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Publication Date

1988-04-01

LBL-25103 c.2
Preprint

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Materials & Chemical Sciences Division

National Center for Electron Microscopy

Submitted to Applied Physics Letters

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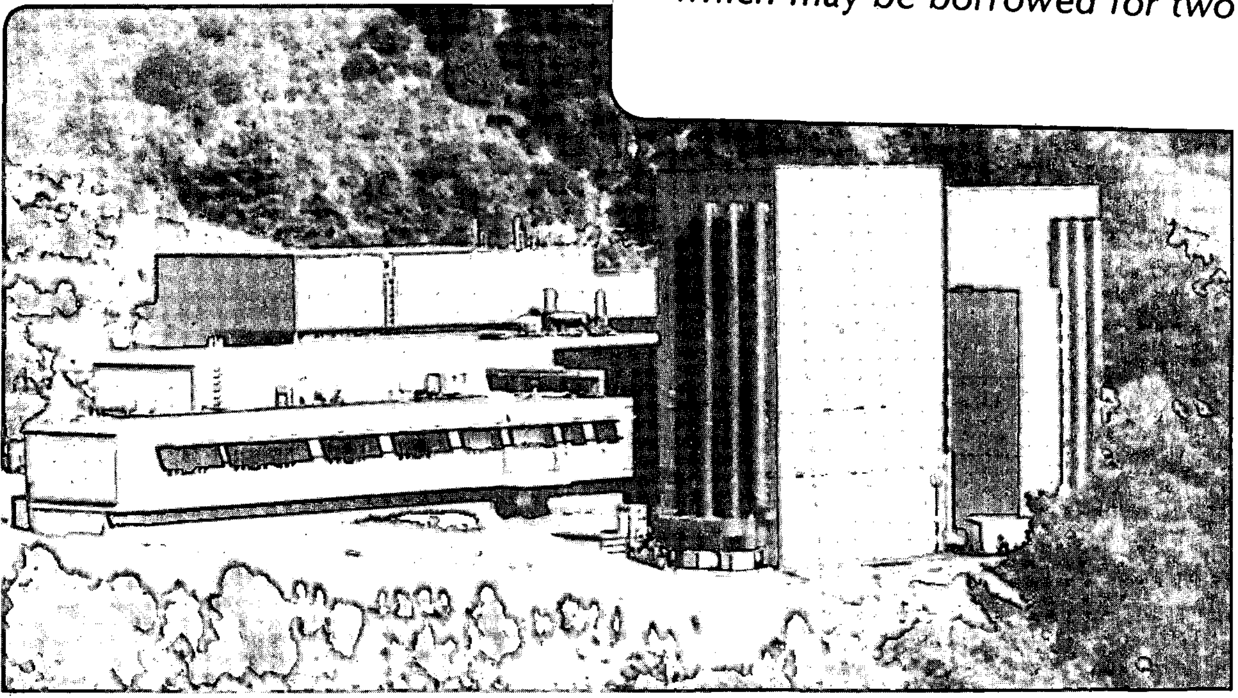
April 1988



Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

Further evidence for the presence of c=38.2Å phase in a Bi-Ca-Sr-Cu-O superconductor

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PACS No. 74.70-b

Results of high resolution electron microscopy, convergent beam electron microscopy and xray microanalysis on the high T_c phase are reported. Local inhomogeneities in the structure and composition have been observed along the c-direction. Both c=30.56Å ($8xa_p$) and c=38.2Å($10xa_p$) have been observed inside the same grain. The regions with the larger c-parameter correspond to regions with higher Ca and Cu concentration suggesting that the range of transition temperatures observed (85K to 115K) is due to the co-existence of such regions of c=38.2Å and c=30.56Å.

