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Pressure effect in the Hg-based superconductors: A structural study

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Energy-dispersive synchrotron x-ray-diffraction studies were performed on powder samples of Hg1212 and Hg1223 in a diamond-anvil cell at pressure up to 300 kbar. High compressibility was found. A reversible structural transition was observed, which is suggested to correspond to a pressure-induced ordering along the c axis. The accommodation of the Ba ion at high pressure is studied, and the effect it might have on the electronic structure of these materials is discussed by employing results from cluster calculations. [S0163-1829(98)03821-1]

INTRODUCTION

The Hg-based high-temperature superconductors (HTSC's) were discovered in 1993 by Putillin *et al.*[1] In close similarity to the previously known thallium HTSC compounds they show a tetragonal structure which follows the general formula $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$. The third member of this family (Hg1223) shows the highest critical temperature (T_c) for a superconducting transition, 135 K at ambient pressure.[2] Soon after the discovery of these compounds an unprecedented increase in T_c under pressure was observed.[3,4] At 31 GPa, a T_c as high as 164 K was measured for Hg1223. Gao *et al.*[4] studied the dependence of the critical temperature on pressure for the first three members of the Hg family. The absolute enhancement of T_c $[T_{c0}(p) - T_{c0}(p=0)]$ was found nearly independent of the number of CuO_2 planes,[5] and it was suggested that the buffer layers may play an important role. In the same work, the dependence of this enhancement on increasing Pb doping at the Hg site was studied. Although the Pb-doped samples showed the same critical temperature at ambient pressure, increasing Pb doping reduced significantly the increase in T_c under pressure. It was suggested that the large $\Delta T_c^{\max}$ (increase of T_c at optimal doping) might have been related more closely to the HgO_δ layer than to the CuO_2 planes. An efficient hole doping of the planes was suggested there and in other studies,[6] however a detailed band-structure calculation[7] showed only a limited pressure contribution to the hole doping of the CuO_2 planes.

While the high-T_c gives hope for new superconductors with high operating temperature at ambient pressure, the pressure dependence might also supply important information regarding the mechanism of high-temperature superconductivity. However, since the discovery of the pressure effect, relatively little has been published on the structural changes under pressure in these compounds.[6,8,9] This is due to a lack of pure enough samples and the difficulty in analyzing the diffraction results. Here we present the results of a synchrotron radiation study under pressure of $HgBa_2CaCu_2O_{6+\delta}$ (Hg1212) and $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg1223).[27,28]

EXPERIMENTAL

The synthesis of the Hg compounds presents major difficulties due to the low decomposition temperature of HgO and the high vapor pressure of Hg. Therefore novel synthetic routes are required. The details of the present route are described elsewhere,[10,11] but the main steps will be given. Hg1212 was synthesized in two steps. A Ba-Ca-Cu-O precursor was prepared by a sol-gel method, starting from an aqueous acetate solution of these materials. Homogeneous gels were obtained by complexing the metal ions with tartaric acid before the gelation process. The decomposition of the precursor was carried out under vacuum at 850 °C. The precursor was then mixed with HgO in a glove box and reacted in an evacuated silica tube at a temperature of 800 °C for 30 h. Oxygen annealing was done at 300 °C for 6 h. The ambient pressure cell parameters (refined from angular-resolved x-ray-diffraction data using an inner standard) were $a=3.8651(1)$ Å, $c=12.713(1)$, and $a=3.8609(2)$ Å, $c=12.701(2)$ Å, for as-prepared and oxidized Hg1212, respectively. The oxygen annealed sample showed an onset of superconductivity at 127 K as determined by ac susceptibility. The synthesis of Hg1223 was performed using a direct reaction of the pure metal oxides in closed ampoules at 665 °C for 70 h. The cell parameters were $a=3.8573(2)$ Å and $c=15.857(2)$ Å.

