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A New Modulated Structure in Pb-doped Bi-Ca-Sr-Cu-O Superconductor

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A new modulated structure has been observed in a Pb-doped Bi-Ca-Sr-Cu-O superconductor (Tc,0=105K), in addition to the incommensurate modulated structure reported by several researchers. This new modulation occurs in the b*-direction and shows up as satellite spots to each of the original diffracted spots. Upon cooling to 88K the diffraction spots due to the original modulation disappear, while the spots due to the new modulation remain. In the case of the un-doped samples, the modulation does not disappear upon cooling to 30K, which is below the Tc,0 of the sample (~75K).

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Recently superconductivity has been observed above 100K in two classes of ceramics, namely Bi(Pb)\textendash Ca-Sr-Cu-O\textdegree and Tl-Ba-Ca-Cu-O\textdegree. While in the case of the Tl compounds zero resistance has been obtained at 125K, in the case of the Bi compounds zero resistance has been obtained only by the addition of small quantities of PbO as a sintering additive\textdegree. Without such an addition, steps are observed in the resistivity plot and zero resistance is obtained only around 75-85K. The corresponding susceptibility measurements show the presence of two superconducting phases with transitions around 110K and 80K respectively. One characteristic feature of the structure of the superconducting phase is the incommensurate modulation in the b-c plane. This is very pronounced in the case of the Bi compounds and weak in the case of the Tl compounds. The origin of this modulation is still not clear. Oxygen/vacancy ordering\textdegree, displacement of the Bi atoms\textdegree, misfit between the Bi-O layers and the perovskite layers\textdegree and the orientation of the Bi\textsuperscript{+3} lone pair\textdegree are some of the causes attributed to the modulated structure. The validity of some of these models is compared in ref.(9). In this communication, we report the existence of a new modulated structure in the case of Pb-doped superconductors.

The nominal composition of the un-doped sample was BiCaSrCu\textsubscript{2}O\textsubscript{y} and the doped sample was Bi\textsubscript{1.4}Pb\textsubscript{0.6}Sr\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{y}. They were processed under identical conditions already reported\textdegree. Samples for transmission electron microscopy (TEM) were prepared from bulk pieces by slicing a 50\textmu m piece followed by mechanical polishing and finally Argon ion milling at liquid nitrogen temperature. Specimens were ion milled at 6kV using a beam current of 0.4mA. The thinned samples were examined at room temperature, at liquid N\textsubscript{2} temperature and by using a liquid He bath at 30K in a Philips 400 TEM at 100kV. High resolution electron microscopy (HREM) was carried out in a JEOL 200CX instrument at 200kV. 

Fig.1(a) is a [100] zone axis selected area diffraction(SAD) pattern from the superconducting phase in the Pb-doped sample. As shown by several workers,
there is the "usual" incommensurate modulation of the structure along the b-c plane. The diffraction spots due to this incommensurate modulation are shown by circles(o) in Fig.1(a). In addition to this modulated structure, extra satellite spots are also observed, which are shown by crosses (x) in Fig.1(a). Corresponding to these extra spots, an intensity modulation is observed in the HREM image, Fig.1(b).

Selected area laser optical diffraction indicated that in some regions, only this new modulated structure exists, while in other regions this is superimposed on the "usual" incommensurate modulated structure. In Fig.1(b), the "usual" incommensurate modulated structure is marked as "A" while the new modulated structure is marked "B". The presence of the new modulated structure was also confirmed from observations of the higher order Laue zone (HOLZ) ring in the [010] zone axis orientation of convergent beam diffraction patterns. The periodicity along the beam direction in this orientation, calculated using the diameter of the first HOLZ, was found to be 45Å, thus corroborating the measurements from the diffraction pattern in Fig.1(a). The extra spots indicated in Fig.1(a) as crosses are not observed in the SAD pattern from the un-doped sample, Fig.2(a), which is the [100] zone axis SAD pattern. The corresponding
same region at 298K and 30K, Figs.4(a&b) respectively. By carrying out the cooling experiment with the electron beam turned off (rather than completely defocussed), it was ensured that the disappearance of the modulation with time was not due to electron beam damage. The same results as in Fig.3(a-c) were obtained. Apparently when both the modulated structures are simultaneously present in relatively small domains (a few hundred to a thousand Å) the “usual” pattern will vanish upon cooling, leaving only the new modulated structure. However, in the unleaded sample the “usual” modulation is present all over the crystal and is stable upto 20K. Note that some areas of the leaded sample show exclusively the new modulated structure even at room temperature, producing a diffraction pattern of the type shown in Fig.3(c). The origin and disappearance of this modulation is not understood at this time but from the diffraction patterns it is long range and may be associated with ordering. The disappearance of the “usual” modulated structure with time at 88K suggests that it may be electronically driven. This aspect needs further examination.