Recently, dramatic advances have been made in raising the transition temperature(T_c) of Cu-O based superconducting ceramics. One of the new classes of alloys in which transition temperatures higher than 100K have been obtained is the Bi-Ca-Sr-Cu-O system. It began with the discovery by Michel[1] et. al who found a compound with a T_c of 22K. Maeda et. al[2] and Chu et. al[3] obtained T_c of about 80K and later 115K. These results have been simultaneously reported by several other groups[4-8]. The orthorhombic structure of the class of compounds responsible for the high T_c consists of layers of Bi_2O_2 between which are sandwiched layers of Sr-O, Cu-O and Ca. The lattice parameters generally reported are a=5.4Å, b=5.39Å (with a modulation of 5x5.39Å) and c=30.56Å. However, in a recent communication[9], we have reported the presence of a compound with c=38.2Å, which shows qualitatively (through observation of the repulsion of the sample by a magnet), better superconducting properties. Shaw et. al[10] and Veblen et. al[11] have observed an incommensurate structure along the b-direction and have also suggested the possible existence of more than two perovskite layers between the Bi layers. Similarly, Parkin et. al[12] have suggested that the range of transition temperatures i.e., 80K to 115K, could be due to the presence of regions with extra Cu-O layers in addition to the two found usually. This increase in the number of Cu-O layers has been attributed by Grant[13] to be the cause of higher transition temperatures. Indeed, in the earlier communication[9], we reported results of convergent beam electron diffraction (CBED) and energy dispersive xray microanalysis (EDXS) wherein the c-parameter was determined to be 38.2Å , i.e., $10xa_p$, where a_p is the fundamental perovskite unit of 3.82Å. The Cu content was also higher than those reported by other workers. In this communication, we present further evidence for the presence of regions with c=30.56Å and c=38.2Å inside the same grain.

The samples were prepared by the usual method described in ref. (9) whichalso reports the characteristics of this sample. Samples for transmission electron microscopy (TEM) were prepared by sectioning the fired crystal parallel and normal to the c-axis. The thin sections were mechanically ground down to 50μm thickness and were Argon ion milled to electron transparency at 6kV at liquid nitrogen temperature. The samples wetre coated with a thin layer of carbon (about 100Å) to prevent damage in the microscope. CBED and EDXS experiments were carried out in a Philips 400TEM/STEM at 100kV. All standard precautions for CBED and microanalysis were taken. High resolution microscopy (HREM) was carried out in the Atomic Resolution Microscope at 800kV. Local diffraction patterns were obtained from the high resolution images by optical diffraction using a laser bench.

Fig.1 shows a high resolution image of two regions, G_1 and G_2. Region G_1 is in the [100] zone axis orientation, while region G_2 is in the [010] zone axis. Thus the two grains share the common c-axis. Of interest is the structure inside region G_1. It can be seen that the spacing of the c-planes is not uniform. Three discrete sub-regions, A,B,C, can be observed inside the region G_1. It should be noted that the change in the c-parameter is not periodic, i,e., the fluctuation is random (polytypoidic). Measurement of the c-parameter from the three sub-regions gave values of 30.4Å, 37.4Å and 37.4Å respectively. These values correspond, within the limits of the measurement error, to $8xa_p$ and $10xa_p$ respectively. To confirm this, optical diffraction patterns were obtained from each of these sub-regions and are shown in Fig.2(a-c) respectively. The patterns were obtained at the same camera length setting of the diffraction bench and hence represent the difference in lattice parameters. The difference between sub-regions A,B and C observed in the image is also reflected in the optical diffraction patterns, although the selected area diffraction pattern shows only a streaking along the c* direction. It is to be noted that the spacing of the Bi layers in region G_2 with the [010] zone axis is also non-uniform. The spacings of the c-planes alternate between 30.4Å and 37.4Å and also values in-between these two. This change in the periodicity along the c-direction is shown more clearly in the modulated type of image in Fig.3. In region A of this image the black spots, corresponding to the Bi layers are separated by three layers while in region B the black spots are separated by two layers. The corresponding optical diffraction patterns, shown in the inset, also reflect this difference in c-parameter.

