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May 1988

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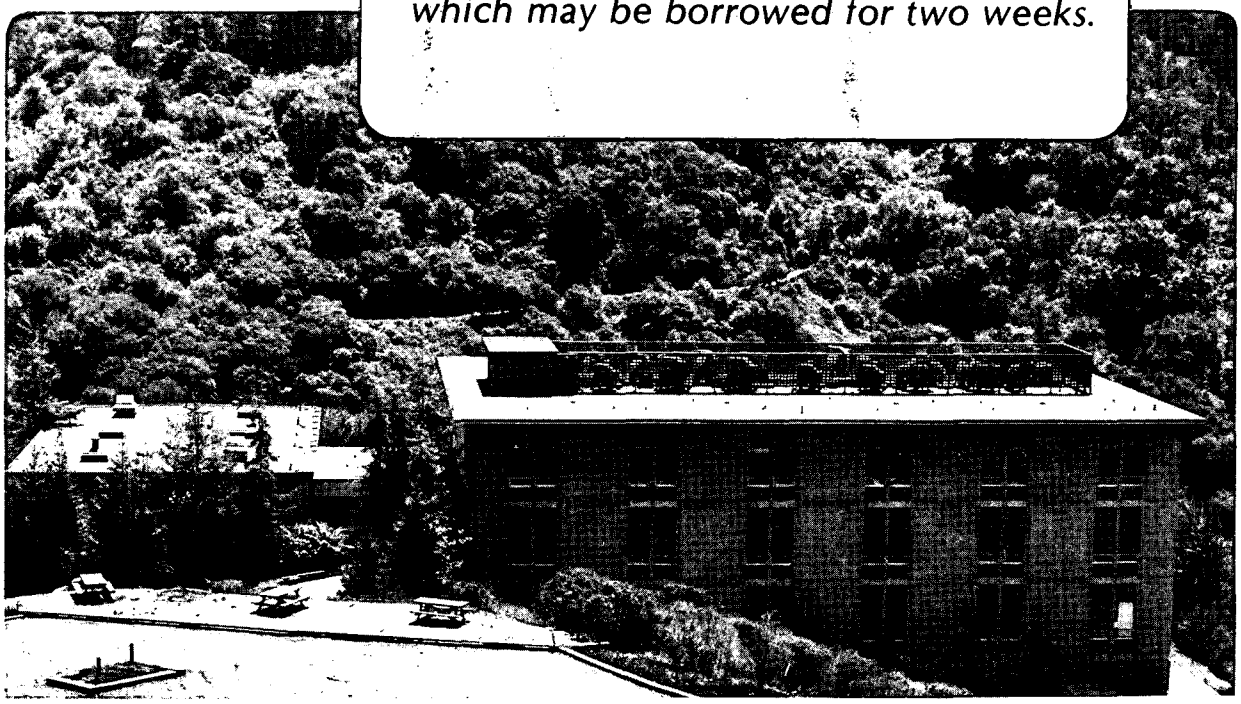

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POLYTYPOID STRUCTURE OF Pb MODIFIED Bi-Ca-Sr-Cu-O SUPERCONDUCTOR

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Pb addition has been found to improve the superconducting properties of a Bi-Ca-Sr-Cu-O superconductor. We report zero resistance at 104K in a $Bi_{1.4}Pb_{0.6}Ca_2Sr_2Cu_3O_y$ alloy with no steps in the resistivity. Pb replaces Bi in the unit cell, as determined by xray microanalysis. The superconducting phase has the same structure as the alloy without lead, with the c-parameter uniformly 38.2Å. The Cu + Ca content of these regions has also been found to be higher than in the un-doped sample, indicating the periodicity is determined by the composition leading to polytypoids. Such polytypoid structures appear to correlate well with the critical temperatures.

INTRODUCTION : The discovery of a new family of superconducting oxides, Bi-Sr-Cu-O by Michel et. al[1] has further fueled the excitement in this area of research since the initial discovery of the Y-Ba-Cu-O compounds. Further improvements by Maeda et. al[2] and Chu et. al[3] resulted in resistive and diamagnetic anomalies in the Bi-Ca-Sr-Cu-O system near 110K, although zero resistance was obtained only around 75-80K. Subsequently other groups have reported similar results, with zero resistance primarily occurring around 75-80K[4-8]. Previously we reported transmission electron microscopy (TEM) results[9,10] suggesting that the steps in the susceptibility and resistivity may be due to the presence of a compound with c=38.2Å along with the c=30.5Å compound. High resolution TEM showed that the regions with c=38.2Å exist as "slabs" inside the c=30.5Å regions. The c=38.2Å regions were richer in Cu+Ca than the c=30.5Å regions. Subsequently it has been found that the controlled addition of Pb to the alloy leads to the elimination of the resistive step, although the step in the diamagnetic susceptibility still remains[11]. In this letter, we report preliminary results of TEM experiments on the lead substituted samples.

