PHYSICAL REVIEW B VOLUME 47, NUMBER 13 1 APRIL 1993-I

$Ba_{2-x}K_xPb_{1-y}Bi_yO_{4-\delta}$: Layered oxides with insulating or conducting properties and possible superconducting properties

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(Received 17 July 1992; revised manuscript received 25 September 1992)

Superconductivity below 14 K has been found by magnetic-susceptibility measurements in a family of layered oxides $Ba_{2-x}K_xPb_{1-y}Bi_yO_{4-\delta}$. The structure is isomorphous of tetragonal La_2CuO_4 but these materials do not contain any magnetic ions. Compounds of this family show a transition from insulator (for example, Ba_2PbO_4, $x=0, y=0$) to conductor by injection of charge carriers induced by substitution of monovalent potassium onto the divalent barium site. The carrier concentrations are estimated from the screening of phonons by the plasmon deduced from the analysis of infrared-reflection spectra. In the tetragonal structure, T_c is found twice higher than in the perovskite with the same bismuth concentration. This is achieved in spite of the fact that the carrier concentration remains low, and that the percentage of bismuth y does not exceed 15% in this series of experiments. A thermal treatment at 450 °C under oxygen improves conducting properties in the normal phase but, at least for low bismuth rate, is detrimental to superconductivity. These materials are expected to help clarify the role played by phonons and possible highly anharmonic fluctuations in the mechanism of superconductivity of oxides since here no magnetic interaction can play any part to mediate Cooper pairing as it is often invoked in copper compounds.

I. INTRODUCTION

One of the most exciting debates since the discovery of Bednorz and Müller[1] of high-T_c superconductivity in a copper oxide compound is whether electron-phonon or magnetic interactions are more important in mediating Cooper pairing within a—possibly renormalized—Bardeen-Cooper-Schrieffer (BCS) framework. "Anything but phonon theories" were developed on account of the low values of the oxygen isotope effect in early reports. However, the recent observations performed independently by two groups of authors[2,3] showing that the isotope exponent α depends *monotonically* on the carrier concentration in (Y,Pr)BaCuO are of importance. At highest carrier concentration which corresponds to the highest T_c in YBaCuO, they recover the low isotope exponents found previously. These results show that phonons possibly play a part at least up to $T_c = 60-70$ K in the superconductivity of praseodymium-substituted YBaCuO. Recently, Ronay, Frisch, and McGuire[4] explained by a nonstoichiometric copper-rich phase the low isotope exponent previously found in $La_{1.85}Sr_{0.15}CuO_4$. In this system also, the critical temperature was previously found dependent on x by Crawford *et al.*[5] Ronay, Frisch, and McGuire reported a much more realistic $\alpha = 0.4$ in the stoichiometric compound showing the highest T_c. Again, this indicates the possible role played by phonons.

The schematic plot in Fig. 1 is reproduced from the data of Ref. 6 just to show three distinct regions observed in the diagram. (i) "Conventional" superconductors are observed in the central hatched region. Most of them obey the BCS relationship. (ii) Heavy fermions are in the right-hand corner. No oxide has been found there. (iii) The upper part shows why the wording "high-T_c" is adequate: compared to most superconductors, T_c's of *certain oxides* are experimentally found roughly one order of magnitude higher than in a conventional superconductors. The upper part contains two subgroups: (i) layered copper-based oxides and (ii) pseudocubic (referred to as "cubic" in this paper, for simplicity) perovskite compounds with lead and/or bismuth (or antimony), ions which are sitting at a +4 site but are expected to prefer (+3+5) disproportionation, because both of these valences are more stable. The disproportionation is not

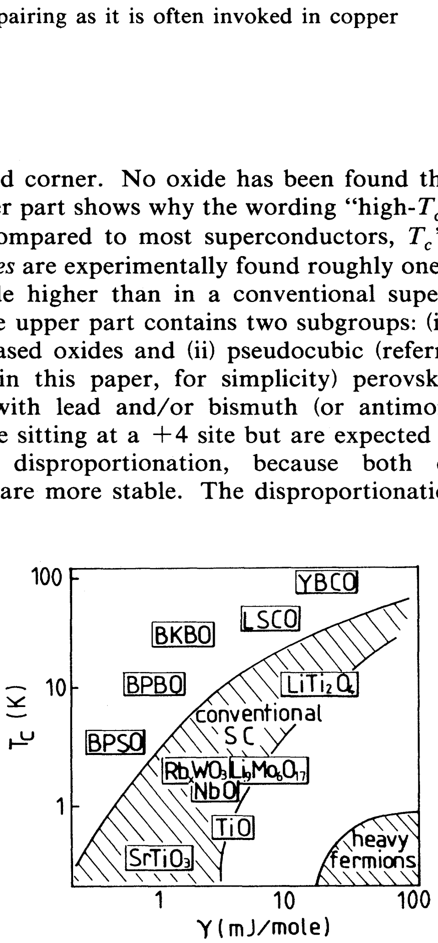

FIG. 1. Schematic trends of critical superconducting temperature vs density of states at the Fermi level (adapted from the review Ref. 6). BPSO: $Ba(Pb,Sb)O_3$; BPBO: $Ba(Pb,Bi)O_3$; BKBO: $Ba_{0.6}K_{0.4}BiO_3$; LSCO: $(La,Sr)_2CuO_4$; YBCO: $YBa_2Cu_3O_7$.

necessarily static but might fluctuate versus time. Hence emerged the idea to combine both ingredients (bidimensionality and the possibility of disproportionation) to reach still higher T_c's. We synthesized new conducting layered oxides, isostructural with La_2CuO_4, but containing bismuth instead of copper. This approach also has the advantage to discard the eventual role played by interaction of magnetic ions in copper compounds and, therefore, make the analysis of the mechanism of superconductivity easier. This study was really a challenge because Ba_2PbO_4 is an insulator and Ba_2BiO_4 was soon shown not to exist in the tetragonal structure but rather to crystallize in a cubic double-perovskite structure.[7] The latter compound is an insulator too.

