ab-plane optical properties of Fe-substituted $Bi_2Sr_2CaCu_2O_{8+\delta}$

M. E. Ziaei,[1] N. L. Wang,[1,2] B. P. Clayman,[1] and G. D. Gu[3]
[1]*Department of Physics, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6*
[2]*Institute of Physics, Chinese Academy of Sciences, P.O. Box 2711, Beijing 100080, People's Republic of China*
[3]*School of Physics, University of New South Wales, Sydney 2052, Australia*

(Received 5 April 2000)

The *ab*-plane reflectance of Fe-substituted $Bi_2Sr_2Ca(Cu_{1-x}Fe_x)_2O_{8+\delta}$ single crystals grown by a floating method was measured above and below T_c and optical conductivity was calculated using a Kramers-Kronig analysis. Detailed studies of the optical parameters of the sample with $x=0.015$ at temperatures 10, 50, 70, 85, 110, 200, and 300 K reveal that the fraction of normal and condensed carriers decrease with increased Fe doping. Furthermore, they show that the decrease in condensed carrier density is a direct result of the reduction of the density of the normal carriers.

The study of the effect of impurities on magneto/optical properties of high-T_c superconductors is an active field of research. It leads, for example, to information about the symmetry of the superconducting order parameter,[1,2] the distinction between *d*- and *s*-wave models,[2–4] pair breaking effects,[5] and plasma frequency and carrier damping.[6]

Most of the studies thus far have been concentrated on Zn and Ni impurities[5,7,8] in $YBa_2Cu_3O_7$ with completely different results. For example while both Ni and Zn preserve the linear temperature dependence of resistivity in normal state,[6,8,9], Zn reduces T_c about three times more quickly than Ni.[10] Doping dependence of the Y substitution in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ (2212:Y) has also been studied.[11]

An early study of the effect of substitution of $3d$ metals for Cu in high-temperature superconductor $Bi_2(Sr_{0.6}Ca_{0.4})_3Cu_2O_y$ was carried out by Maeda *et al.*[12] by measuring lattice constants, dc resistivity, Hall effect, and magnetic susceptibilities in normal and superconducting phases. For all kinds of impuritis, including nonmagnetic Zn, the superconducting transition temperature T_c was found to decrease with increasing impurity concentration. They concluded that the decrease of T_c caused by the doping of $3d$ impurities was a result of the pair breaking effect due to these magnetic and nonmagnetic impurities.

In this paper, we report on the effects of Fe doping on the optical properties of $Bi_2Sr_2Ca(Cu_{1-x}Fe_x)_2O_{8+\delta}$ (2212:Fe) single crystals for temperatures of 10–295 K. The 2212:Fe crystals were grown by the floating-zone method.[13,14] An infrared radiation furnace was used[14,15] to grow single crystals

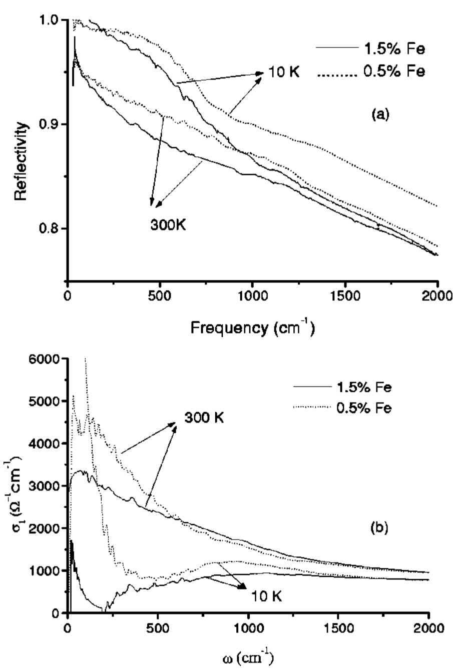

FIG. 1. (a) The measured *ab*-plane reflectivity for different doping levels at 10 and 300 K. (b) The calculated real part of conductivity for the same samples and temperatures.