The samples were prepared by the usual technique described in ref.(11). The alloy compositions and final sintering temperature and time are given in Fig.1, which shows the resistivity and susceptibility versus temperature plots for the two alloys. Note that the Pb-doped sample does not show a step in the resistivity while the un-doped sample does. Both the samples are comprised of almost similar fractions of the 110K and 75K polytypoids, as evidenced from the susceptibility plots.

Samples for TEM were prepared by the Argon ion milling technique under conditions described earlier[10], in order to obtain foils with the c-axis in plane. High resolution TEM (HREM) was carried out in a JEOL 200CX at 200kV and analytical TEM (AEM) was carried out in a Philips 400TEM at 100kV.

Figs.2(a&b) show HREM images of the superconducting phase in the un-doped and doped samples respectively, in the [310] zone axis. Since the sample tilt was limited to ±10°, lower index zone axes were not accessible in this microscope. In Fig.2(a), the regions with c=38.2Å and c=30.5Å are indicated. In an earlier paper also it was shown that such regions of c=38.2Å exist over several tens of unit cells. Fig.2(b) shows a HREM image in the case of the Pb-doped sample, in the [310] zone axis. The c=parameter was measured to be 38.2Å. This periodicity is very uniform unlike that in the un-doped sample which showed frequent variations in the c-parameter inside each grain. Fig.3(a) shows a lattice fringe image close to a grain boundary of the un-doped sample. It is seen that adjacent to the grain boundary the c-parameter is lower than that inside the grains. In the case of the Pb-doped sample, the c-parameter is uniformly 38.2Å upto the grain boundary, as evidenced from the lattice fringe image in Fig.3(b).

The existence of regions of different c-parameter periodicities can also be derived by convergent beam diffraction (CBED), as described previously[9,10]. CBED patterns were acquired under the same lens setting from both doped and un-doped samples. Fig.4(a) shows a [001] CBED pattern from the un-doped sample while (b) is a [001] pattern from the Pb-doped sample. The c-parameter determined from the HOLZ rings was 30.5Å for (a) and 38.2Å for (b), thus corroborating the HREM results. Another interesting feature in the pattern in Fig.4(a) is that the first order ring is broadened, suggesting that there is a distribution of c-parameters within the probe size of about 500Å. However, in the case of the Pb-doped sample, this is not observed, consistent with the observation of constant 38.2Å periodicity.

Energy dispersive xray (EDX) microanalysis of the two samples showed that the Cu+Ca content of the Pb-doped sample is higher in the c=38.2Å region than that of the c=30.5Å regions in the un-doped sample. The

quantitative data are given in Table I. The Cu+Ca content of this region agrees well with the composition reported for the 38.2Å region in the earlier paper[10]. It was also found that Pb occupies Bi sites in the unit cell. This phenomenon of adjustment of structural periodicity without change in crystal structure to accomodate compositional changes is not unusual in ceramic alloys and results in structures referred to as polytypoids[12].

DISCUSSION : In this paper it has been shown that the steps in the susceptibility remain while the steps in the resistivity disappear when Pb is added to the alloy. Inside each grain the composition and hence the c-parameter is uniform unlike the un-doped sample, which shows frequent fluctuations in the Cu+Ca content and the c-parameter[10]. In subsequent experiments, it has been found, by direct atomic imaging, that the increase in the c-parameter from 30.5Å to 38.2Å is due to the insertion of two Cu-O and two Ca layers inside the intergrowth structure, as speculated earlier by us and by several others[7,10,13-15]. Fig.5 shows a model of the structure consistent with the observed data. The 30.5Å and the 38.2Å periodicities differ only in the number of intercalated Cu+Ca layers in the structure. This is also consistent with the xray microanalysis results in Table I. It is important to note that it is possible, by suitable modification of the alloy composition (and heat treatment), to obtain a superconducting compound with a uniform composition comprising 3 Cu-O units between the Bi bi-layers.
The observation of a step in the susceptibility plot can be rationalized in terms of the presence of the two polytypoids with c=30.5Å (T_c~65-75K) and c=38.2Å(T_c~110K), either inside the same grain or as discrete grains of uniform c-parameters. The HREM results suggest that the latter is more likely in the case of the Pb-doped sample while both occur in the un-doped sample. The presence of the step in the resistivity plot in the