II. SYNTHESIS AND PRELIMINARY CHARACTERIZATION

In a first step, we have synthesized compounds belonging to the solid solution $Ba_2Pb_{1-y}Bi_yO_4$. They adopt the K_2NiF_4 tetragonal structure only if y remains smaller than 0.3, and all compounds are insulating.[8] Other groups reported results of similar experiments and absence of superconductivity.[9] Preliminary attempts by solid-state reaction to substitute Ba for K did not arrive to a successful outcome. These experiments were performed in the open air or under oxygen flow. But using a modified sol-gel route[10] and performing the final reaction under oxygen, the synthesis of potassium-substituted compounds was achieved.

The modified sol-gel process consists of a gelation of an aqueous solution containing the appropriate ratios of the required elements through an organic polymer network. The gel is calcinated in a furnace under air flow at the desired temperature. The stability of the aqueous solution against hydrolysis or condensation is improved by complexing the actions by a chelating agent such as one citric acid $C_6H_8O_7 \cdot H_2O$ per valence unit of each cation. The pH is raised to 7 by addition of ammonia, and distilled water is added to obtain 1 ℓ of solution. The gelation of the solution is achieved by creating a hydrophilic polymeric polyacrylamide network *in situ*. The monomers acrylamide and N,N′-methylene-bis-acrylamide are soluble in water. The polymerization is initiated by free radicals afforded by azobisiobutyronitrile (AIBN) and is promoted by radical transfer agents like N,N,N′,N′-tetramethyl-ethylenediamine (TEMED). In 150 mℓ of precursor solution (0.092 mol L^{-1}) were dissolved 7.5 g of acrylamide, 0.75 g of N,N′-methylene-bis-acrylamide, 1 mℓ of TEMED and 4 mℓ of a 3% hydrogen peroxide solution (AIBN). By heating this solution in a water bath at 80 °C, a gel is obtained. The gel is then calcinated during 5 h in a ventilated furnace at 600 °C until all water and organic species are removed. The small-grain powder is then annealed at 1060 °C during 17 h under oxygen, a process which allows the chemical reaction to be completed as shown by x-ray patterns.

However, in most cases, further treatment of the final powder under oxygen at 450 °C is necessary to ensure optimum conducting behavior. Conversely, heating up to the same temperature under nitrogen cancels conducting properties as probed by the plasmon signature (detailed in the next paragraph). Thus, these new materials are extremely sensitive to the oxygen partial pressure during thermal treatments. Up to now, the synthesis of potassium-substituted compounds with a concentration of bismuth larger than $y = 0.15$ failed. Indeed, a multiphase product is obtained, as indicated by x-ray diffraction. Samples are routinely characterized according to the methods detailed in Ref. 8. Energy dispersive x-ray analysis (EDX) of the powders observed by scanning electron microscopy in particular allows us to check the homogeneity of potassium and bismuth concentrations. *Only compounds showing a single phase as probed by x-ray diffraction were studied further.* Examples of characterization of perovskite and tetragonal phases by x-ray diffraction are shown in Fig. 2.

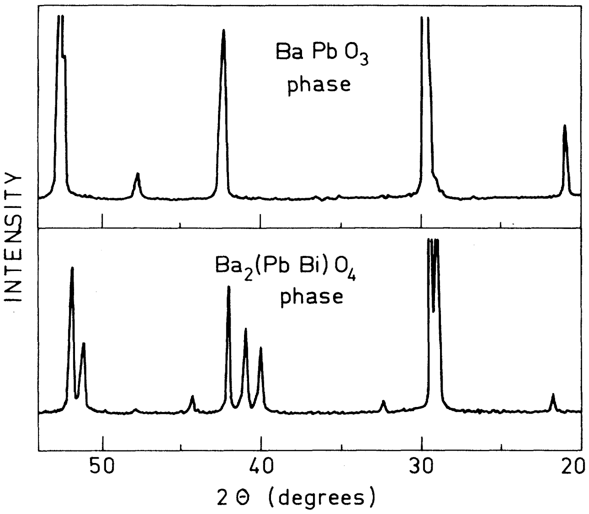

FIG. 2. X-ray diffraction patterns typical of perovskite and tetragonal phases.

III. INFRARED REFLECTIVITY AND CHARGE CARRIER CONCENTRATION

A. Experiment and data reduction

For certain compositions, the sintering process starts at a temperature 10 °C below the melting point (between 1200 and 1385 °C depending on x and y). Since preliminary tests have shown that this process can modify the electrical properties of these new materials drastically, in our first step we decided to characterize the materials in the powdered state only. Within these conditions, only a limited number of techniques can be used. X-ray diffraction and electron scanning microscope combined with EDX have been mentioned above. To prove electrical properties, we performed infrared reflectivity measurements at the surface of powders compacted under 4 kbar. We have studied the degree of screening of phonons by the plasma wave, which gives information about the electronic concentration and the eventual anisotropy of the conducting properties as is detailed below.