This observation was independently confirmed by CBED experiments on samples with the c-axis normal to the foil. Fig.4(a) is an [001] zone axis pattern from one region while Fig.4(b) is a CBED pattern from a region quite close to it, inside the same grain. Use of the Higher Order Laue Zone (HOLZ)rings to measure the periodicity along the beam direction was alluded to in the earlier communication[9]. The details of the analysis is given in ref. (14) and will not be described here. In this case, the first and second order Laue zone rings were used to determine the c-axis spacing. The average c-spacing, within a probe of size 400Å, corresponding to Fig.4(a) was found to be 31.13Å while in the case of Fig.4(b) it was found to be 37.88Å. EDX spectra were also obtained from these two regions and are shown in Fig.5. From the ratios of the Bi:Cu peak heights, it can be clearly seen that the region corresponding to Fig.4(a) has lower Cu and Ca content compared to the region corresponding to Fig.4(b). This is shown in the chemical analysis shown in the right hand corner of Fig.5. In both cases, oxygen has not been detected since a Be window detector was employed. The difference in Cu+Ca content between the two regions, about 6at.%, is significantly higher than the error bars in the microanalysis. The modulation in structure due to local changes in composition are often seen in other ceramic systems, e.g., Al_2O_3-AlN[15] and Zirconia alloys[16]. However, the HREM images of layers between the Bi-layers are not well resolved indicating that these composition variations are not periodic. Further work is in progress.

DISCUSSION AND CONCLUSIONS

The presence of regions of different c-parameters inside the same grain has been conclusively demonstrated by HREM as well as CBED. It has also been shown by EDX microanalysis that the regions with larger c-parameter correspond to regions with a higher Cu+Ca content . This agrees with the observation of more than two layers between the Bi layers in the image shown in Fig.3. It is thus concluded that the increase in the c-parameter is due to the introduction of one or more extra Cu-O layers and also due to the introduction of extra Ca layers. Such variations in the composition and consequently the c-parameter were observed quite frequently during our experiments . It is however interesting that such an inhomogeneous composition distribution should occur locally inside a single grain. This may explain the range of transition temperatures that is generally observed for a polycrystalline sample. The existence of such inhomogeneities inside the grain may have implications in terms of nucleation of flux penetration, similar to the case of the twin interfaces in the 1-2-3 compounds. The observation of regions with an higher Cu+Ca content (and larger c-parameters) however suggests that it may be possible to tailor the composition and treatments such that the majority of the compound has the higher c-parameter or even larger c-parameters with the inclusion of more Cu-O layers. This, as has been pointed out by Grant[13], may be accompanied by an increase in the T_C.

ACKNOWLEDGEMENTS : Stimulating discussions with Professor R.Gronsky are and the technical assistance of Mr.C.Nelson are gratefully acknowledged. 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 work at UC, San Diego is supported by the California, MICRO program and Hughes Aircraft Co.

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FIGURE CAPTIONS

Figure 1 : High resolution image of two regions, G_1 and G_2 with the c-axis in the plane of the foil. Region G_1 is in the [100] zone axis while region G_2 is in the [010] zone axis. Note the non-uniform spacing of the c-planes in both the regions.

Figure 2: Laser optical diffraction patterns from the sub-regions A,B,C in region G_1. Note that the spacing in A is different from that in B and C for the same value of camera length.

Figure 3: High magnification image of region G_1 showing the difference in spacing along the c-direction due to the introduction of an extra plane between the Bi layers. Note that this change is not periodic.

Figure 4: (a) [001] CBED pattern from a region with lower Cu and Ca content ; (b) [001] CBED pattern from a region with higher Cu and Ca content. Note that the radii (and hence the c-parameter) of the first and second order Laue zones are not the same in both.

Figure 5: EDX spectra from the regions corresponding to Figures 4(a&b) along with the quantified data.