case of the un-doped sámple, suggests that the presence of regions of reduced c-parameter near the grain boundaries, Fig.3(a), lead to a loss of connectivity. Due to the homogeneous composition (and hence c-parameter),in the Pb-doped sample, Fig.3(b), connectivity between the grains is attained and the step in the resistivity plot vanishes.

ACKNOWLEDGEMENTS : This work is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under contract No. DE-AC03-76SF00098. The research at UC, San Diego is supported by the California MICRO program and the Hughes Aircraft Co. We also appreciate a grant-in-aid from Engelhardt Corporation which supports TEM specimen preparation.

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FIGURE CAPTIONS

Figure 1: A Plot of resistivity and susceptibility versus temperature for the two samples used in this study.
(O , _____ : $Bi_2Sr_2Ca_2Cu_4O_y$, 870-875°C, 72 hours) ;
(+ , _ _ _ _ : $Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_3O_y$, 860-865°C, 60 hours)

Figure 2: (a) [310] zone axis high resolution image of the un-doped sample showing the presence of interpenetrating regions of c=30.5Å and c=38.2Å. (b) [310] zone axis high resolution image of the Pb-doped sample showing a uniform c-parameter of 38.2Å.

Figure 3: (a) High resolution lattice fringe image of the un-doped sample showing the decrease in the c-parameter close to the grain boundary ; the 24Å spacing corresponds to the polytypoid with no Ca while the 30.5Å and 38.2Å correspond to the cation sequences shown in Fig.5. (b) high resolution lattice fringe image of the Pb-doped sample showing the uniform c-parameter upto the grain boundary.

Figure 4: (a) [001] zone axis convergent beam electron diffraction (CBED) pattern from the un-doped sample showing the higher order Laue zones (HOLZ) from the diameter of which the c-parameter was calculated to be 30.5Å ; (b) [001] zone axis CBED pattern from the Pb-doped sample from which the c=-parameter was calculated to be 38.2Å. Note the width in the diameter of the first order ring in (a) suggesting a range of c-parameters selected by the probe of nominal size of 500Å.

Figure 5: Schematic model showing the [001] cation stacking sequence in the Bi(Pb)-Ca-Sr-Cu-O alloy for (a) c=30.5Å and (b) c=38.2Å.