The synchrotron-diffraction data were collected at beam line F3 of HASYLAB-DESY in Hamburg. A diamond-anvil cell was used to obtain pressures in the range of 0.001–300 kbar. To obtain quasihydrostatic conditions, the sample was placed in silicon oil. A mixture of 4:1 methanol and ethanol was used first, but it reacted with the sample at high pressures. The pressure was determined by the nonlinear ruby fluorescence method.[12] The sample was placed in an inconel gasket with a 200 μm hole together with the ruby crystal. All measurements were done at room temperature.

Analysis of the diffraction data was performed using both a version of the PURUM program converted to treat energy-dispersive data[13] and the modules Characterize and Structure_Refine of the Biosym package.[14] Rietveld refinement of the diffractograms converted to angular-dispersive data was performed for some of the measurements using the GSAS code.[15] Comparing the complete diffractogram to model calculations at each step, including intensity ratios allowed us to treat both preferred orientation effects and structural transitions which were observed in the measurements. The spectra were processed by escape correction, background subtraction, and deconvolution by the maximum entropy method.[13]

RESULTS

Figures 1 and 2 present typical diffractograms at different pressures. The ambient pressure data [Fig. 1(a)] corresponds very closely to the angular-dispersive data. Profile parameters corresponding to the energy-dispersive measurement were refined at this stage. The peaks at 31.86, 32.22, 36.37, and 37.30 keV correspond to Ba fluorescence lines. As the pressure increases a preferred orientation effect is observed [Fig. 1(b)]. The Ba fluorescence lines were subtracted for clarity. The 001 direction was found to be the main preferred orientation direction in all of the samples, corresponding to the platelike growth of these materials. Similar intensity ratios were observed for the final ambient pressure measurement while structural changes were found to be reversible, supporting the preferred orientation nature of these intensity ratios changes. A high-pressure splitting of the 102 line in Hg1212 and the 103 line in Hg1223 are shown in Fig. 2. A correlated irregularity is observed at higher energy peaks (not shown in the figure). This splitting is suggested to correspond to a pressure-induced structural transition, which is related to the partial occupation of oxygen at the HgO layer and the position of the Ba^{2+} ions.

Following the variation of the different Bragg reflections with pressure gives a general picture of the structural changes involved. Figure 3 presents such a picture for the highest intensity peaks. The continuos contraction of the unit cell is changed around 150 kbar, where a splitting of the 102 peak indicates the onset of a structural phase transition. Several studies[16,17] report a change in dT_c/dP around that pressure. The circled dots designate repeated measurements with decreasing pressure. The recovery of most of the peaks shows that this structural transformation is reversible.

Figure 4 shows the dependence of the lattice parameters on pressure for the three samples. An absolute scale was kept to allow comparison with neutron-diffraction results.[6] The splitting shown in Fig. 2 is suggested to correspond to a structural transition along the c axis. Apart from other disagreements with the data, a transformation along the a axis would cause a splitting of the 200 peak which is well observed and unsplitted along the whole pressure range. A detailed description of this transformation follows in the discussion part. The c-axis lattice parameter for Hg1212 after the phase transition, plotted in Fig. 4, is the average c parameter. For Hg1223 and optimally doped Hg1212, lattice parameters up to the transition point are given.