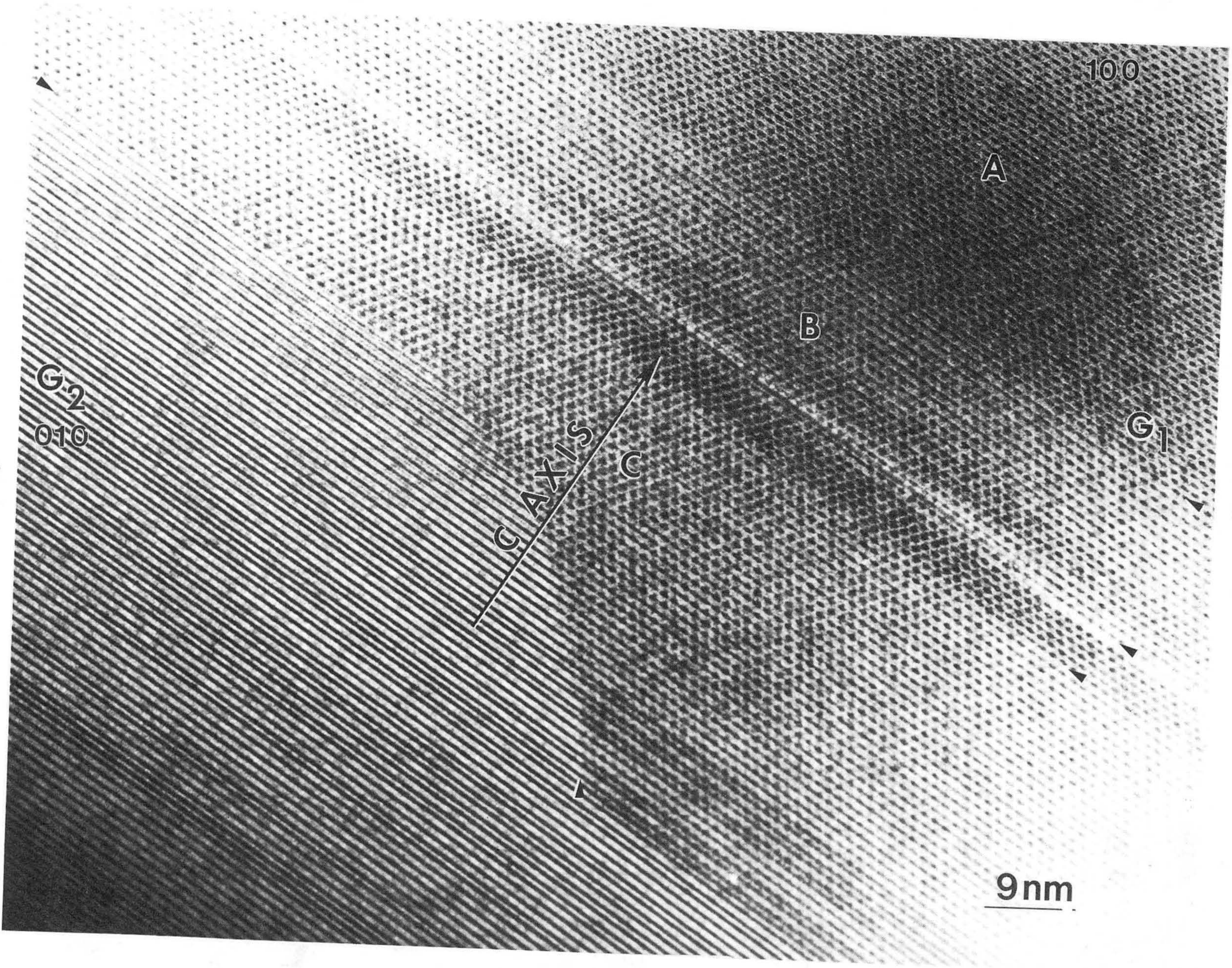


Fig. 1