TABLE I

ELEMENT	UN-DOPED SAMPLE	Pb-DOPED SAMPLE
Cu	35.66	40.55
Ca	15.36	18.16
Sr	22.32	22.09
Bi	26.65	15.58
Pb	-- --	3.62

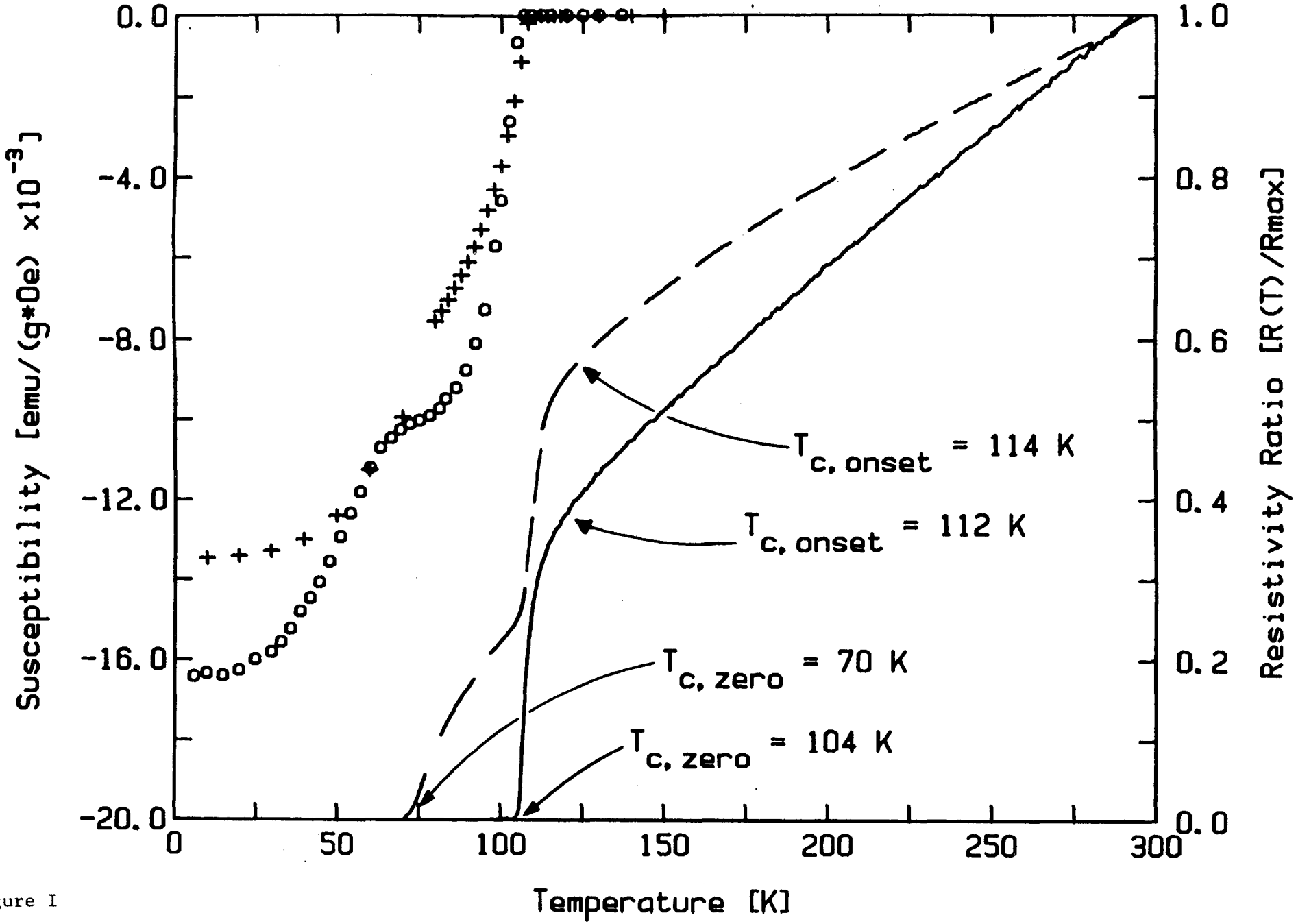

0.0
-4.0
-8.0
-12.0
-16.0
-20.0
Susceptibility [emu/(g*Oe) x10^{-3}]
1.0
0.8
0.6
0.4
0.2
0.0
Resistivity Ratio [R(T)/Rmax]
0
50
100
150
200
250
300
Temperature [K]
$T_{c, onset}$ = 114 K
$T_{c, onset}$ = 112 K
$T_{c, zero}$ = 70 K
$T_{c, zero}$ = 104 K