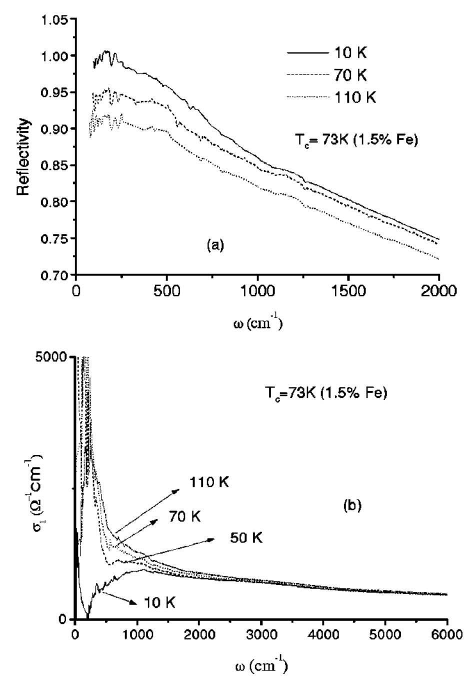

FIG. 2. (a) The measured *ab*-plane reflectivity for $x=0.015$ Fe doping for temperatures of 10, 70, and 110 K. (b) The calculated real part of conductivity for the same sample and the same temperatures. Note that the reflectivity and conductivity data for $T=85$ K are similar to those of 110 K and have not been included in the figure for clarity.

0163-1829/2000/62(14)/9818(4)/$15.00 PRB 62

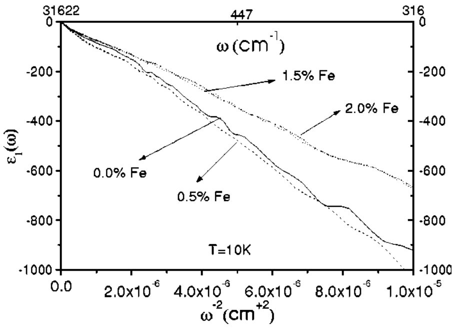

FIG. 3. Graphs of $\epsilon_1(\omega)$ versus ω^{-2} for a temperature of 10 K, for samples with x=0.0, 0.005, 0.015, and 0.02 for $\omega > 316\ \mathrm{cm}^{-1}$.

of 2212:Fe. Nominal Fe levels of 0.005, 0.015, and 0.02 were used. For Fe levels of equal or smaller than 0.01, all Fe actually enters into 2212 crystal as substitution. However, for x greater than 0.01, some Fe segregates into secondary phases in the grain cellular boundaries.[14] There is little difference in the photograph of the Laue x-ray backscattering and the transmission between pure and Fe-substituted single crystals. This indicates that the crystal structure does not change much upon substitution of Fe in the Cu site.[14] The superconducting transition temperature decreases with an increase of Fe content progressively from 91 K (for $x=0$) to 83 K (for $x=0.005$), 73 K (for $x=0.015$), and 69 K (for $x=0.020$), respectively.[15]

Freshly cleaved crystals of about $3\times2\times0.5\ \mathrm{mm}^3$ were mounted on optically black cones, and the *ab* reflectance was measured in the frequency range of 50–9000 cm^{-1} at different temperatures on a Bruker IFS113 spectrometer using an *in situ* overcoating technique.[16] The temperature was controlled by a LakeShore 330 autotuning controller. The measured reflectance was extended to high frequency (40 eV) using data from Terasaki *et al.*[17] The real part of the conductivity and other optical parameters such as dielectric function ϵ_1 (ω) were calculated from these extended data using Kramers-Kronig analysis and extrapolation techniques explained elsewhere.[11]

The measured *ab*-plane reflectivity and calculated real part of the conductivity for $x=0.005$ and $x=0.015$, are shown in Fig. 1. The reflectivities and conductivities for $x=0.0$ and $x=0.02$ samples are similar to those of $x=0.005$ and $x=0.015$, respectively, and have not been included in the figure for reasons of clarity.