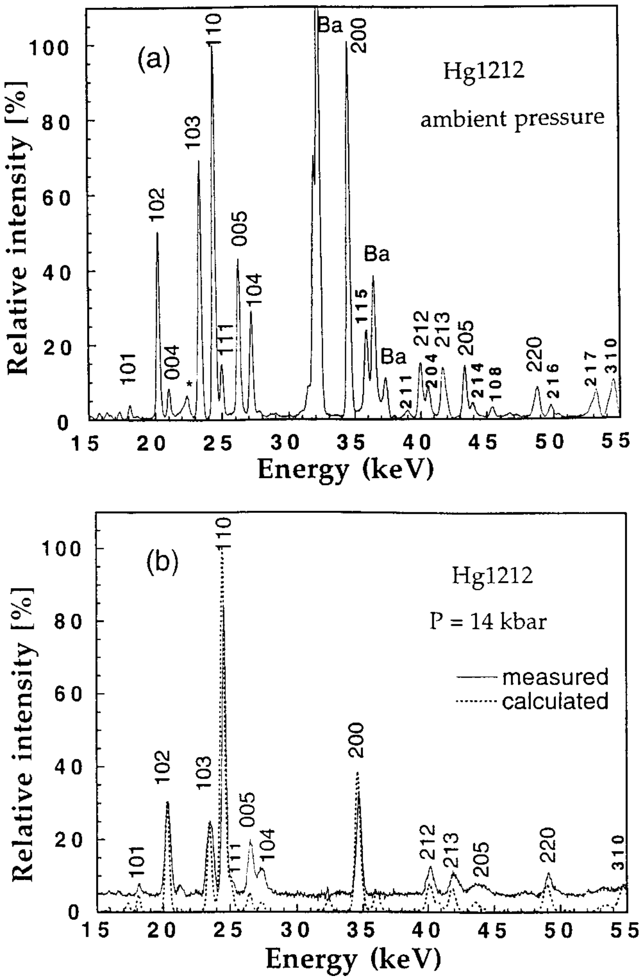

FIG. 1. Energy-dispersive diffraction patterns for the as-synthesized Hg1212 superconductor. (a) Ambient pressure, (b) 14 kbar.

DISCUSSION

The structure of the Hg compounds, with the large Cu-apical oxygen separation and the linear coordination of Hg, presents an integration of three components: CuO_2 $[CaCuO_2]$ blocks, Ba^{2+} ions, and HgO_2 dumbbells (see Fig. 5). Oxygen doping is achieved through the partial occupation of the O(3) [O(4)] site in Hg1212 [Hg1223], with the crystallographic coordinates (0.5, 0.5, 0). (Hg is taken at the origin.) This site is referred to below as the O_δ site.[18] We discuss below two pressure effects related to the position of the Ba ion and the occupation of the O_δ site: A shift of the Ba ion away from the CuO_2 plane observed around 20 kbar, and a high-pressure superstructure observed above 150 kbar. While the HgO_2 dumbbells present rigidity in the c direction, the CuO_2 planes present rigidity along the a direction. This

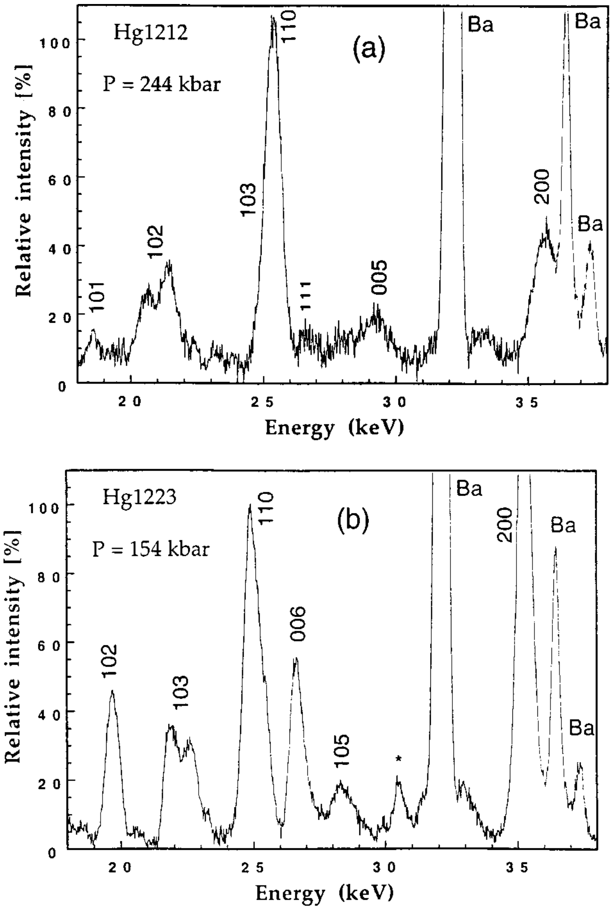

FIG. 2. Enlarged energy-dispersive diffraction patterns of the low-energy range. (a) Hg1212 superconductor, as synthesized. A splitting of the 102 peak is observed. (b) Hg1223 superconductor, as synthesized. A splitting of the 103 peak is observed.

behavior is preserved under high pressure as is seen from the stable Cu-O in-plane bond length and the Hg-O (apical) bond length observed by neutron diffraction.[6] Such a behavior leads to structural defects when packing the $Ba_2(HgO_2)_4$ cluster at high pressures, due to the partial occupation of the O_δ site. Thus, efficient compressing of the structure cannot take place without heavily distorting the CuO_2 planes. As far as we learn from the T_c increase in that pressure range it seems that the CuO_2 planes are not significantly affected.