Figure I

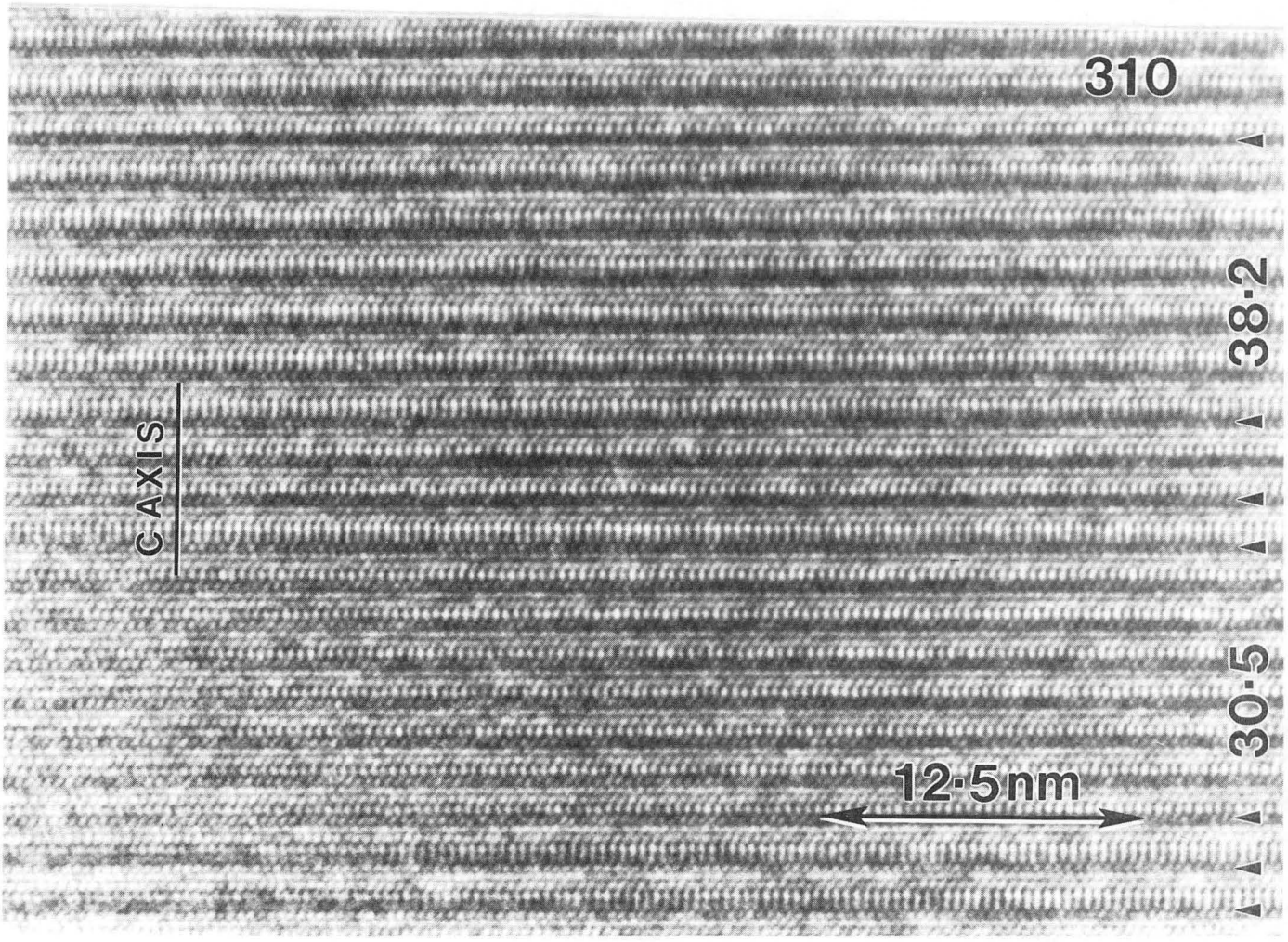


Figure 2(a)