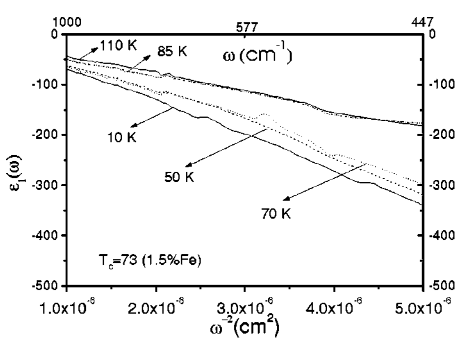

FIG. 4. Graphs of $\epsilon_1(\omega)$ versus ω^{-2} for $x=0.015$ Fe-doped sample ($T_c=73$ K) for temperatures of 10, 50, 70, 85, and 110 K for $\omega > 447\ \mathrm{cm}^{-1}$.

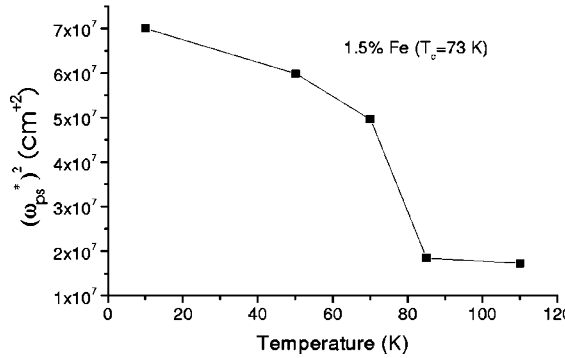

FIG. 5. Slope of $\epsilon_1(\omega)$ versus ω^{-2} for $x=0.015$ Fe-doped sample ($T_c=73$ K) for temperatures of 10, 50, 70, 85, and 110 K.

A summary of the preliminary measurements have been presented earlier and show a reduction of low-frequency spectral weight in the normal state and a suppression of the strength of superconductivity condensate (see 6th International Conference on Materials and Mechanisms of Superconductivity and High-Temperature Superconductors. Proceedings of M2S-HTSC-VI 2000 to be published in Physica C).

To obtain more insight about pair breaking effects of Fe doping, we made a detailed temperature dependence study of one of the samples ($x=0.015$, $T_c=73$ K) at temperatures of 10, 50, 70, 85, 110, 200, and 300 K. Figure 2 shows the reflectance and real part of the conductivity for this sample. For reasons of clarity, not all the temperatures have been included in the figure.

The plots of $\epsilon_1(\omega)$ for different samples show a linear ω^{-2} dependence at $T \ll T_c$. This can be seen in Fig. 3 for a temperature of 10 K and $\omega > 316\ \mathrm{cm}^{-1}$. In Fig. 4, a plot of ϵ_1 versus ω^{-2} for $x=0.015$ and for temperatures of 10, 50, 70, 85, and 110 K for $\omega > 450\ \mathrm{cm}^{-1}$ is shown. The linear behavior holds even for temperatures above T_c. This is usually the case[18] when the scattering rate $\tau^{-1} \ll \omega$. Then slope of ϵ_1 versus ω^{-2} gives $(\omega_{PD})^2$ (ω_{PD} is Drude plasma frequency) which in turn is proportional to the normal carrier density. Thus a study of this slope for different samples may be used to investigate the effect of impurity doping on the carrier concentration.

Before doing this, however, it is worthwhile to consider the slope of ϵ_1 versus ω^{-2} for $x=0.015$ as a function of temperature in more detail. Figure 5 shows a plot of this slope for temperatures of 10, 50, 70, 85, and 110 K. From

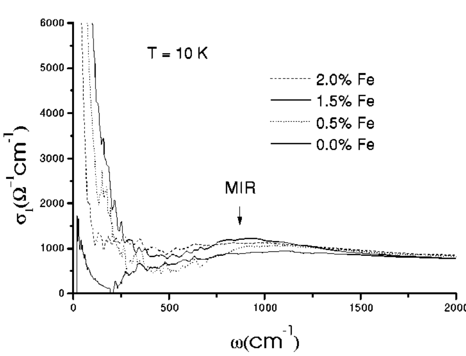

FIG. 6. The calculated real part of conductivity at 10 K for several Fe-doping levels.

TABLE I. Fractions of normal and condensed carriers for different Fe-doping levels in $Bi_2Sr_2CaCu_2O_{8+\delta}$.

