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Optical investigation of the valency of Pr in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$

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We have investigated the dependence of the visible-ultraviolet dielectric function of $Y_{1-x}Pr_xBa_2Cu_3O_7$ on the Pr content x using rotating analyzer ellipsometry. Based on recently published band-structure calculations, we believe that the valency of Pr can be deduced from the optical properties in this spectral region. Interband transitions should shift to higher energies for Pr^{4+} and to lower energies for Pr^{3+} when compared to the optical spectra of $YBa_2Cu_3O_7$. In the case of tetravalent Pr ions, transitions into unoccupied Pr 5d levels should be observable. Since the experimental energies for interband transitions shift down with increasing x and no additional structure can be seen, we conclude that Pr is trivalent in $Y_{1-x}Pr_xBa_2Cu_3O_7$.

I. INTRODUCTION

Not only is the mechanism of superconductivity in $MBa_2Cu_3O_7$ (Ref. 1) (M = Y, Nd, Sm, Gd, Dy, etc.) still unclear, but so also is the reason why it is suppressed for M = Pr. The solid-solution system $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ is of particular importance for several reasons: It offers solubility, stability, and formation of one single isostructural phase for the whole range of x. These properties allow one to gradually decrease T_c with x, reaching $T_c = 0$ for $x \approx 0.55$.[2] The recently reported[3] increase of the isotope effect with increasing x (thus decreasing T_c), leading to standard BCS behavior for $x = 0.5$, is another unsolved riddle of this system. Two kinds of reasons for the decrease in T_c with x can be adduced: those leaving the normal electronic state unchanged (i.e., pair breaking by the magnetic moments of the Pr ions) and, on the other hand, those which involve modifications of the normal-state electronic structure.

Since $PrBa_2Cu_3O_7$ shows no superconducting transition and, moreover, displays a temperature dependence of its resistance typical for insulators, the following discussion will exclusively focus on the latter group of explanations, namely possible changes of the electronic normal state induced by the Pr ions. Its detailed understanding may lay the foundation for answering the fundamental question regarding the superconductivity mechanism.

Pr is not only found as a trivalent ion [e.g., in PrF_3 (Ref. 4)] but also as a tetravalent one [e.g., in PrO_2 (Ref. 5)], thus offering a possible explanation for the decrease in T_c: if the Pr ions in $Y_{1-x}Pr_xBa_2Cu_3O_7$ were indeed tetravalent, holes in the Cu-O planes would be filled and T_c suppressed via a reduction of the number of carriers in the material. The Cu-O planes in $PrBa_2Cu_3O_7$ should then have an electronic structure similar to that of $YBa_2Cu_3O_6$ rather than that of $YBa_2Cu_3O_7$. Evidence for this model was reported from experiments probing the magnetic moments of the Pr ions,[2] and from transport measurements.[6]

Results from high-energy spectroscopies,[7-9] however, suggest the presence of trivalent Pr ions thus casting doubts about the hole-filling mechanism. X-ray absorption[8] at the Pr $M_{IV,V}$ thresholds indicated that Pr is trivalent, and led the authors of Ref. 8 to propose some fundamental change in band structure due to the Pr substitution. Using high-energy transmission electron-energy-loss spectroscopy Fink *et al.*[7] could show directly that the number of holes remains unchanged with varying x. They therefore proposed that the holes were not being filled but rather localized due to hybridization with the Pr 4f levels, thus allowing one to reconcile the trivalency result with previous Hall measurements.[6] In addition, the investigation of the ionic radii[10] of Pr via Raman spectroscopy and x-ray measurements of the lattice constants are also consistent with trivalent Pr.

Recently Guo and Temmerman[11] performed local-density-approximation–based calculations of the electronic band structure of $MBa_2Cu_3O_7$ (M = Y, Gd, Pr) using the linear-muffin-tin-orbital (LMTO) method in the atomic sphere approximation (ASA). According to their calculation dramatic changes in the electronic band structure can only be expected for tetravalent Pr, thus weakening the proposal in Ref. 8. They discussed the differences in electronic structure between $Pr^{3+}Ba_2Cu_3O_7$ and $Pr^{4+}Ba_2Cu_3O_7$ and could also show that it is energetically favorable for the Pr ions to be trivalent.

Optical measurements are a very direct way to probe the electronic structure and have not yet been performed on these materials. Guo and Temmerman's band-structure calculations[11] should help in the interpretation of the optical response of $PrBa_2Cu_3O_7$, especially in view of the existing information on the anisotropic optical properties of $YBa_2Cu_2O_{7-\delta}$ (Refs. 12 and 13) and the rather detailed microscopic understanding of its dielectric function.[12-14] In the present work we report measurements of the optical response of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ as a function of x. Special attention has been paid to the interband transitions in the CuO_2 plane and the Pr 5d bands. Our results can be explained in the framework of the work of Guo and Temmerman[11] under the assumption of trivalent Pr ions.