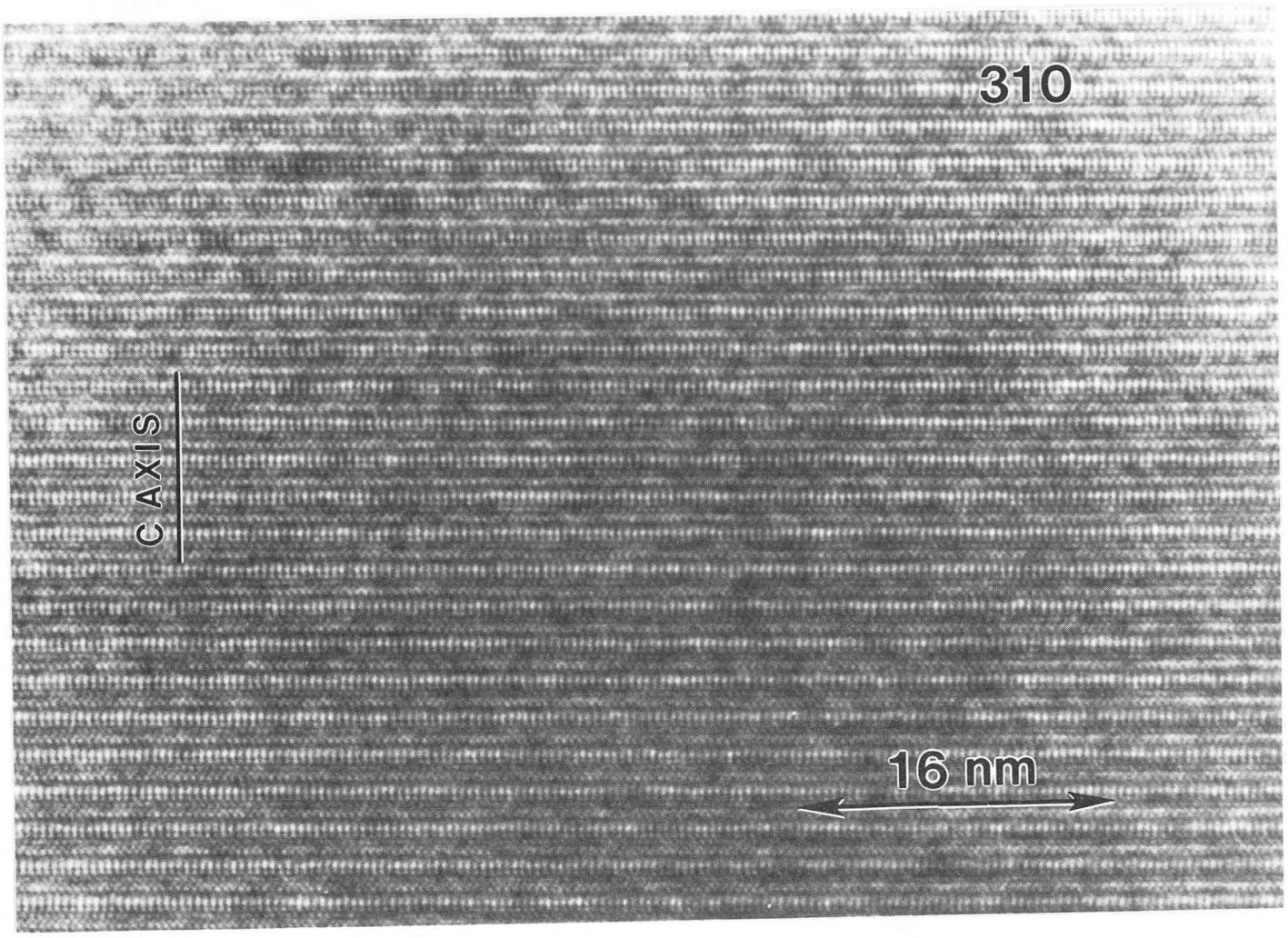
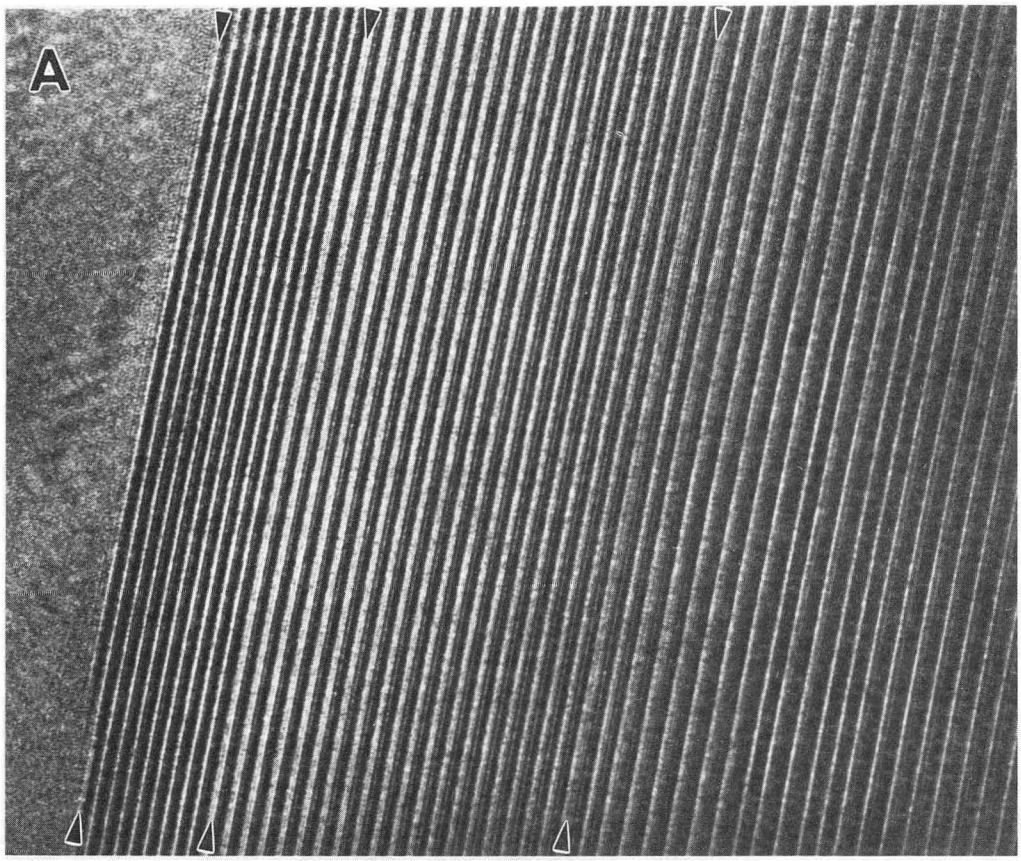