Several supercell models were constructed in order to reproduce the observed splitting of the peaks shown in Fig. 2 and additional variations in the diffractograms. Thus, for a supercell of five unit cells representing the pressure-induced distortions in Hg1212, a doublet followed by a triplet splitting of the 102 peak is obtained on decreasing supercell volume when the structural defect corresponding to the occupation of the O_δ site is localized to the fifth unit cell (see Fig. 6). Similar results are obtained with a six-unit supercell. Figure 6 presents two examples of such models with the calculated and observed diffractograms. Due to the high strain induced in the samples at these pressures, the distinction between the different possibilities is below the measurement resolution in the present time. However, several features are common to all the models that we could fit to the data:

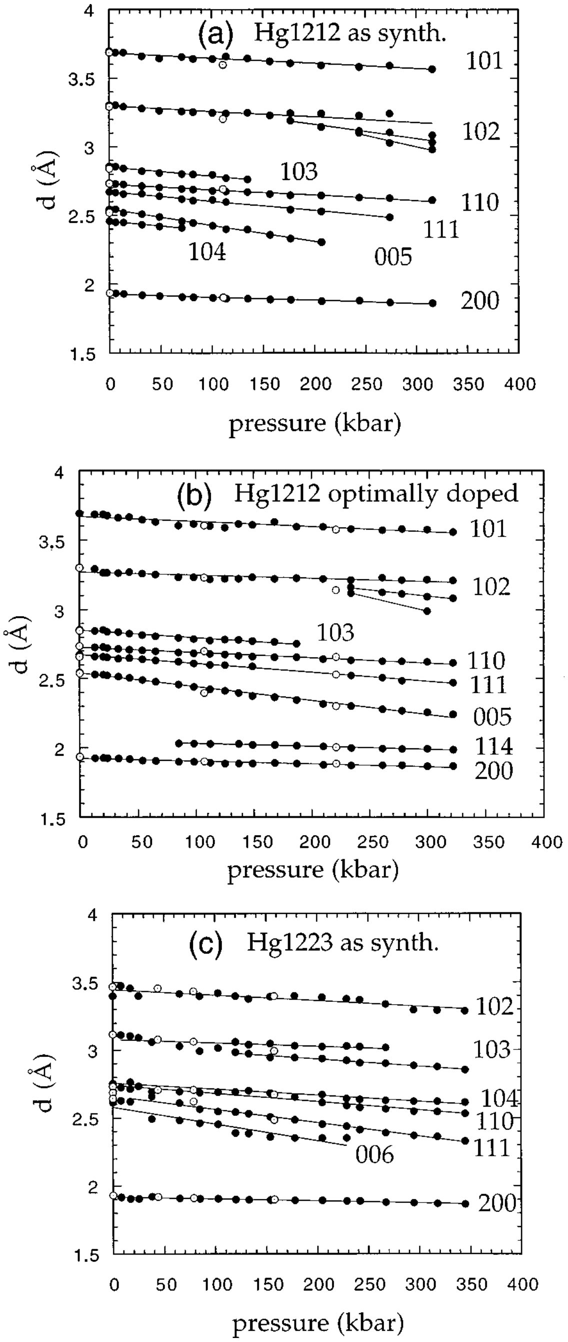

FIG. 3. Observed Bragg reflections as function of pressure. Circled dots denote measurements at decreasing pressure. Miller indices for the tetragonal structure are given to the right. (a) As-synthesized Hg1212, (b) optimally doped Hg1212, (c) as-synthesized Hg1223.