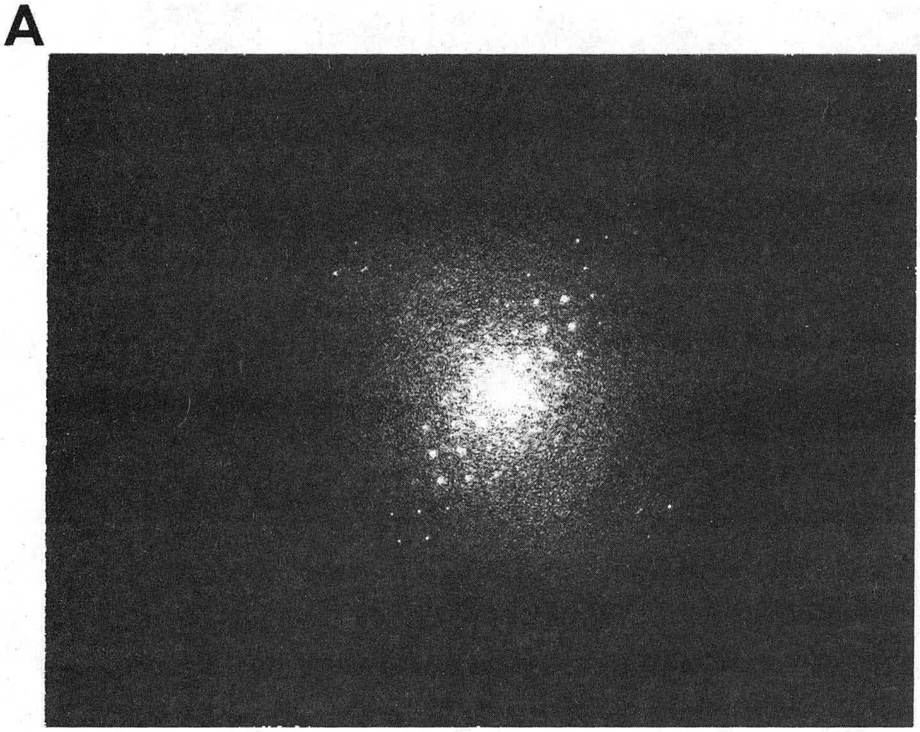
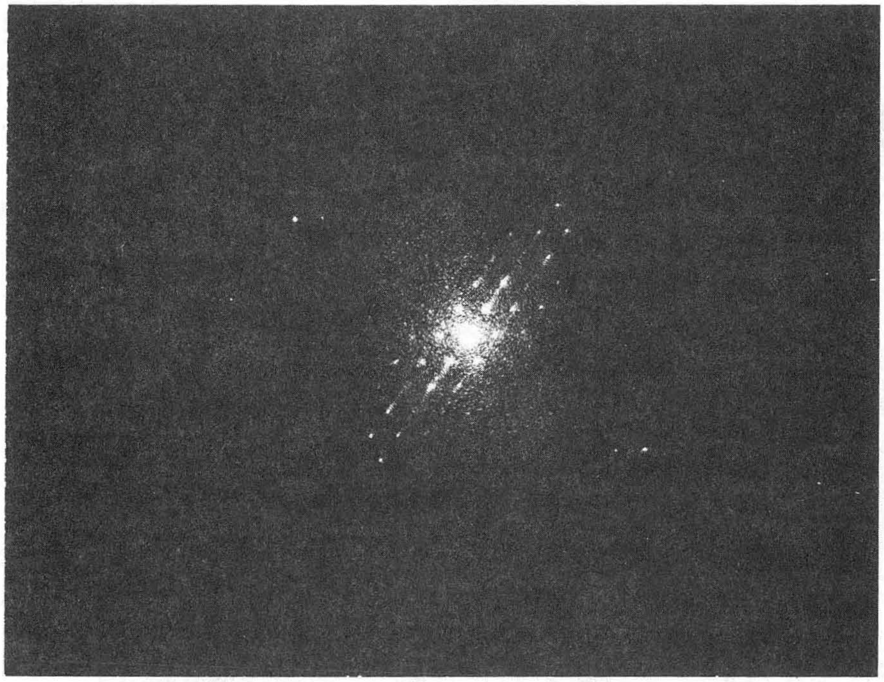