T_c(K)	91	83	73	69
$n_n(x)/n_n(0)$	1.0	0.93	0.64	0.63
$n_s^*(x)/n_s^*(0)$	1.0	0.90	0.63	0.60

this figure, we note that for temperature range of 85–110 K, the change of slope is very small, which may be associated with a small change of scattering rate in normal state. On the other hand, the slope changes sharply in 70–85-K region. We believe that this sharp change in slope is closely related to the condensation of normal carriers into superconducting state. As Fig. 5 indicates, the bulk of the process of transition from the normal state into the superconducting state takes place in the temperature range of $T_c \pm 10$ K. On decreasing temperature further, below T_c, the change of the $\epsilon_1 - \omega^{-2}$ slope becomes more gradual and is probably associated with change of scattering rate, effective mass, and further condensation.

The plot of ϵ_1 versus ω^{-2} includes contributions from Drude carriers and excitations of bound electronic states in the mid-infrared (MIR) region. While the Drude component is temperature dependent, the MIR part consists of a weak broad band and is essentially temperature independent. For this reason, it is expected that the temperature behavior of the slope in Fig. 5 will be mainly determined by the Drude-like carriers. In particular, it is interesting to note that if the slope of ϵ_1 versus ω^{-2} at 85 K (i.e., 17.5×10^6 cm^{-2}) and 70 K (i.e., 50×10^6 cm^{-2}) are associated with the normal and the condensed carrier densities respectively, then the slope at 10 K (i.e., 70×10^6 cm^{-2}) may be expressed as

$$(\text{slope})_{10\text{K}} = (\text{slope})_{70\text{K}} + (\text{slope})_{85\text{K}} \tag{1}$$

from which, using the terminology of Ref. 18, we may conclude that $(\text{slope})_{10\text{K}}$, $(\text{slope})_{70\text{K}}$, and $(\text{slope})_{85\text{K}}$ are reasonable representations of $(\omega_{ps}^*)^2$, $(\omega_{ps})^2$, and $(\omega_{pn})^2$, respectively. Using the two-fluid model,[19] $(\omega_{ps})^2$ and $(\omega_{pn})^2$ are proportional to the densities of superconducting and normal carriers, respectively. $(\omega_{ps}^*)^2$ represents contributions from superconducting carriers as well as residual components. However, as mentioned earlier, the MIR effect is temperature independent and thus will not significantly infulence our conclusions.

The association of the slope at 70 K with the condensed carrier density is consistent with the idea that at temperatures close to T_c, (say 70 K in our case), the optical estimates for the density of condensate are accurate.[18] As the temperature is lowered further below T_c, (say 10 K in our case), then

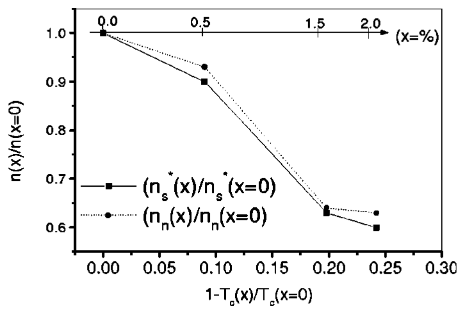

FIG. 7. Ratios of normal and condensed carrier densities of doped samples with respect to the pure sample.

because of the residual component, optical results would be an overestimate[18] and in our notation is represented by $(\omega_{ps}^*)^2$. The above data for $x=0.015$ doping level show that at 10 K, about 75% of the normal carriers have condensed and about 25% remains.

In materials under study, the MIR absorption is weak and cannot be unambiguously resolved.[6] Our data do not show appreciable MIR changes due to Fe substitution as can be seen in Fig. 6. Therefore, within the limits of our experiments, and assuming that Eq. (1) is valid for the other Fe-doping levels too, and neglecting variations of effective mass and scattering rates for different doping levels, we find the ratios of $[n_n(x)/n_n(0)]$ and $[n_s^*(x)/n_s^*(0)]$ in Table I, where $n_n(x)$ and $n_s^*(x)$ are densities of normal and superconducting carriers, respectively.