II. EXPERIMENT

Rotating analyzer ellipsometry[15] was employed to measure the pseudodielectric function (i.e., the dielectric function calculated from the measured complex reflectance modeling the sample as semi-infinite, isotropic, and homogeneous) of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$. In the energy range between 1.66 and 5.66 eV, we used an ellipsometer with the optical path in air and a Xe high-pressure lamp as light source, as has been described previously.[16] The search for the higher lying Pr 5*d* levels, however, made it necessary to extend the region of optical studies to higher photon energies. This was done by using a newly developed synchrotron radiation UHV ellipsometer at the BESSY electron storage ring in Berlin.[17]

Because of the anisotropy of these materials the orientation of the samples is crucial. For the experiments reported here we used a series of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ thin films ($x = 0$, 0.1, 0.2, 0.3, 0.4, 0.6, 0.65, 1; $\delta = 0$) grown by laser ablation.[18,19] X-ray and Raman measurements showed the *c* axis to be perpendicular to the film surface. The quasidielectric function (as defined above) determined by ellipsometry is mainly the dielectric tensor component along the line of intersection between sample surface and plane of incidence (assuming anisotropic but homogeneous and clean samples).[20] More accurate data for the dielectric tensor component can be obtained by fitting the results of various measurements with different polarization configurations to the ellipsometric equations. This, however, has not been done in the present work.

Thus we assume that the ellipsometric measurements on the film samples yield approximately $\varepsilon^{\perp c}$, i.e., the dielectric tensor component for polarization parallel to the CuO_2 planes. Since the *a* and *b* axes have random orientation in the film surface the effects of chains and planes cannot be separated.

III. RESULTS AND DISCUSSION

Figures 1 and 2 display the real (Fig. 1) and imaginary (Fig. 2) parts of the dielectric function of $Y_{1-x}Pr_xBa_2Cu_3O_7$ thin-film samples in the region between 1.6 and 10 eV for different values of x. At first glance these figures show that, apart from small shifts, no fundamental changes occur with increasing x. This fact already suggests that only small changes in band structure are present.

In the range between 2 and 5 eV the interband transitions for all polarizations of the incident light have been carefully analyzed for $x = 0$.[12,14,21] Most sensitive to hole filling in the Cu-O planes seems to be a peak in $\varepsilon^{\perp c}$ at ~2.5 eV (for $x = 0$) that has been assigned to an interband transition between two bands having plane character for *a* polarization and mixed (plane-chain) character for *b* polarization. In a band-structure picture, these transitions are concentrated around the *S* point of the Brillouin zone.[21] The final state is the antibonding band with plane character; the initial state can be found in the strongly dispersive bands ~2.5 eV below the final states and nearly parallel to these. The matrix elements for these transitions are largest for final states close to the Fermi level, making this structure ideal for probing changes in E_F. In order to experimentally observe this peak it is necessary to use a (001) surface, since otherwise the peak is hidden by a much stronger *c*-polarized peak at 2.7 eV, which has been assigned to a plane-to-

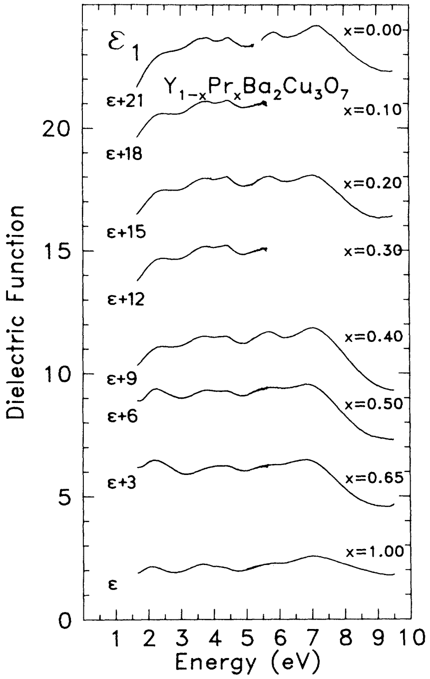

FIG. 1. Real part of $\varepsilon^{\perp c}$ for $Y_{1-x}Pr_xBa_2Cu_3O_7$ as determined by rotating analyzer ellipsometry.