Typical infrared reflectivity spectra are shown in Fig. 3. The insulating compound (no potassium) shows bands related to polar phonons, whereas conducting samples display in addition a broad "Drude-like" profile which screens the phonons partially. Spectra have been fitted with an average dielectric function

$$\epsilon=(\varepsilon_{\parallel}+2\varepsilon_{\perp})/3 \ .$$

Other models exist[11] but this one has the advantage of simplicity and it has been checked to yield correct results by comparing a single crystal and polycrystalline sample of La_2NiO_4, an isomorphous system. Each component of the dielectric response is modeled with phonons (plus the Drude component only for $\varepsilon_{\perp}$) in the form[12]

$$\frac{\varepsilon(\omega)}{\varepsilon_{\infty}}=\prod_j \frac{\Omega_{j\mathrm{LO}}^2-\omega^2+i\gamma_{j\mathrm{LO}}\omega}{\Omega_{j\mathrm{TO}}^2-\omega^2+i\gamma_{j\mathrm{TO}}\omega}-\Omega_p^2/\omega(\omega-i\gamma_p) \ .$$

The reasons for this modified version with respect to the more usual expression are detailed in Ref. 12, referring to previous analyses of other conducting oxides. We did not perform the Kramers-Kronig (KK) transformation because the dispersion is unknown below 10 cm^{-1}, but it is expected to play a major part in the response. Also, the anisotropy of the system raises a specific problem from the point of view of the KK analyses of a powder.

The decrease of reflectivity related to the onset of the scattering of light when the wavelength of radiation becomes the order of magnitude of the grain size can be, in the first step, estimated by compensating the spectrum with a calculated diffusion profile. We have also measured diffusion losses by deposition of a thin metallic coating upon the surface of the granular sample and remeasured the spectrum. The last spectrum is then used as the reference of the uncoated-sample spectrum. This last method tends to overestimate the high-frequency reflectivity whereas diffusion losses underestimate it. Results are inaccurate in terms of the plasma edge because the responses are very broad, but the rate of screening of phonons provides information sufficient in itself. To get more accurate results, we would need to grow single crystals because the plasmon is expected to be bi-dimensional as in La_2NiO_4 or $(La,Sr)_2CuO_4$.[13,14]

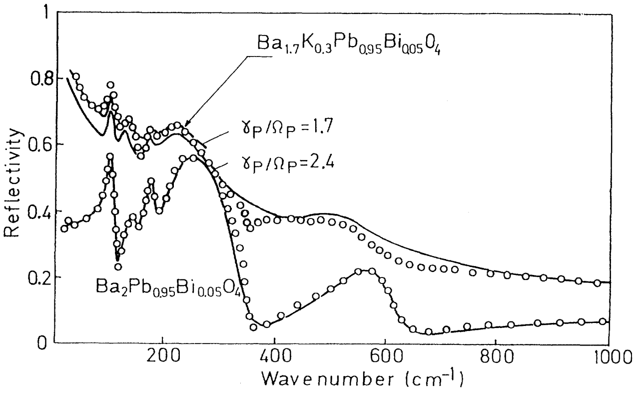

FIG. 3. Infrared reflectivity of insulating and conduction oxides (dots). Best fit with the model Eq. (1) (full curves).

In the example of Fig. 3, best results of data fitting were obtained with *no charge-carrier contribution to* $\varepsilon_{\parallel}$. The same was true for all conducting samples we have investigated. Note the general tendency at mode softening upon injection of charge carriers. The Drude expression is known to be a rough model used to describe metallic properties of oxides and the agreement with experimental data of $Ba_{1.7}K_{0.3}Pb_{0.95}Bi_{0.05}O_{4-\delta}$, for example (Fig. 3), is only fair. The plasmon is overdamped, $\Omega_p=3,300$ cm^{-1}, $\gamma_p/\Omega_p=2.4$. Note that a better fit of the part of the spectrum below 300 cm^{-1} is obtained with $\gamma_p/\Omega_p=1.7$ at the expense of a larger disagreement with the data at higher frequency. This means that a frequency-dependent plasma damping function would be more appropriate than a constant γ_p.

B. Phonon mode assignment

In spite of the fact that this study is performed with powdered samples, the phonon mode assignment is made easy by the knowledge of those phonons which are screened by the plasmon and belong, therefore, to the basal plane, and by comparison with cuprate and nickelate with the same structure. For the polarization parallel to the c axis, the mode with the (largest) dielectric strength of 18, which corresponds to the vibration of lead (bismuth) against oxygen, is found at 225 cm^{-1}. In this discussion, numeric data refer to the compound $Ba_{1.7}K_{0.3}Pb_{0.95}Bi_{0.05}O_{4-\delta}$. This is to be compared to 275 cm^{-1} in La_2NiO_4 and 240 cm^{-1} in La_2CuO_4 (dielectric strength 15).[14,15] The second mode is observed at 535 cm^{-1} and at a frequency again not very far from that, 574 cm^{-1}; both found in La_2NiO_4 and La_2CuO_4. Slightly lower frequencies found here are related to the larger mass of lead (bismuth) with respect to nickel or copper, taking into account that oxygen plays a dominant part in the reduced mass. This means that lattice force constants are comparable. The third mode predicted by group theory for this direction of polarization is unobserved. It was also hardly observed in La_2NiO_4 and La_2CuO_4 (see Refs. 13 and 14, and compare to Ref. 15).

Within the basal plane, we observe four modes at frequencies (102, 141, 176, 565) also systematically lower than those found in Ni (151, 224, 351, 656) or the Cu (162, 220, 363, 671) parent compounds. The sequence of oscillator strengths (4.9, 1.3, 1.3, 0.8) is also found compatible with what was observed previously (5.2, 1, 3.2, 0.34 for La_2NiO_4 and 4.9, 1.9, 2, 0.22 for La_2CuO_4). Both the lattice dynamics and the dielectric response thus appear compatible with that in the nickelate and cuprate compounds. This is of importance because complete phonon dispersion curves have been measured by inelastic neutron scattering in both crystals,[16,17] and analyzed with a shell model, which will be most helpful in the discussion.

