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Infrared study of relevance of Nd_2CuO_4 structure to superconductivity of La-Sr-Cu-O system

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A comparative study of the infrared spectra of $Nd_2Cu_{1-x}Ag_xO_4$ and $La_{1.8}Sr_{0.2}Cu_{1-x}Ag_xO_4$ is reported. It is shown that the appearance of an absorption peak at ~680 cm^{-1} is due to local distortions around the Ag impurities, and the appearance of this peak need not imply a structural transformation from Nd_2CuO_4 type of K_2NiF_4 type. It is shown that Nd_2CuO_4 structure is not important for the superconductivity of La-Sr-Cu-O system. © *1999 Kluwer Academic Publishers*

1. Introduction

After the exciting discovery of superconductivity in $La_{1.8}Ba_{0.2}CuO_4$ by Bednorz and Muller [1], there has been great interest in oxide superconductors both from applied as well as basic points of view. Although there are now several different superconducting oxide systems known, an understanding is still lacking due to conflicting experimental evidences. Infrared reflectance and transmittance experiments [2–4] have shown energy gaps in the range $2\Delta/k_BT_c \sim 1.3$–2.7 well below the BCS prediction of $2\Delta/k_BT_c = 3.53$. Tunneling measurements [5–8] have shown gaps in the range $2\Delta/k_BT_c \sim 3.5$–6, at least as large as the BCS prediction. No isotope shift has been observed [9] in $YBa_2Cu_3O_7$, while very small shift has been observed in La-Sr-Cu-O system [10]. These facts suggest that superconductivity of these systems may not be of the conventional BCS type. The superconductivity of Y-Ba-Cu-O and La-Sr-Cu-O systems has been related to the antiferromagnetism of the parent compounds [11–13]. We may note, however, that all these systems contain planes of Cu-O to which the superconductivity seems to be connected. In the present context, it becomes important to investigate the oxide superconductors using various techniques that can probe the electronic system and the lattice and their interaction.

Shortly after the discovery of La-Sr-Cu-O system, Stavola *et al.* [14] reported an interesting result from infrared absorption measurements on $La_{2-x}Sr_xCuO_4$. Of the two strong absorption peaks at $\nu_1 = 677$ cm^{-1} and $\nu_2 = 517$ cm^{-1}, the first one gradually decreases in intensity and finally disappears at $x = 0.15$ which is found to be the optimum concentration for the occurrence of superconductivity. Ohbayashi *et al.* [15] have compared the IR spectra of $La_{1.8}Ba_{0.2}CuO_4$ to that of tetragonal (T_t phase) La_2CuO_4 and tetragonal Nd_2CuO_4 (T_x phase) and they conclude that $La_{1.8}Ba_{0.2}CuO_4$ has Nd_2CuO_4 type structure and not K_2NiF_4 type. They go further to say that the Nd_2CuO_4 structure of $La_{1.8}Ba_{0.2}CuO_4$ is important for the superconductivity of this compound. It is natural that their arguments must also apply to $La_{1.8}Ba_{0.2}CuO_4$ as well, since the IR spectra are essentially similar. In this paper, through a comparative study of Ag substituted $La_{1.8}Ba_{0.2}CuO_4$ and Nd_2CuO_4, we show that the above conclusion of Ohbayashi *et al.* is not valid. Our data shows that $La_{1.8}Ba_{0.2}CuO_4$ does not necessarily have Nd_2CuO_4 structure, and even if it does, the structure is not important for superconductivity of the La-Sr-Cu-O system. The features of the IR spectra may be explained on the basis of local distortions produced around the Ag impurities.

2. Experimental

The samples of $Nd_2Cu_{1-x}Ag_xO_4$ ($x = 0.05$, 0.1) were prepared by mixing Nd_2O_3, CuO and Ag_2O in stoichiometric proportions, calcining them at 700 °C for 6 h and then at 1000 °C for 12 h. Afterwards they were pressed into pellets and heated for 4 h at 1050 °C. From X-ray diffraction the samples were found to be single phase with Nd_2CuO_4 structure. The lattice parameters are found to be $a = 3.943$ Å and $c = 12.154$ Å for $x = 0.05$ and $a = 3.945$ Å and $c = 12.157$ Å for $x = 0.1$ samples. Infrared spectra were recorded in KBr matrix using a commercial cw IR spectrometer. The samples for IR were prepared by mixing 0.1 wt % of the sample with KBr and grinding and pressing into pellets.

