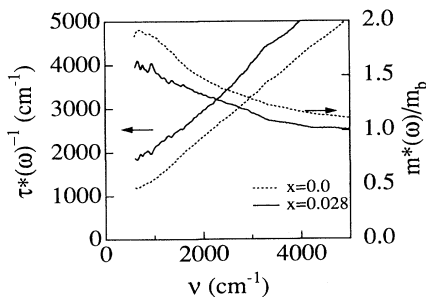In conclusion, we have measured the reflectivity of

FIG. 3. The renormalized scattering rate and the effective mass enhancement obtained from the a-axis spectra of $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$.
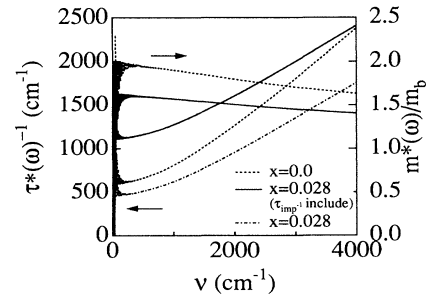
FIG. 4. The renormalized scattering rate and the effective mass enhancement calculated by the antiferromagnetic spin-fluctuation theory of Fermi liquids.

twinned and untwinned $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ single crystals. Through Zn substitution, $\sigma_b(\omega)$ shows a broad peak at 2000 cm^{-1}, which suggests localization of carriers in the chains. The one-component analysis of $\sigma_a(\omega)$ shows that the main effect of Zn substitution is to increase the impurity scattering rate. It also shows that the carrier is reduced by a small amount and enhancement of $m^*(\omega)$ at low frequency is suppressed. Using the antifer-romagnetic spin-fluctuation theory of Fermi liquids, the suppression of $m^*(\omega)$ was explained by the Zn-induced destruction of the magnetic correlation. However, it could not explain the constant increase in $\tau^*(\omega)^{-1}$. Some explanations for this discrepancy are also discussed.

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