Figure 2(b)



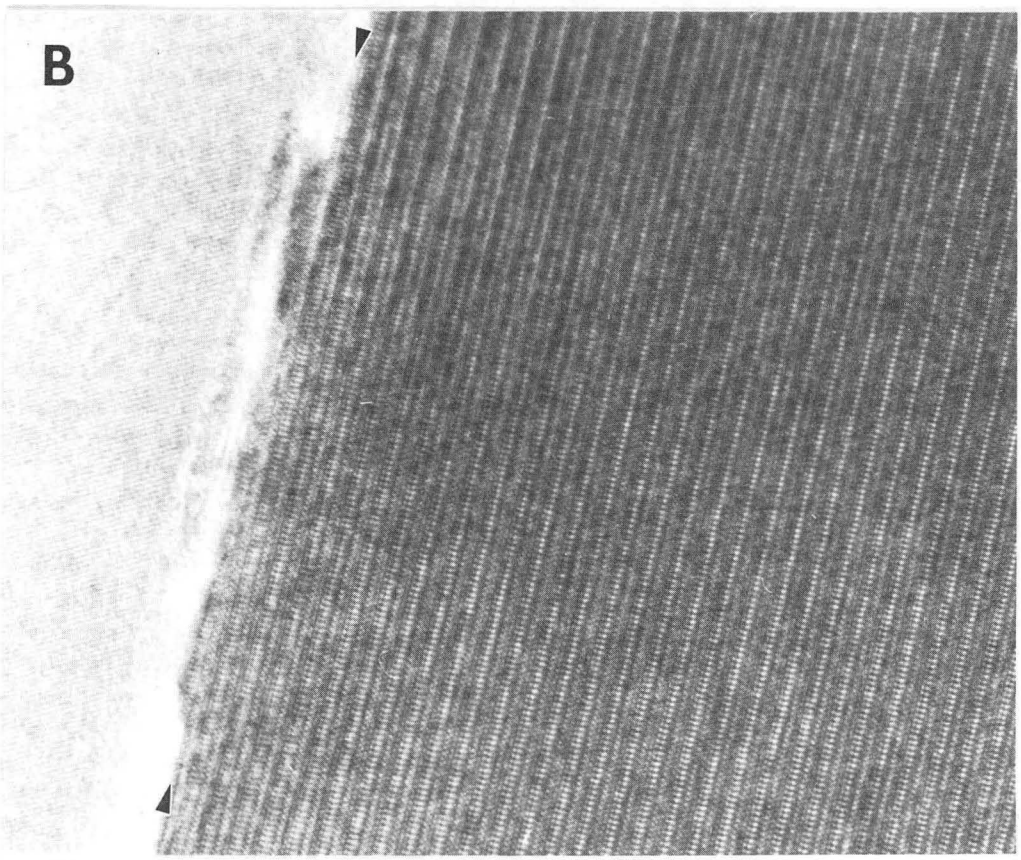
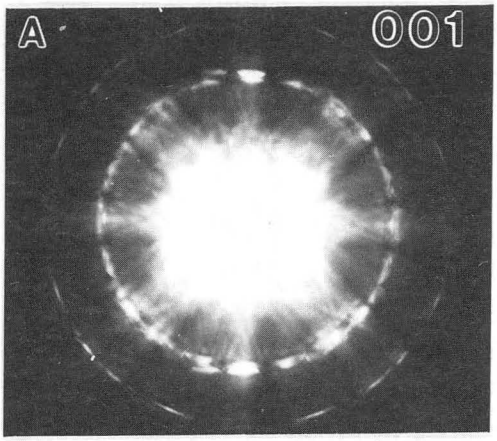