The large dielectric strength of the main polar mode at 225 cm^{-1} in $Ba_{1.7}K_{0.3}Pb_{0.95}Bi_{0.05}O_{4-\delta}$ in the direction parallel to the c axis should be emphasized. Even more important is to realize that this frequency is softened by

20 cm^{-1} when the compound becomes a conducting compound. The frequency shift reaches 30 cm^{-1} in $Ba_{1.7}K_{0.3}Pb_{0.9}Bi_{0.1}O_{4-\delta}$. We have checked that *the frequency shift is related to the change of carrier concentration* and not the cationic substitution. (The electronic concentration can be monitored by annealing under a controlled atmosphere as will be discussed below.) This may indicate that the apical oxygen is highly sensitive to the local electric field as will be discussed in Sec. V A. Also, the frequencies of the polar vibrations within the basal plane soften appreciably with the onset of metallicity. This is consistent with the softest character of the in-plane vibrations compared to La_2NiO_4 or La_2CuO_4. The average ratio of TO frequencies in lead-bismuth compared to nickel or copper compounds is indeed ~ 0.9 for the direction parallel to the c axis whereas it falls down to ~ 0.65 within the basal plane.

C. Effective charges

The modulus of the effective charge of oxygen evaluated within the basal plane, $|0.9e|$, is found much lower than in the direction parallel to the c axis, $|1.6e|$. These data refer to insulating compounds without potassium. They do not vary significantly with bismuth substitution. A similar situation was encountered in both lanthanum nickel and copper oxides.[13,14] This evaluation is a straightforward application of the principle of infrared spectroscopy which is based upon the coupling of an instantaneous dipole moment with the electric field of an electromagnetic radiation. The dipole moment is an effective charge times a relative atomic displacement. In practice, it is calculated from the experimental knowledge of the TO-LO splittings in the form[18]

$$\sum_j (\Omega_{j\mathrm{LO}}^2 - \Omega_{j\mathrm{TO}}^2)_p = (1/\varepsilon_v V) \sum_k (Ze)_{kp}^2 / m_k ,$$

where p denotes a direction of polarization and the summation on the right-hand side extends over all atoms k contained in the elementary volume V. ε_v is the dielectric constant of vacuum. The highly anisotropic effective charges found in La_2NiO_4 and La_2CuO_4 were thought to reflect the shorter cation-anion bond lengths within the conducting plane compared to the c-axis direction (see also the discussion in Ref. 18). Here, octahedra are nearly regular, $d_{M\text{-}O\parallel}/d_{M\text{-}O\perp} = 0.98 \pm 0.02$ (M=Pb,Bi) and the anisotropy of the effective charge may simply reflect the hybridization within the basal plane. Injection of charge carriers enhances the effect (metallicity added to covalence) with a modulus of the oxygen effective charge which decreases to $|0.69e|$ in $Ba_{1.7}K_{0.3}Pb_{0.95}Bi_{0.05}O_{4-\delta}$ and even down to $|0.64e|$ in $Ba_{1.7}K_{0.3}Pb_{0.9}Bi_{0.1}O_{4-\delta}$ in the conducting plane. A decrease of the oxygen effective charge with the increase of charge-carrier concentration was also observed in La_2NiO_4 based on the same method.

D. Electronic concentration

Compared to copper-based oxide superconductors, the plasma frequency is low and the electronic concentration is estimated to be in the range $1-3 \times 10^{20}$ cm^{-3} for the compound $Ba_{1.7}K_{0.3}Pb_{0.95}Bi_{0.05}O_{4-\delta}$. In this calculation, the carrier effective mass is assumed to be of the same order of magnitude as that of other high-T_c oxide superconductors. In $Ba_{1.7}K_{0.3}Pb_{0.9}Bi_{0.1}O_{4-\delta}$, the carrier concentration reaches $\sim 4 \times 10^{20}$ cm^{-3}. But this estimation implies a large error bar (absolute uncertainty 50%, but the relative accuracy is better).

If each potassium atom provides one free carrier, their expected number corresponding to the composition with 0.15 atm.% of potassium would be 2.4×10^{21} cm^{-3}. The actual electronic concentration is found at least 5 times lower. Annealing of this compound at 450 °C under oxygen increases this value, but to a level which remains below the expected value. To compensate this discrepancy, the charge balance may be achieved via oxygen vacancies or oxidation of bismuth to the formal valence +5. Since Bi^{5+} is smaller than Bi^{3+}, we would then expect a decrease of the unit-cell parameters. Experimentally, the unit-cell parameter a is found weakly sensitive to the insulator-metal phase transition (0.2% at most). A thermal treatment under reducing atmosphere (nitrogen or argon) decreases **a** whereas reoxidizing increases it, but only by 0.7%. Note that an eventual slight zigzag of M-O bonds within the a-b plane would minimize a and would not be detected by x-ray diffraction.

IV. SUPERCONDUCTIVITY

One of the problems which is raised by this study is the possible existence in our samples of impurity perovskite phase $BaPb_{1-y}Bi_yO_3$ which is known to superconduct when $0.05 \leq y \leq 0.35$ with a maximum $T_c = 13$ K for $y = 0.25$,[20] and may give spurious signature of superconductivity. [We did not succeed in preparing $(Ba,K)BiO_3$ with the same sol-gel route.] We have measured, therefore, the magnetic susceptibility of powders of perovskite compounds for several values of y, *prepared with the same method and in the same conditions of observations as the layered materials studied presently*, for comparison. Results are shown in Fig. 4. In the perovskite compounds, we recover the onset of supeconductivity at 12 K for $y = 0.3$, 10 K for $y = 0.2$, and 7 K for $y = 0.1$. This is consistent with published data.[21] With the susceptometer with which the measurements have been performed, a magnetic field of 450 G is required to get an appropriate signal-to-noise ratio. We attribute the relative weak amplitude of the negative part of the susceptibility observed in perovskite and layered compounds to the fact that, most likely, the critical field H_{C1} is below the field of 450 G under which the experiments have been performed. We believe, therefore, to observe bulk superconductivity but limited to those regions outside vortices, as in any type II superconductor above H_{C1}. In brief, the modest amplitude of the susceptibility is limited by the unavoidable conditions of our experiment and not by the chemistry of the materials which appear as single phase by x-ray diffraction.