(1) The existence of a superstructure along the *c* axis.
(2) A supercell of least five unit cells was needed.
(3) The appearance of two unit cells of which one is more contracted than the other.
(4) The Ba-Ba separation is much shorter in the contracted unit as the Ba ions are being pushed into the $(HgO_2)_4$ cluster.

It should be stressed that each of the models reproduces fairly well the diffractograms over the whole pressure range, while other distortions such as in-plane modulations failed to

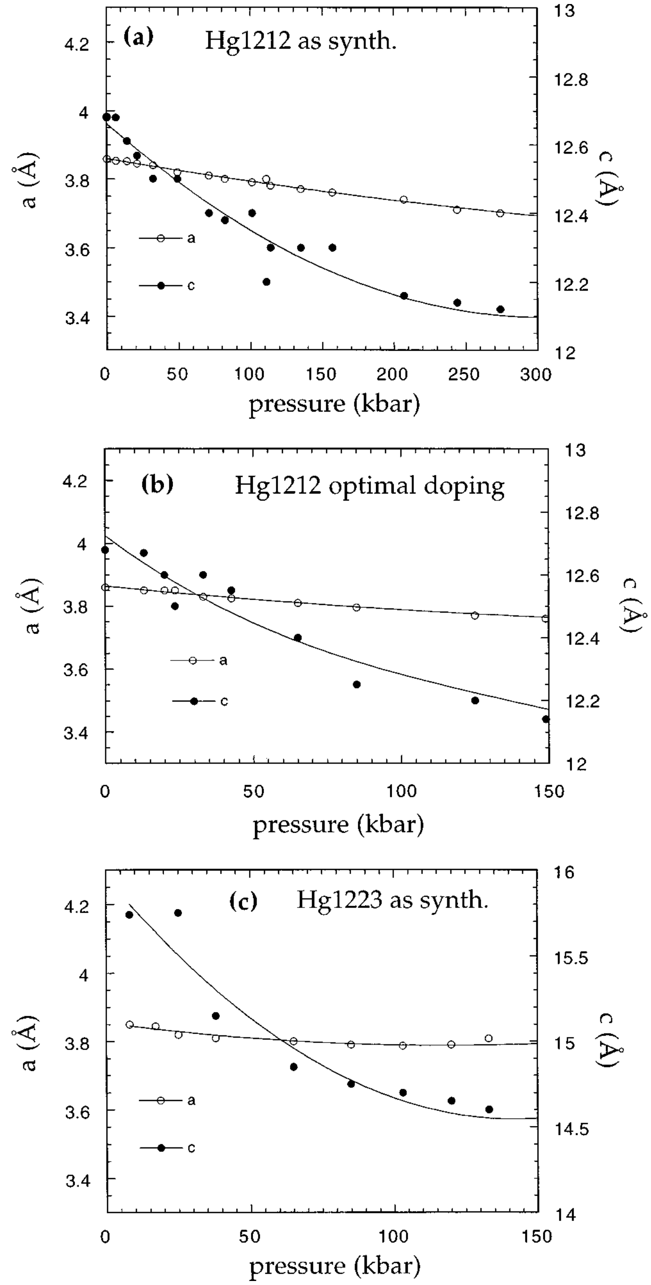

FIG. 4. The dependence of lattice parameters on pressure for the three samples. (a) As-synthesized Hg1212, (b) Optimally doped Hg1212, (c) As-synthesized Hg1223. Lines are guides to the eye.

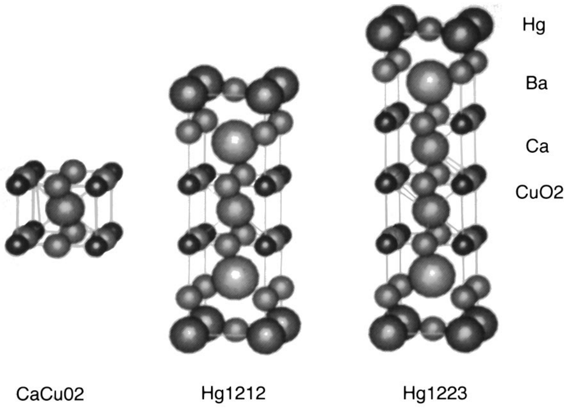

FIG. 5. The crystal structure of Hg1212, Hg1223, and the infinite layer $CaCuO_2$.