Fig. 3



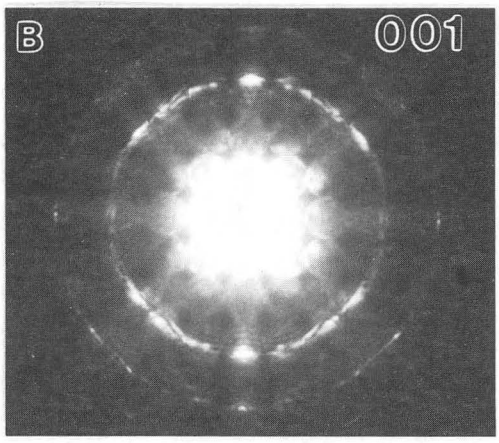


Figure 4

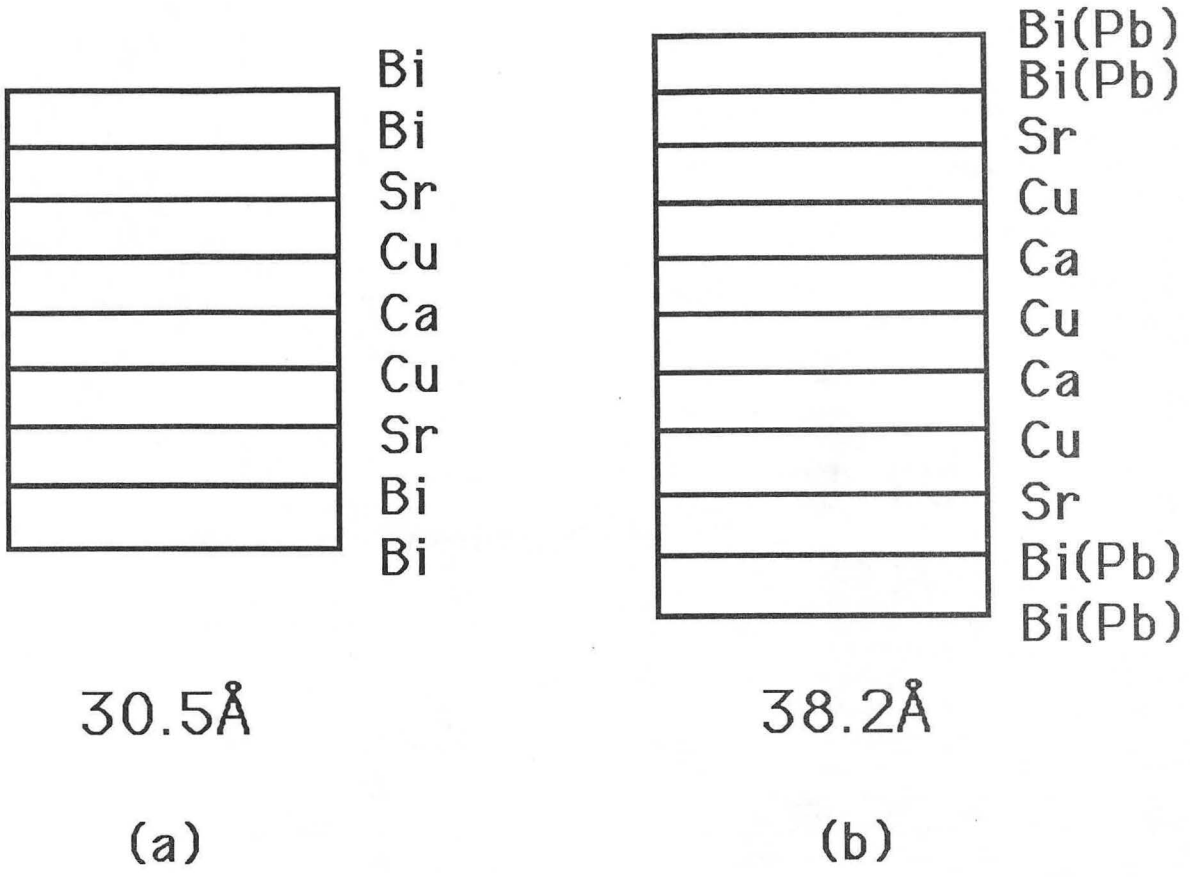

Bi
Bi
Sr
Cu
Ca
Cu
Sr
Bi
Bi
30.5Å
(a)
Bi(Pb)
Bi(Pb)
Sr
Cu
Ca
Cu
Ca
Cu
Sr
Bi(Pb)
Bi(Pb)
38.2Å
(b)

Figure 5

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