A first signature of superconductivity below 9 K was observed for $x = 0.3$ and $y = 0.05$ (T_c's reported here correspond to the onset of superconductivity). T_c reaches 12.5 K for $x = 0.3$ and $y = 0.1$. This last compound

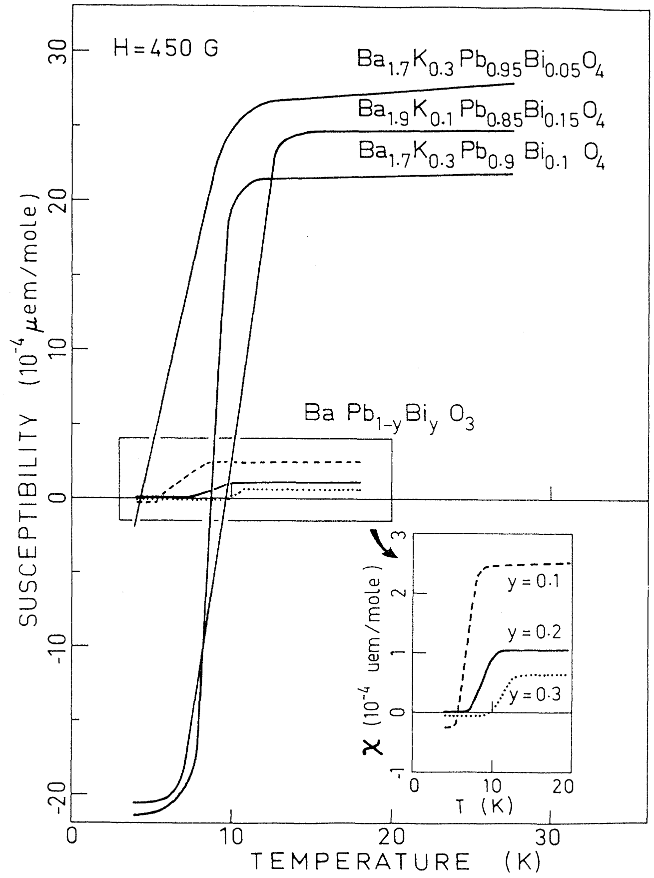

FIG. 4. The temperature dependence of the magnetic susceptibility of the tetragonal conducting compounds compared to that of perovskites measured in the same conditions.

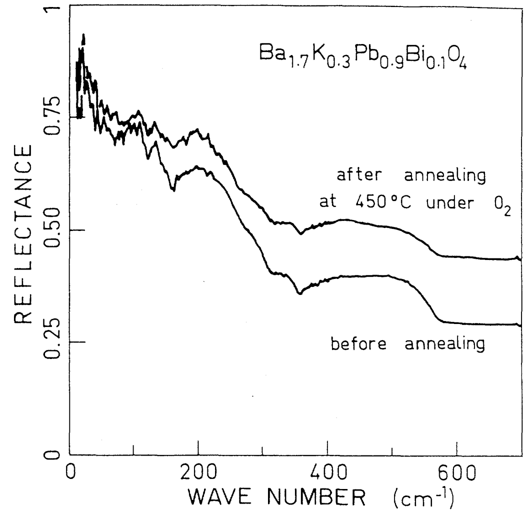

FIG. 5. Annealing at 450 °C under oxygen increases the plasma background level and increases the rate of screening of phonons.

which annealed to 450 °C under oxygen, shows higher charge-carrier concentration which manifests itself by (i) larger screening of phonons by plasmon (Fig. 5) and (ii) decrease of magnetic susceptibility in the normal phase down to a level as low as in $BaPb_{0.9}Bi_{0.1}O_3$. *T_c of the annealed compound is depressed down to 6* K. One possible explanation is that the treatment under oxygen not only fills the oxygen vacancies but also forces the formal bismuth valence to +5 to ensure electric neutrality, and the concomitant deficiency of Bi^{3+} would be detrimental to superconductivity. We decided, therefore, to decrease the potassium in subsequent syntheses. The sample with $x=0.1$ and $y=0.15$ shows superconductivity below 14 K.

We emphasize that all compounds studied in these experiments have been checked by x-ray diffraction to show a single phase (perovskite or tetragonal) as shown in Fig. 2. The amplitude of the response in samples with the tetragonal structure which is larger than that of perovskite compounds by a factor as large as 10–20 in the normal phase shows that the result has nothing to do with perovskite phase impurities. More interesting is to emphasize that, given a bismuth rate, *T_c is found larger by a factor of roughly 2 in a bi-dimensional structure compared to the cubic perovskite.* And this is obtained in spite of the fact that the charge-carrier concentrations remain lower in our tetragonal samples compared to perovskite compounds. This is also seen in Fig. 4 with the much lower levels of magnetic susceptibility in the normal phase of more metallic perovskite compounds, and confirmed by the respective plasma frequencies and the degree of phonon screening they induce.