3. Results and discussion

The IR study of $La_{1-x}Sr_xCuO_4$ system by Stavola *et al.* reveals that the ν_1 line of La_2CuO_4 gradually decreases in intensity and finally disappears at $x = 0.15$. This concentration also happens to be the optimum for the occurance of superconductivity. Fig. 1 shows the IR spectra of $La_{1.8}Sr_{0.2}Cu_{1-x}Ag_xO_4$ compounds. We find that

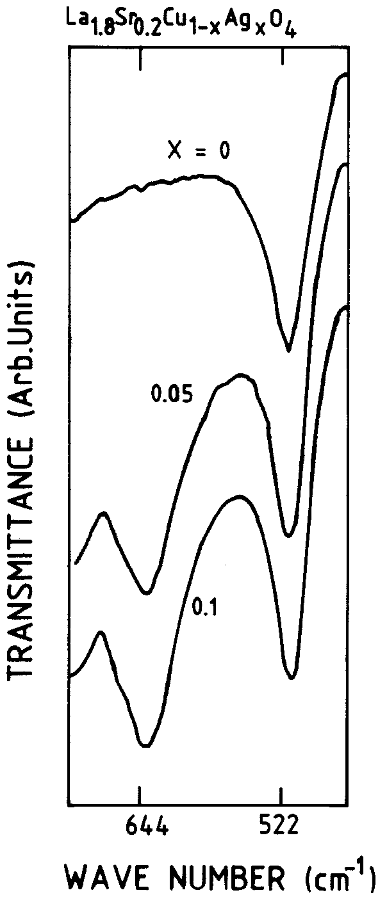

Figure 1 Infrared spectra of $La_{1.8}Sr_{0.2}Cu_{1-x}Ag_xO_4$ compounds.

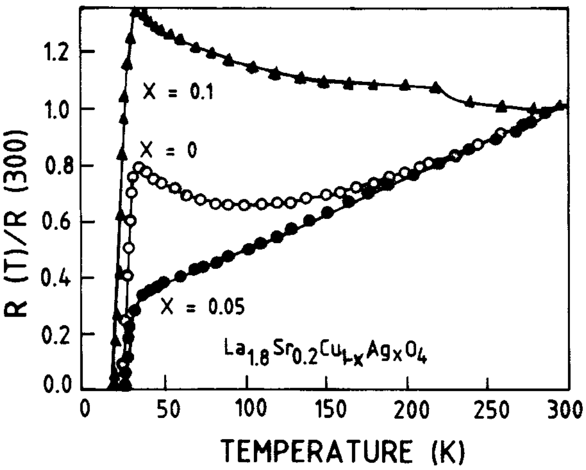

Figure 2 Electrical resistivity of $La_{1.8}Sr_{0.2}Cu_{1-x}Ag_xO_4$ as a function of temperature. Note that T_c is nearly the same for $x = 0.0$ and 0.05 while for $x = 0.1$ it is clearly lower. The transition becomes broader with increasing Ag concentration.