do so. Thus, the exact type of superstructure cannot be resolved by our measurements, although the existence of a superstructure in the material is unambiguous. This (possibly partial) ordering allows volume reduction, while preserving the strong in-plane Cu-O bond. Similar ordering along the c axis has been observed also in other systems,[19] though not induced by pressure as in this case. It is also possible that the high-pressure contraction reveals a pre-existing order of the O_δ ions.

These results should be compared with the neutron-diffraction studies of Marezio *et al.*[6,9] In agreement with our results, the absolute c-axis compression was found significantly higher than the a-axis compression. (Although it should be pointed out that the preferred orientation effect might contribute to the observed compression.) The main reduction was observed in the Cu-apical oxygen distance. The strong Hg-O bond induces a large Cu-apical oxygen distance at ambient pressure. This distance was found to contract while the Hg-O bond length was found stable at high pressures. An important observation[6] was a shift in the Ba position away from the CuO_2 plane at comparatively low pressure (20 kbar). A corresponding large decrease in the Ba-O_δ distance shown in their data supports this observation. Thus, an increase in pressure seems to induce an instability of the Ba equilibrium position with respect to the two energy minima, touching the CuO_2 plane oxygen ions or the apical oxygen ions. Such instability and its dependence on O_δ occupation are observed already for the ambient pressure structure of Hg1223.[20]

This effect was studied by means of electronic-structure calculations. A cluster model representing the structural surrounding of the Ba^{2+} ion is depicted in Fig. 7(a). In contrast to a detailed model addressing the fine electronic structure of the CuO_2 planes, to be presented below, we focus here on the ionic nature of the local interactions. Thus, ionic replacements are performed to preserve ionic charge and overlap repulsion effects while saving computation effort. The Hg^{2+} and Cu^{2+} ions are thus replaced by Mg^{2+} ions, the Ba^{2+} ion is represented by Ca^{2+} and O^- is represented by F^-. Figure 7(b) presents the results of Coulomb hole augmented Hartree-Fock calculations.[21,22] The equilibrium position of Ca is well reproduced for an oxygen vacancy site. The effect of the dumbbell was found small and the equilibrium position to be identical for a calculation where the dumbbell was not included. A shift of the energy minimum towards larger distances from the plane is seen to depend on the occupation of the O_δ site. This effect is studied for two Cu-apical oxygen distances representing low and high pressure, and for two possible oxygen charges. While the low-pressure results indicate a static shift to depend on oxygen charge, the high-pressure results (short apical distance) suggest a possible dynamic effect where a buffer ion oscillation is accompanied by a charge transfer.

An important issue to address is how variation of pressure affects the electronic structure so that T_c is increased. In looking for important structural changes under pressure with relation to the CuO_2 planes we observe that in addition to the reduction of the Cu-apical oxygen distance,[6] the Ba to plane