Fig. 2a

B



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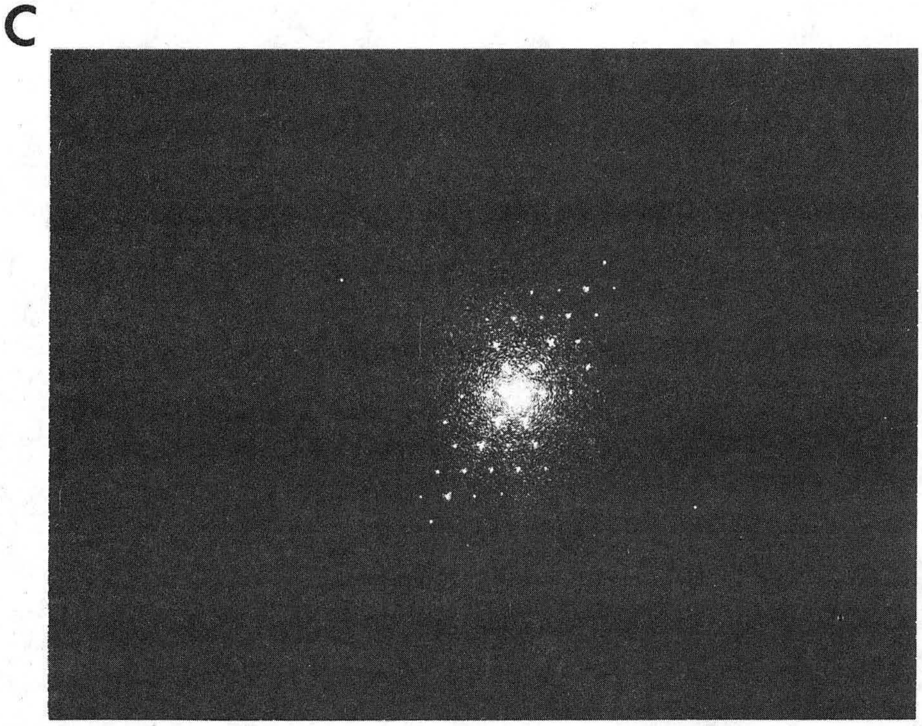