V. DISCUSSION

A. A model of harmonic to anharmonic crossover

The schematic plot of Fig. 1 refers to the BCS formula

$$T_c \propto \Omega \exp[-1/\lambda N(E_F)] \ .$$

Since the oxygen breathing vibrational mode is a promising candidate to explain superconductivity, at least in compounds like $Ba(Pb,Bi)O_3$ or $(Ba,K)BiO_3$,[22] and since oxygen is light, one may wonder whether the T_c, found higher than in conventional superconductors for the oxides of the upper part of the diagram, is related to BCS predictions via the prefactor Ω. Within a *harmonic* description, an approximation inherent to the BCS formalism, the dependence of a phonon frequency upon the reduced atomic mass M is

$$\Omega \propto M^{-\alpha} \ ,$$

with $\alpha = 1/2$. The search for accurate isotope exponents during the five past years was aimed to check the validity of the BCS prediction. Their departure from 0.5 as T_c increases weakens the argument that harmonic vibrations of oxygen would play a major role. Also, the argument that data of several oxides lie within the central region of conventional superconductors in Fig. 1 rules out this over simple view. Another "booster" might be an exceptionally large electron-phonon coupling λ in certain oxides.

Data of Sec. III B support this conjecture (see also the discussion in Ref. 19). The analysis of ferroelectric properties of oxidic perovskites concluded to the origin of the phenomenon in the large anisotropic polarizability of oxygen.[23] The possible connections between the origins of the phenomena of ferroelectricity and superconductivity in oxides derived from the perovskite structure, have been discussed by several authors.[24–27] Note, however, that strontium titanate lies in the central region, far from the high-T_c domain. Apart from Ba(Pb,Bi)O_3 or (Ba,K)BiO_3, for which the isotope exponent is consistently not far from BCS predictions,[22] the general opinion is that pairing of electrons of the Cooper pairs via phonons cannot explain very high T_c's. A few authors, however, defend the opposite thesis,[28] and the community did not arrive to any consensus yet. The clue is currently searched in the phonon dispersion curves. But the situation is not entirely clear for a lack of *large* single crystals necessary for *accurate* inelastic neutron scattering measurements. Available data show a general tendency at the softening of lattice branches with the increase of charge-carrier density in the family of oxides containing copper, among which specific compositions show the onset of superconductivity.[16,17] This tendency was shown in Sec. III B to hold at the Brillouin zone center for present materials too.

The progressive decrease of the oxygen isotope exponent observed in (Y,Br)BaCuO[2,3] may be understood within a model of harmonic to anharmonic crossover.[26,27] In high-T_c copper compounds, the apical oxygen is sitting sandwiched between a conducting plane and a reservoir sheet (Fig. 6). Apical oxygen sees, therefore, an electric field which increases with carrier concentration. This electric field may act on the oxygen polarizability to increase anharmonicity of motions implying apical oxygen, hence the decrease of the isotope exponent related to passage from parabolic well (harmonic vibration) to double-well potential. A double-well potential

$$V(x)=-ax^2+bx^4 ,$$

where a and b are positive coefficients, is the simplest way to describe a huge anharmonicity. Extended x-ray absorption fine structure (EXAFS) measurements[29] interpreted in terms of the double-well potential at the apical site support this model. Anomalously large dielectric strengths for certain modes polarized parallel to the c axis also support this conjecture.[27] Highly anharmonic "crenel"-like oxygen motions rather than harmonic sine vibrations are able to polarize the lattice more efficiently and, therefore, capture mobile charge carriers to higher temperatures. Several authors have shown that anharmonic interactions in general[30] and quartic anharmonicity in particular[31] do favor high T_c and decrease the isotope exponent. The fact that no clear-cut signature of mode softening has been observed in neutron scattering experiments until now does not rule out the mechanism proposed here. (i) Σ_1 phonon branches display large anticrossing behavior and signature of partial mode softening is difficult to visualize in this case. (iii) Harmonic models with screening of phonons within the basal plane have great difficulties in reproducing the experimental data. (iii) Unusually large line broadenings occur; even disappearance of the line at wave vectors where branches "anticross" have been observed.[16] (iii) More important within the scope of the present work, the prediction[32] (and observation in barium titanate)[33] of a double peak response related to a double-well potential, should be recalled. The response consists of an oscillatory component within one well which softens partially and saturates at a finite frequency, and a long time scale corresponding to jumps from one well to another. This second component is the signature of the double-well potential and is conjectured to be one possible origin of low isotope exponent and increased efficiency of superconductivity.

Does our anharmonic model apply to 3D lead-bismuth compounds? Bismuth (also antimony) is sitting at a +4 site but Bi^{3+} and Bi^{5+} configurations would be chemically more stable. The relaxation motion which periodically exchange a supposed chain of Bi^{3+}-Bi^{5+}-Bi^{3+}-Bi^{5+} octahedra to the reverse configuration Bi^{5+}-Bi^{3+}-Bi^{5+}-Bi^{3+} is nothing but the highly anharmonic component of an oxygen-breathing-type mode at the Brillouin zone boundary. Indeed Bi^{3+}-O are longer than Bi^{5+}-O bond lengths. This periodic motion favors superconductivity. In other words, the periodic fluctuation of bond length renormalizes the instantaneous bonding itself, and induces a huge electron-"phonon" coupling. Here, the wording "phonon" refers to an oxygen breathing-type fluctuation having a time scale longer than conventional harmonic phonons, just the second time scale predicted by motions in a double-well potential.[32] It should manifest itself by an oxygen isotope exponent lower than 0.5, which was just observed.[34] The model of crossover from harmonic to