These ratios are plotted in Fig. 7 as a function of $1-[T_c(x)/T_c(0)]$. As the doping level is increased, both normal and condensed carrier densities are suppressed. This is consistent with Fig. 1 where, by increasing the Fe substitution, the area under $\sigma_1(\omega)$ decreases in the normal state. At 10 K, Fig. 1 also shows that by adding more Fe, the missing area in $\sigma_1(\omega)$ is reduced, which implies a reduction of n_s^*. It is interesting to note that in Fig. 7, variation of n_s^* and n_n are very similar. In other words, it seems that the change of n_s^* is a direct result of change of n_n.

In conclusion, doping of Fe in $Bi_2Sr_2CaCu_2O_{8+\delta}$ samples reduces the density of free carriers in normal state which in turn suppresses superconductivity. This reduction and suppression is increased by increasing the doping level from 0 up to $x=0.01$. However, above $x=0.01$, the effect is more gradual which may be attributed to the fact that for x bigger than 0.01 as mentioned earlier, some of Fe enters into secondary phases in the grain boundaries.

This work was supported in part by Natural Sciences and Engineering Research Council of Canada (NSERC), Simon Fraser University (SFU), and Northern Lights College (NLC).

[1] C. Bernhard, J.L. Tallon, C. Bucci, R. De Renzi, G. Guidi, G.V.M. Williams, and Ch. Niedermayer, Phys. Rev. Lett. **77**, 2304 (1996).
[2] L.S. Borkowski and P.J. Hirschfeld, Phys. Rev. B **49**, 15 404 (1994).
[3] J.P. Carbotte, C. Jiang, D.N. Basov, and T. Timusk, Phys. Rev. B **51**, 11 798 (1995).
[4] Eric R. Ulm, Jin-Tae Kim, Thomas R. Lemberger, S.R. Foltyn, and X. Wu, Phys. Rev. B **51**, 9193 (1995).
[5] N.L. Wang, S. Tajima, A.I. Rykov, and K. Tomimoto, Phys. Rev. B **57**, R11 081 (1998).
[6] N.L. Wang, A.W. McConnell, and B.P. Clayman, Phys. Rev. B

60, 14 883 (1999).
[7] C.C. Homes, D.A. Bonn, Ruixing Liang, W.N. Hardy, D.N. Basov, T. Timusk, and B.P. Clayman, Phys. Rev. B **60**, 9782 (1999).
[8] D.A. Bonn, S. Kamal, Kuan Zhang, Ruixing Liang, D.J. Baar, E. Klein, and W.N. Hardy, Phys. Rev. B **50**, 4051 (1994).
[9] Michael J. Sumner, Jin-Tae Kim, and Thomas R. Lemberger, Phys. Rev. B **47**, 12 248 (1993).
[10] B. Jayaram *et al.*, Phys. Rev. B **38**, R2903 (1988).
[11] N.L. Wang, A.W. McConnell, B.P. Clayman, and G.D. Gu, Phys. Rev. B **59**, 576 (1999).
[12] A. Maeda, T. Yabe, S. Takebayashi, M. Hase, and K. Uchinokura, Phys. Rev. B **41**, 4112 (1990).
[13] G.D. Gu, T. Egi, N. Koshizuka, P.A. Miles, G.J. Russel, and S.J. Kennedy, Physica C **263**, 180 (1996).
[14] G.D. Gu, K. Takamuku, N. Koshizuku, and S. Tanaka, J. Cryst. Growth **137**, 472 (1994).
[15] G.D. Gu, G.J. Russell, and N. Koshizuku, Physica C **282-287**, 2107 (1997).
[16] C.C. Homes, M. Reedyk, D.A. Crandles, and T. Timusk, Appl. Opt. **32**, 2976 (1993).
[17] I. Terasaki, T. Nakahashi, S. Takebayashi, A. Maeda, and K. Uchinokura, Physica C **165**, 152 (1990).
[18] C.C. Homes, S. Kamal, D.A. Bonn, W.N. Hardy, and B.P. Clayman, Physica C **296**, 230 (1998).
[19] C.J. Gorter and H.B.G. Casimir, Z. Phys. **35**, 963 (1943).