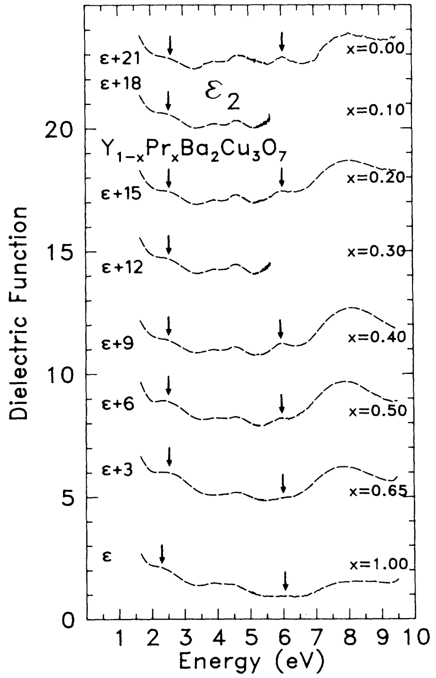

FIG. 2. Imaginary part of $\varepsilon^{\perp c}$ for $Y_{1-x}Pr_xBa_2Cu_3O_7$ as determined by rotating analyzer ellipsometry.

chain charge transfer.[12,14] The experimental finding from Figs. 1 and 2 is that the 2.5-eV peak does not weaken with increasing x as one would expect if hole filling were relevant. Instead, a shift towards lower energies can be observed.

In the case of trivalent Pr the additional charge in the Pr $4f$ shell would lower the energies of the other Pr orbital levels and, correspondingly, the initial states for the 2.5-eV peak that have minority Y (Pr) character.[14,21] Thus the calculations of Guo and Temmerman predict a shift of the 2.5-eV peak towards lower energies for Pr^{3+} and towards higher energies for Pr^{4+}. *Both experimental findings concerning the 2.5-eV peak, the constant amplitude of the peak and its shift towards lower energies, indicate that Pr is trivalent.* In $YBa_2Cu_3O_7$, between the antibonding $pd\sigma$ band and the lowest-lying completely empty conduction band a small "gap" is found. Features in $\varepsilon_2^{\perp c}$ at 3.7 eV and around 5.5 eV reflect transitions across that gap around Γ (at 3.7 eV) and around Y (5.5 eV) from states roughly 0.5 eV below the Fermi level.[21]

As discussed by Guo and Temmerman,[11] if one Pr $4f$ electron is promoted to the conduction band, the center of the Pr $5d$ band is lowered-by about 4.2 eV and the "gap" is filled by two low-lying but still empty Pr $5d$ bands. These states should, if present, serve as final states for transitions. Initial states for dipole allowed optical matrix elements are supplied by the occupied $4f$ levels and thus the traces of tetravalent Pr would be detectable by the presence of new peaks in the optical spectrum. In the case of trivalent Pr, only a shift of the 3.8-eV transition towards lower energies is predicted. The experiment shows such a downward shift of the 3.8-eV peak, however, no traces of transitions into the two empty Pr $5d$ bands could be found in $\varepsilon_2^{\perp c}$ up to 10 eV. Around 6 eV one structure becomes much less prominent with increasing x. The weakening of that structure is predicted from the work of Guo and Temmerman[11] and Gopalan *et al.*:[21] In both works[11,21] only three bands in the band structure of $YBa_2Cu_3O_7$ cross the Fermi energy, namely the two antibonding $pd\sigma$ plane bands and the antibonding chain band.

If Pr were tetravalent the Fermi level would be shifted considerably to higher energies (by 0.51 eV) without any qualitative change of the situation.[11] For Pr^{3+}, in contrast, the calculation predicts a small ($\sim$0.03 eV) shift towards lower energies.[11] Although this shift seems small, it bears delicate consequences since it would allow two additional bands to cross E_F around the S point. According to Gopalan *et al.*,[21] a major contribution to the 6-eV feature comes from a transition centered around the S point in the Brillouin zone having the lower one of these two bands as initial states. Thus the weakening of this transition does not come as a surprise. Moreover, one could argue that further work on the origin of this peak might provide a valuable tool for the investigation of this detail in band-structure calculations for $YBa_2Cu_3O_7$. (At this point we should note that other electronic structure calculations[22] not making use of the ASA obtain a small pocket of holes even for $YBa_2Cu_3O_7$. They place the Fermi level between these two bands, leaving this detail of the electronic structure even more susceptible to tiny changes in the Fermi energy.)

The optical spectra presented here thus indicate that the Pr ions are trivalent, but we feel, however, that a calculation dealing with the effects of the presence of the Pr $5d$ bands on the optical spectra is desirable to ascertain this conclusion. As Fink *et al.*[7] remarked, hole immobilization could be one possibility to reconcile the contradicting results of no hole filling and insulating behavior. Infrared measurements could help to clarify matters.

IV. CONCLUSIONS

We have measured the in-plane component of the dielectric function of $Y_{1-x}Pr_xBa_2Cu_3O_7$. Small shifts of all features towards lower energies are observed with increasing x. No weakening of the 2.5-eV in-plane interband transition and no new transition into low-lying Pr $5d$ bands are found. The weakening of a structure around 6 eV is interpreted as the manifestation of a tiny shift of E_F towards lower energies, which would be incompatible with hole filling. All these observations indicate that Pr is trivalent in $YBa_2Cu_3O_7$ and the mechanism suppressing superconductivity in $PrBa_2Cu_3O_7$ is *not* hole filling.

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