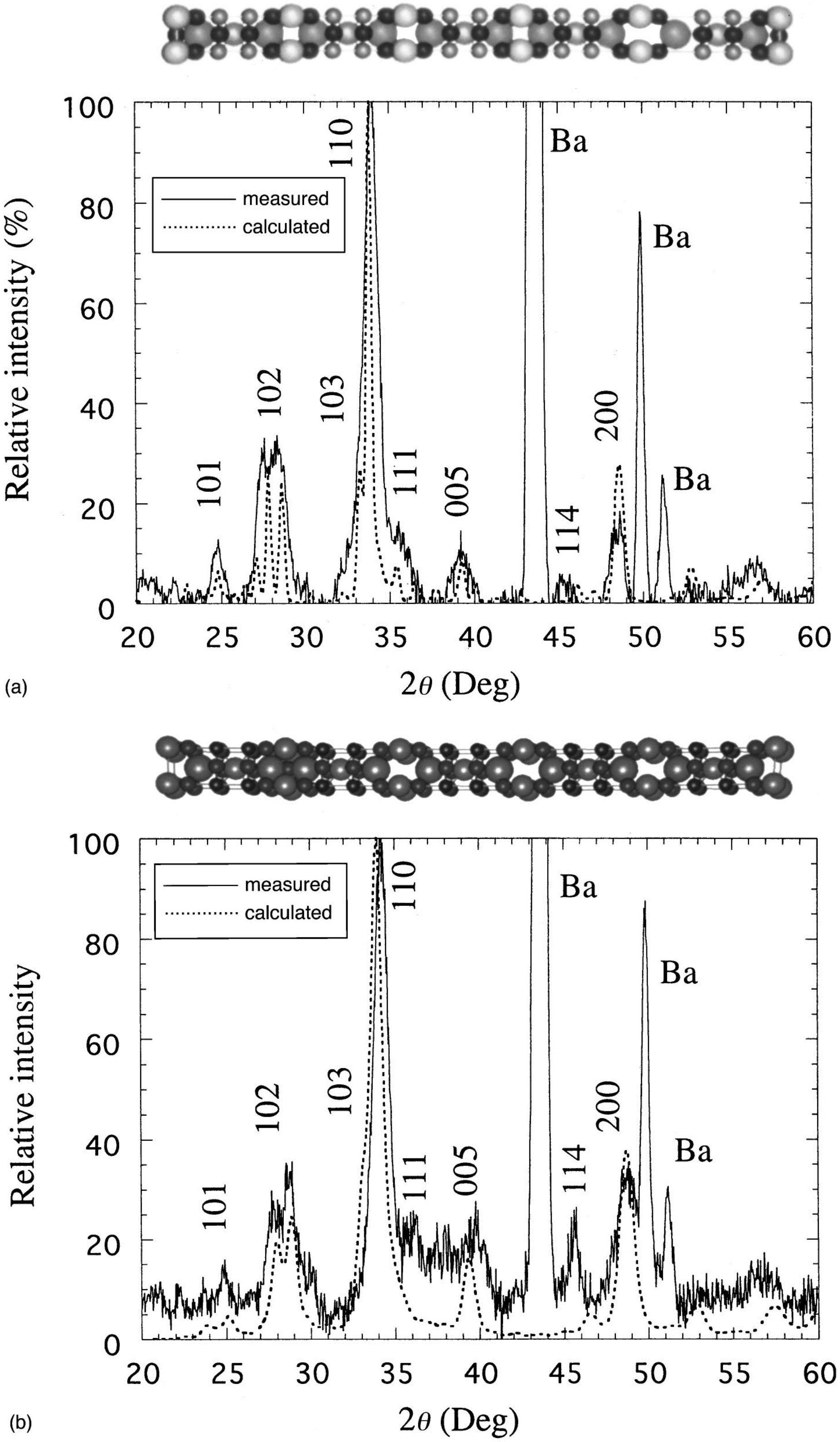

FIG. 6. Diffraction patterns and model calculation results. (a) As-synthesized Hg1212 at 207 kbar. A supercell model with expanded fifth unit. (b) Optimally doped Hg1212 at 278 kbar. A supercell model with contracted fifth unit. The inset shows the structural model in both cases.

distance changes significantly. Additional neutron-diffraction studies under pressure are required in order to study this effect.

In order to be able to relate such structural changes with the electronic structure of a highly correlated system like the cuprates, an adequate treatment of local correlations is necessary. In a recent work,[23] we have studied the fine electronic properties in a $Ca_2(CuO)_4$ cluster model, representing the