The absence of the new modulated structure along the b-direction in the unleaded sample indicates that this modulated structure is typical of the leaded samples. This new modulated structure can be rationalized on the basis of the difference in oxidation state of Bi (+3) and Pb(+2). Energy dispersive x-ray microanalysis of the c=38.2Å polytypoid in the unleaded and the leaded samples has shown that\(^{10}\): (i) Pb exclusively replaces Bi in the unit cell; (ii) the ratio Pb:Bi is always in the range of 1:3 to 1:4, i.e., the lead content varies from 20-25% of the total Bi content. Corresponding to the upper limit of 25%, one out of every four Bi atoms will be replaced by Pb due to which there will be a charge imbalance of +1. Thus, for every eight Bi atoms a charge imbalance of +2 is created. This can be neutralized by one of the following mechanisms: (i) by the loss of an O\(^{-2}\) ion for every eight oxygen ions, thus creating an oxygen vacancy. If this oxygen vacancy is ordered, then a superlattice corresponding to 8x(O-O distance along the b-direction, the direction of ordering), should be observed. The O-O distance
along the b-direction is 5.4Å, and hence the superlattice spacing is $8 \times 5.4 = 43.2\text{Å}$. This is very close to the experimentally measured value of 43.8Å, from the SAD pattern in Fig.1(a). This mechanism is quite feasible since the samples are prepared in air and loss or gain of oxygen from the atmosphere should be quite easy.

Another possible mechanism by which the charge imbalance of +2 can be neutralized is by the oxidation of a Bi$^{+3}$ to Bi$^{+5}$. Thus, one out of every 8 Bi atoms can be oxidized to the +5 state. If this Bi$^{+5}$ ion is ordered, then again a superlattice will occur with a periodicity of $8 \times (\text{Bi-Bi spacing})$, i.e., $8 \times 5.4\text{Å} = 43.2\text{Å}$. Such arguments concerning the formation of the +5 state from the +3 state to accommodate the presence of the +2 Pb ion, and the subsequent ordering of the +5 ion, have been put forward by Khachaturyan$^{11}$ to explain the superconducting properties of BaPb(Bi)O$_3$.$^{12}$ A third mechanism by which this can take place is by the increase in the oxidation state of the Cu-ions in the perovskite units that are sandwiched between the Bi-O bi-layers. In this case, however, the cause for a superstructure is not very transparent, although this may have significant implications in terms of the superconducting properties.

It has been postulated that the incommensurate modulated structure is due to the presence of a deformation of the Bi-O bi-layers, presumably due to the introduction of oxygen atoms or due to the misfit between the Bi-O bi-layers and the perovskite units. The fact that the new modulated structure exists in some regions of the sample without the existence of the incommensurate modulated structure, suggests that the difference in the sizes of the Pb$^{+2}$ ion (1.20Å) and the Bi$^{+3}$ ion (0.96Å) may also have an important role to play, in addition to the charge difference, in the existence or absence of the incommensurate modulated structure. This 25% difference in ionic radii between Bi$^{+3}$ and Pb$^{+2}$, may be sufficient to reduce the effect of the deformation of the Bi-O bi-layers, thus reducing the feasibility for the formation of a deformation induced modulated structure. Detailed experiments, in which the nominal Pb content of the alloy has been systematically increased, are in
progress, in order to study the effect of different lead concentrations on the nature of the two different modulations. However, the disappearance of the incommensurate modulation below the \( T_c \) for the leaded sample while still persisting in the unleaded sample suggests that its existence may not be related to superconductivity in this class of materials. The increased zero resistance temperature in the case of the leaded sample can be explained in terms of the connectivity of the 110K regions of the sample, due to the absence of lower \( T_c \) polytypoid structures adjacent to grain boundaries\(^{10}\).

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FIGURE CAPTIONS

FIGURE 1: (a) [100] Selected area diffraction (SAD) pattern from the lead doped sample showing the presence of extra satellite spots; (b) [100] zone axis high resolution image showing the co-existence of the "usual" incommensurate (regions marked A) and the new modulated structure (regions marked B) in the lead doped sample.

FIGURE 2: (a) [100] zone axis SAD pattern from the undoped sample showing the absence of satellite spots due to the incommensurate modulation; (b) high resolution image corresponding to (a), again showing only the incommensurate modulation.

FIGURE 3: (a) [100] SAD pattern from the leaded sample after 5 minutes at 88K; (b) 15 minutes after cooling to 88K; (c) 45 minutes after cooling to 88K. Note the progressive disappearance of the diffraction spots due to the "usual" incommensurate modulation.

FIGURE 4: (a) [100] SAD pattern from the unleaded sample; (b) SAD pattern from the same region as in (a) showing the unchanged diffraction pattern.
Figure 3(a-c)