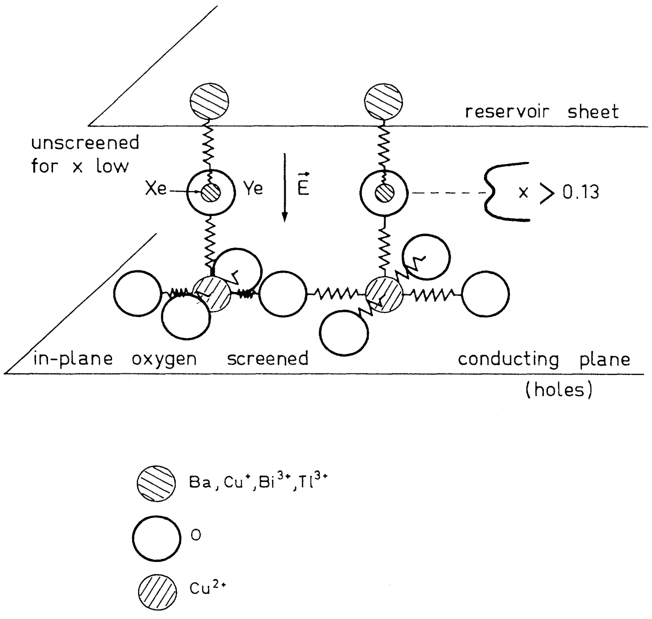

FIG. 6. A schematic plot of the conjectured origin of crossover from harmonic to highly anharmonicity regimes related to the increase of electronic concentration in the conducting plane of bi-dimensional systems.

highly anharmonic regime monitored by the charge-carrier concentration is thus consistent with the two kinds of oxides (bismuth-antimony perovskites or layered copper) of the upper part in the diagram Fig. 1. And *only the oxides among those plotted in Fig. 1, which fulfill the criteria developed in the model, do appear in the upper "high-T_c" regime.*

B. Application of the model to layered lead-bismuth oxides

The infrared reflectivity study has indicated that the trends of the lattice dynamics and the bi-dimensionality of conducting properties previously observed in nickel and copper oxides with the same structure, also apply in layered lead-bismuth oxides. We therefore expect enhanced anharmonicity related (i) to the existence of apical oxygen sitting in sandwich between an insulating sheet and a conducting plane, and (ii) to dynamic bismuth disproportionation. If anharmonicity does play a part in the mechanism of high-T_c superconductivity as conjectured by the model developed in the previous paragraph, then T_c should be enhanced with respect to the perovskite compounds. The results reported in Sec. IV show that the experiments support this expectation (doubling of T_c). The effect is even more striking if one realizes that such a high T_c is obtained with a lower charge-carrier concentration compared to the perovskites. Remember indeed that the perovskite $BaPbO_3$ is metallic whereas Ba_2PbO_4 is an insulator, and our bismuth concentrations are low. We face, however, several problems which prevent a more convincing demonstration. (i) Increasing the bismuth rate would be highly desirable but difficulties of synthesis are not overcome yet. Mattheiss[35] suggests that $Ba_{2-x}K_xBiO_4$ would be a promising high-T_c candidate, consistent with the experimental trend reported here, provided it could be elaborated.[7] (ii) The charge-carrier concentrations remain modest. As discussed in Ref. 8, the increase of the ratio (insulating sheets)/(conducting planes) in barium lead (bismuth) oxides is accompanied by a slight increase of the Pb-O bond length. The concomitant decrease of the metal-oxygen hybridization weakens the incipient metallicity of the bonding. As a result, large charge-carrier concentrations become hardly accommodated.

Preliminary measurements of the temperature dependence of infrared reflectivity spectra indicate little dependence of the plasma frequency on temperature, consistent with a metallic-type behavior. Electrical conductivity measurements on sintered materials (not yet available as mentioned previously) are planned in the future. Preliminary observations[36] indicate that the resistivity does not vary much upon cooling, consistent with the small upshift of the plasmon. In La_2NiO_4, the behavior is semiconducting (thermally activated) and the rapid decrease of the plasma frequency upon cooling[14] prevents the compounds to become superconductor. Conversely, the situation in the present layered lead-bismuth oxides is comparable to La_2CuO_4 which does not show much temperature dependence of the plasma frequency.[14] This is consistent with the fact that $BaPbO_3$ shows metallic properties too. The resistivity measurement performed on a sintered sample with $x=0.3$, $y=0.1$ also indicated onset of an abrupt decrease at 12.5 K, consistent with magnetic susceptibility measurements. The decrease is not sharp enough to ensure zero resistivity at liquid-helium temperature.

VI. SUMMARY

With no superconductivity reported in $Ba_4Pb_3O_{10}$,[9] nor in $(Ba,K)_3Bi_2O_7$,[37] the discovery of the first family of layered oxide superconductors without magnetic ion is worth mentioning. We have shown that superconductivity may be found in a compound isostructural of La_2CuO_4 but in absence of antiferromagnetic or related magnetic interactions. Superconductivity is obtained at a temperature which is roughly twice as large as in the cubic perovskite with the same bismuth rate. This is achieved in spite of the fact that the carrier concentration estimated from both Drude reflectivity and magnetic susceptibility level in the normal phase is significantly lower than in the perovskite analogues. The bi-dimensionality of the structure is thus confirmed to be a favorable ingredient and results support our anharmonic model which focus in particular on the specific role possibly played by the apical oxygen and dynamic bismuth disproportionation.

ACKNOWLEDGMENTS

Part of this work was performed under European Economic Community Contract ESPRIT Basic Research 3327. Kind assistance of J. M. Bassat, P. Odier, and P. Odier, and P. Simon and technical help of A. Blin, J. Coutures, G. Jouan, and N. Raimboux is acknowledged. We thank Dr. P. Odier and Dr. P. Echegut for a critical reading of the manuscript. One of us (M.L.) acknowledges financial support from the Regional Council (Région Centre).