the ν_1 line reappears upon Ag substitution. This has been attributed by us to local distortions around the Ag ions [16]. These defects give rise to local charge disproportionation and hence to some infrared activity. The Ag impurities lower the T_c slightly and make the transition broader (see Fig. 2). Ohbayashi *et al.* have presented in their paper [15] the IR spectra of La_2CuO_4 which changes from an orthorhombic phase to a tetragonal phase (T_t) that is of K_2NiF_4 structure. The structure of $La_{1.8}Ba_{0.2}CuO_4$ has been deduced from X-ray diffraction to be $K_2NiF_4(T_t)$ type. However, Ohbayashi *et al.* propose another tetragonal structure (T_x phase) for $La_{1.8}Ba_{0.2}CuO_4$ which cannot be easily distinguished from T_t phase by X-ray diffraction. According to Ohbayashi *et al.* the striking difference between T_t and T_x phases is that the T_t phase shows two absorption peaks (at $\nu_1 \sim 680$ cm^{-1} and $\nu_2 \sim 510$ cm^{-1}) while in the T_x phase the ν_1 line is absent. The T_x phase, they point out, has the same structure as Nd_2CuO_4 as this compound also has a similar IR spectrum. From this they go further to say that the superconductivity is specifically related to the Nd_2CuO_4 type structure of $La_{1.8}Ba_{0.2}CuO_4$. Naturally the same arguments also apply to the La-Sr-Cu-O system. If we apply the arguments of Ohbayashi *et al.* to $La_{1.8}Sr_{0.2}Cu_{1-x}Ag_xO_4$ system it implies that by Ag substitution, we have switched the structure from T_x to T_t and yet retained superconductivity in the system. This immediately contradicts their contention that Nd_2CuO_4 structure is important for the superconductivity. We therefore, suggest that superconductivity is not related to the Nd_2CuO_4 structure at all. What, however, is related to superconductivity is the drastic change in the electronic structure brought about by Sr substitution which turns the material into a metallic one. Therefore, it appears that it is incorrect to correlate the appearance/disappearance of the ν_1 line to a structural transformation. The explanation based on local distortions is more likely from this point of view. The results of IR absorption on $Nd_2Cu_{1-x}Ag_xO_4$ strongly support this explanation. Nd_2CuO_4 shows an absorption peak at around 510 cm^{-1} and no line corresponding to ν_1 [17]. We find that upon Ag substitution a second absorption line appears (see Fig. 3) which corresponds to the ν_1 line. From the data we find that $\nu_1 = 675$ cm^{-1} for $x = 0.05$ and 670 cm^{-1} for $x = 0.1$ compounds. Since we are directly substituting Ag into the T_x phase, we

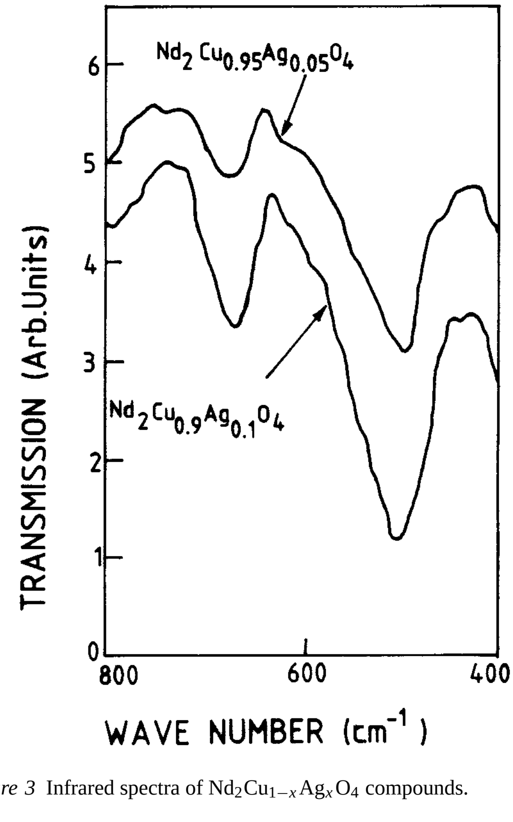

Figure 3 Infrared spectra of $Nd_2Cu_{1-x}Ag_xO_4$ compounds.

can assume that the Ag substituted compounds are of the same structure as the parent Nd_2CuO_4. The fact that a ν_1 line appears in the T_x phase implies that the absence of this line is not characteristic of the T_x phase. Rather, it appears due to local distortions of the lattice produced by the Ag impurities.

4. Conclusions

To conclude, we have shown that in Nd_2CuO_4 an absorption line at about 680 cm^{-1} appears upon Ag substitution due to local distortions around the Ag impurities. By relating this data to that on superconducting $La_{1.8}Sr_{0.2}Cu_{1-x}Ag_xO_4$ we have shown that Nd_2CuO_4 structure is not essential for the superconductivity of La-Sr-Cu-O and La-Ba-Cu-O systems as suggested by Ohbayashi *et al.* [15].

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