Fig. 2c

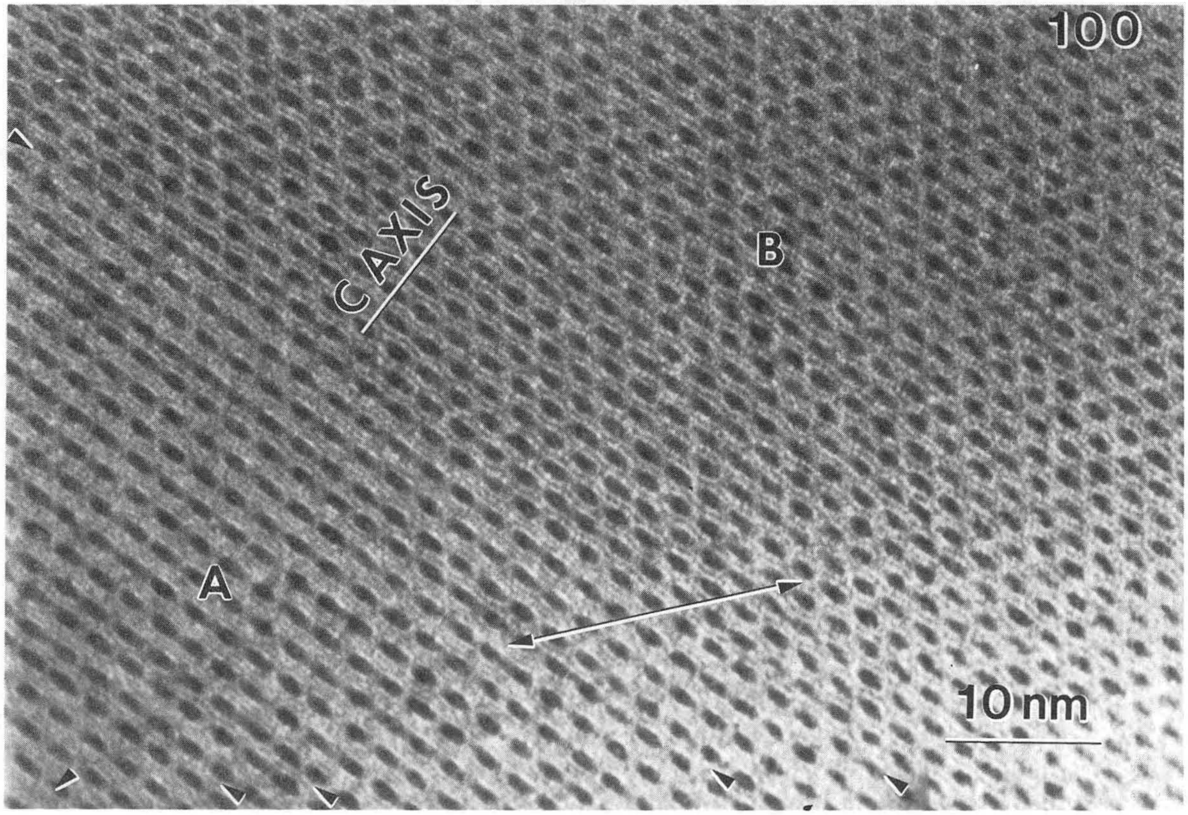


Fig. 3

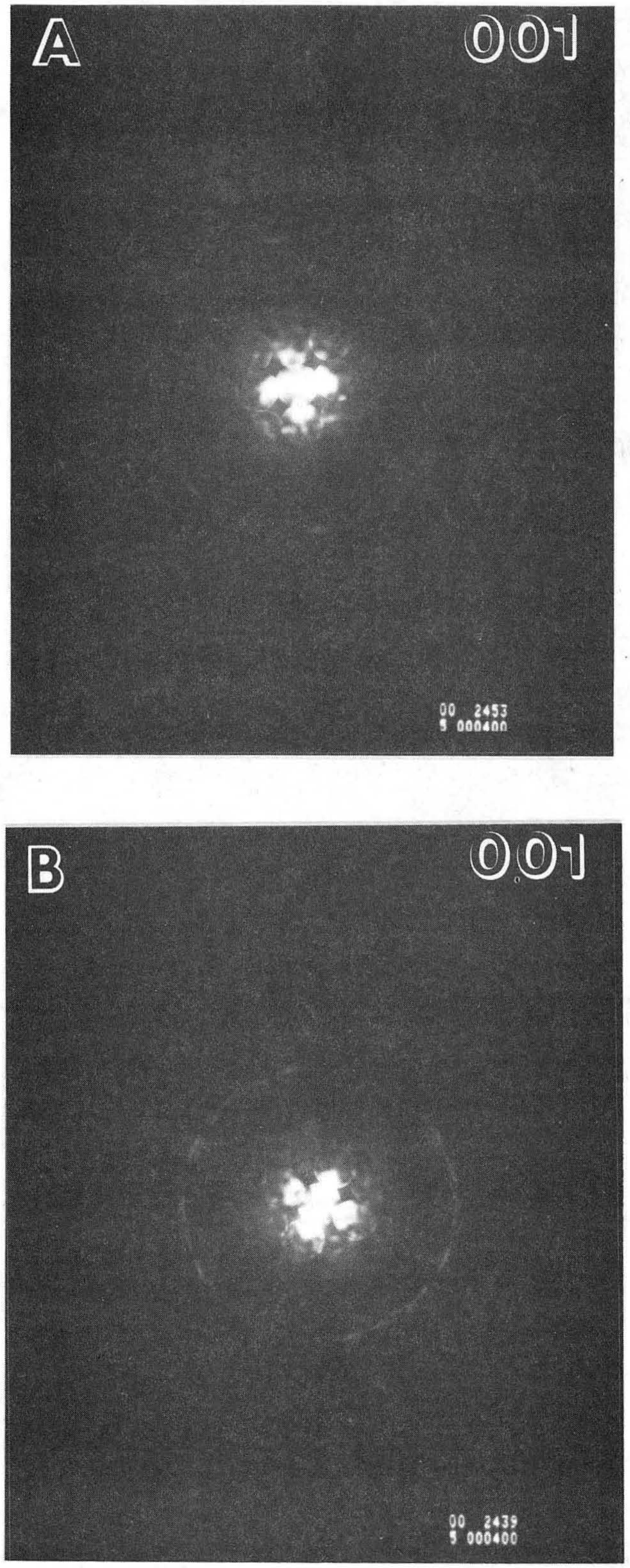
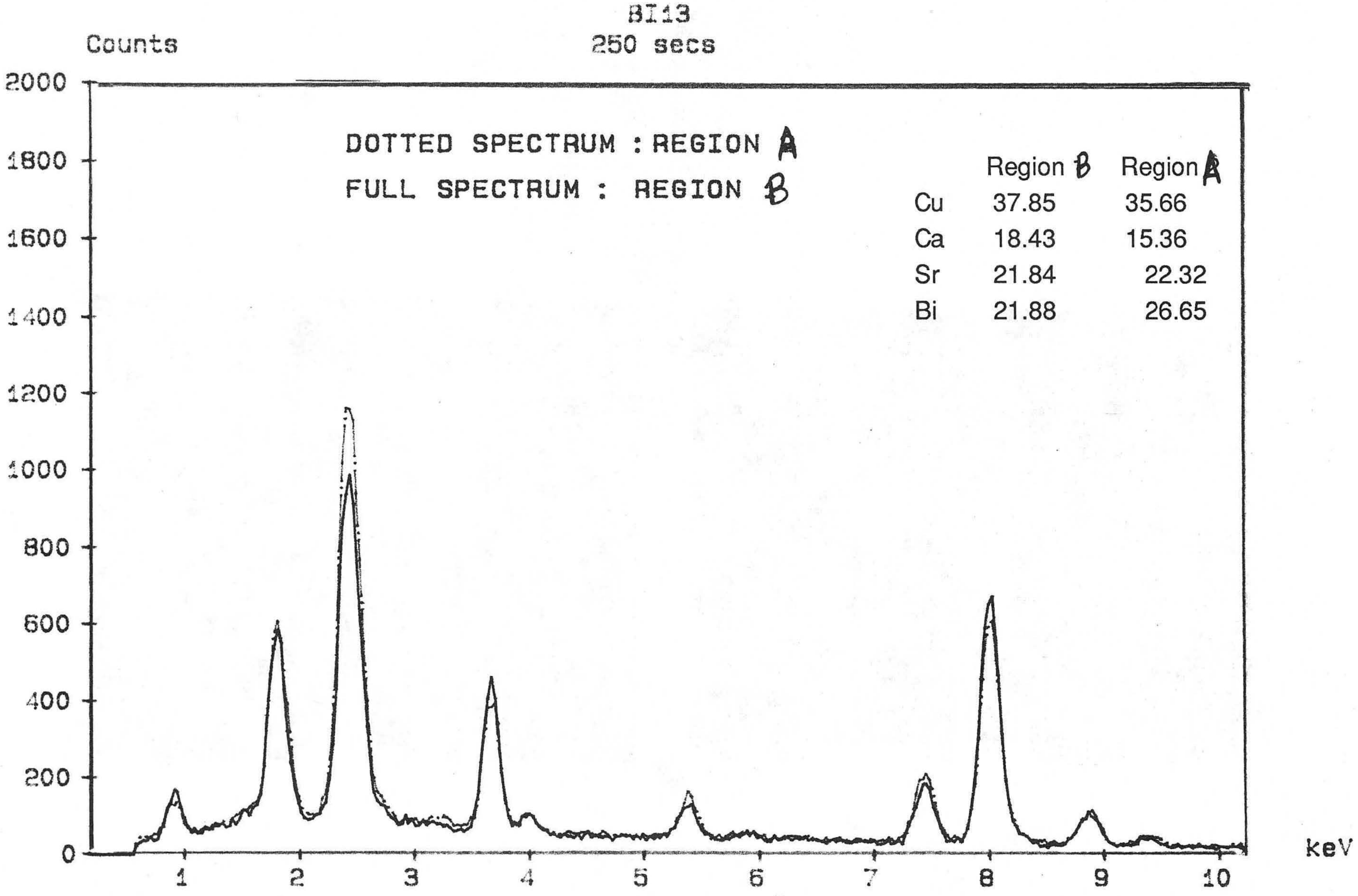


Fig. 4



	Region B	Region A
Cu	37.85	35.66
Ca	18.43	15.36
Sr	21.84	22.32
Bi	21.88	26.65

Fig. 5

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