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[1] G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2] J. P. Franck *et al.*, Phys. Rev. B **44**, 5318 (1991).

[3] H. J. Borneman and D. E. Morris, Phys. Rev. B **44**, 5322 (1991).

[4] M. Ronay, M. A. Frisch, and T. R. McGuire, Phys. Rev. B **45**, 355 (1991).

[5] M. K. Crawford *et al.*, Phys. Rev. B **41**, 282 (1990).

[6] B. Batlogg, in *Proceedings of the International Conference on Materials and Mechanisms of Superconductivity High Temperature Superconductors III, Kanazwa* [Physica C **185**, 18 (1991)].

[7] M. Licheron, F. Gervais, J. Coutures, and J. Choisnet, Solid State Commun. **75**, 759 (1990).

[8] M. Licheron and F. Gervais, Mater. Sci. Eng. B **6**, 61 (1990).

[9] W. T. Fu *et al.*, Solid State Commun. **70**, 1117 (1989); X. Qu *et al.*, J. Less-Common Metals **165**, 948 (1990).

[10] A. Douy, patent FR8803370 (1988).

[11] P. E. Sulevski, T. W. Noh, J. T. McWhirter, and A. J. Sievers, Phys. Rev. B **36**, 5735 (1987).

[12] F. Gervais, in *Infrared and Millimeter Waves,* Vol. 8, edited by K. J. Button (Academic, New York, 1983), pp. 279–339.

[13] J. M. Bassat, P. Odier, and F. Gervais, Phys. Rev. B **35**, 7126 (1987).

[14] F. Gervais, P. Echegut, J. M. Bassat, and P. Odier, Phys. Rev. B **37**, 9364 (1988).

[15] R. T. Collins, Z. Schlesinger, G. V. Chandrashekhar, and M. Schafer, Phys. Rev. B **39**, 2251 (1989).

[16] L. Pintschovius, J. M. Bassat, P. Odier, F. Gervais, G. Chevrier, W. Reichardt, and F. Gompf, Phys. Rev. B **40**, 2229 (1989).

[17] L. Pintschovius, in *Proceedings of the International Conference on Materials and Mechanisms of Superconductivity High Temperature Superconductors III, Kanazawa* [Physica C **185**, 156 (1991)].

[18] F. Gervais, Solid State Commun. **18**, 191 (1976); F. Gervais and H. Arend, Z. Phys. B **50**, 17 (1983).

[19] S. Tajima *et al.*, Phys. Rev. B **43**, 10 496 (1991).

[20] A. W. Sleight, J. L. Wilson, and P. E. Bierstedt, Solid State Commun. **17**, 27 (1975).

[21] J. C. Phillips, *Physics of High-T_c Superconductors* (Academic, Orlando, 1989).

[22] M. Shirai, N. Suzuki, and K. Motizuki, J. Phys. Condens. Matter **2**, 3553 (1990); O. V. Ivanov, E. G. Maksimov, and I. I. Mazin, Solid State Commun. **76**, 1267 (1990); A. I. Liechenstein *et al.*, Phys. Rev. B **44**, 5388 (1991).

[23] R. Migoni, H. Bilz, and D. Baüerle, Phys. Rev. Lett. **37**, 1155 (1976); H. Bilz *et al.*, Ferroelectrics **25**, 339 (1980); F. Gervais, Jpn. J. Appl. Phys. **24-2**, 198 (1985).

[24] K. A. Müller, Z. Phys. B **80**, 193 (1990).

[25] A. Bussman-Holder, A. Simon, and H. Büttner, Phys. Rev. B **39**, 207 (1989).

[26] F. Gervais, in *Les Nouveaux Supraconducteurs,* edited by E. Lavoiser (Lavoiser, Paris, 1991).

[27] F. Gervais, Mater. Sci. Eng. B **8**, 71 (1991); Ferroelectrics **130**, 117 (1992).

[28] R. E. Cohen, W. E. Pickett, and H. Krakauer, Phys. Rev. Lett. **64**, 2575 (1990); Y. Shiina and Y. O. Nakamura, Solid State Commun. **76**, 1189 (1990); W. Pint and E. Schachinger, Phys. Rev. B **43**, 7664 (1991).

[29] S. D. Conradson *et al.,* Science **248**, 1394 (1990); J. Mustre de Leon *et al.*, Phys. Rev. Lett. **65**, 1675 (1990).

[30] N. M. Plakida *et al.*, Europhys. Lett. **4**, 1309 (1987); J. R. Hardy and J. W. Flocken, Phys. Rev. Lett. **60**, 2191 (1988); S. Flach *et al.*, Solid State Commun. **75**, 647 (1990); M. Frick *et al.*, Z. Phys. B **82**, 339 (1991).

[31] T. Galbaatar *et al.*, Physica C **176**, 496 (1991); K. Nasu, Phys. Rev. B **44**, 7625 (1991).

[32] S. Aubry, J. Chem. Phys. **62**, 3217 (1975); **63**, 3392 (1976).

[33] K. A. Müller, Y. Luspin, J. L. Servoin, and F. Gervais, J. Phys. Lett. **43**, 537 (1982).

[34] D. G. Hinks *et al.*, Nature **335**, 419 (1988); H. C. Zur Loye *et al.*, Science **239**, 3553 (1990); B. Battlogg *et al.*, Phys. Rev. Lett. **61**, 1670 (1990); C. K. Loong *et al.*, Phys. Rev. Lett. **66**, 3217 (1991).

[35] L. F. Mattheiss, Phys. Rev. B **45**, 12 528 (1992).

[36] J. M. Bassat (private communication).

[37] R. J. Cava *et al.*, Phys. Rev. B **44**, 9746 (1991).