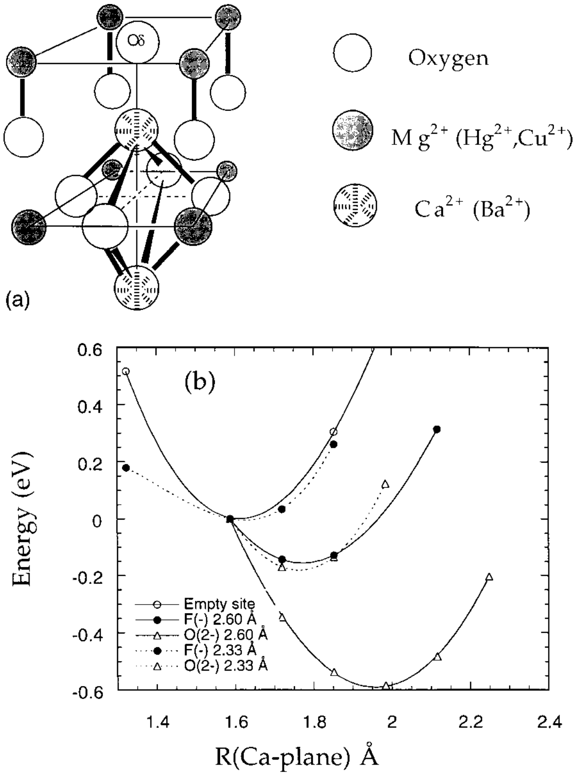

FIG. 7. (a) Cluster model replacing Cu^{2+} and Hg^{2+} by Mg^{2+}, and Ba^{2+} by Ca^{2+}, addressing the effect of oxygen at the δ position; (b) O_δ induced shifts of Ca^{2+} equilibrium position for two apical oxygen distances. Open circles: empty site. Filled circles indicate F^- at the δ position. Open triangles indicate $O(2-)$ at the δ position. Solid line indicates the low-pressure structure: Cu-apical oxygen distance$=2.60$ Å. Dashed line is the high-pressure structure: Cu-apical oxygen distance$=2.33$ Å.

infinite layer core of the mercury compounds. Holes were found to localize on in-plane oxygen $2p_\pi$ orbitals, in proximity to the Ca^{2+} ions. Pure in-plane oxygen $2p_\pi$ hole-pair states were identified. The pairing was found to result from screening of buffer ions repulsion through the $(CuO)_4$ loop and to originate from independent particle states of anisotropic *s* and *d* symmetries with similar weights. The pair-breaking energy was found small (0–60 meV) and sensitive to the Ca-plane distance. The interplay between buffer ion position and pairing energy is understood to give rise to phonon-assisted hopping between nearly localized states. In a subsequent chemical study,[24] several candidates for in-plane and buffer cations were compared. Implications for the influence of a large cation at the Ba^{2+} position were obtained by addressing the trend in the Na^+, K^+, Ca^{2+}, and Sc^{3+} series. If a ‘‘free’’ Ba position is associated with the pressure effect on T_c in the mercury cuprates, then Pb substitution at the Hg site would tend to reduce this effect by introducing an additional structural constraint, as Pb tends to prefer four-coordination in the Hg-Pb plane. Thus, Pb doping, while not reducing the ambient pressure T_c may reduce the increase in T_c at high pressures.

CONCLUSIONS

The synchrotron study under pressure was performed on powder samples of Hg1212 and Hg1223. High compressibility of these compounds was found. A reversible structural transition was observed and was suggested to correspond to a pressure-induced ordering along the *c* axis. The structural importance of an observed Ba shift was demonstrated, and the effect to result from Ba-O_δ attraction. The influence of the Ba ion position on the fine local electronic structure was discussed by employing results from cluster calculations. We suggest that the buffer layer plays an important role in increasing T_c by ‘‘fine tuning’’ the Ba position. This local understanding is in accordance with the observed independence of the pressure-induced increase in T_c on the number of CuO_2 planes in the mercury cuprates. A crucial role in enabling the Ba shift is played by the HgO_δ layer at high pressures. Consequently, Pb doping may reduce severely the pressure effect on T_c by introducing and locking additional oxygen at the δ position. Further neutron-diffraction studies under pressure are required in order to test the proposed structural effects. In particular, Andersen *et al.*[25] propose the dimpling of the CuO_2 planes as an important structural feature. We did not find any signs for such dimpling, although increased strain in the planes is expected due to the partial occupation of oxygen as demonstrated above, and the decreasing Cu-apical oxygen distance under pressure.

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