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Structure and composition of the 115°K superconducting phase in the Bi-Ca-Sr-Cu-O system

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Results of convergent beam electron diffraction (CBED) and energy dispersive xray (EDX) microanalysis of a $Bi_{1.2}Ca_{0.9}Sr_{0.9}Cu_2O_y$ superconductor are reported. The structure is orthorhombic with a=5.63Å, b=5.4Å and c=38.2Å. The c-parameter is different from those reported by other workers and suggests that two extra perovskite units, a_p, where a_p = 3.82Å, have been introduced leading to c= 10 xa_p. EDX microanalysis shows that the Cu content of this phase is higher than that reported by other workers. It is suggested that the phase with c=38.2Å may be the higher temperature (115K) superconductor.

The observation of superconductivity at temperatures at and above liquid nitrogen temperature in certain classes of oxide ceramics has led to an explosion of research and development activity all over the world (see for example refs.1,2). One of the new classes of alloys to capture the interest of researchers is the Bi-Ca-Sr-Cu-O alloy system. Michel et. al[3] reported superconductivity in this system with a transition temperature of 22K. Maeda et. al[4] found a compound with a well defined resistivity drop at 115K and they claimed a composition of $CaSrBiCu_2O_x$ (1-1-1-2). This observation of superconductivity has also been confirmed by several other groups[5-10]. Hazen et. al[5] reported an orthorhombic unit cell with lattice parameters of 5.44 x 27.2 x 30.78 Å. Shaw et. al[11] reported that the molar ratios of the four elements other than oxygen was Bi:Sr:Ca:Cu = 8: 6.7: 3: 7.2. Zandbergen et. al[12] reported the presence of at least two phases in alloys of nominal composition of $BiSrCaCu_2O_x$. In this paper, we report results of transmission electron microscopy experiments on the structure and composition of the superconducting phase responsible for the drop in resistivity at 115K.

The sample analysed in this work was prepared with a nominal composition of $Bi_{1.9}Ca_{0.9}Sr_{0.9}Cu_2O_8$. The sample was lined up on a Pt foil and fired at 800°C in air, reground, pressed at 70kpsi and re-fired in an open end tube furnace at 875°C for 72 hours. Fig.1 schematically shows the cross-section of this sample. Approximate magnetic characteristics were observed by cooling the sample in liquid nitrogen and placing it on a $SmCo_5$ magnet. The region in contact with the Pt foil showed a brownish coloration and was not repelled very well. The central region was moderately repelled, while the exposed region acquired a crystalline appearance and was very strongly repelled for several seconds. The resistivity was measured from 300K down to 77K with a calibrated Si-diode in the usual four-point arrangement. A 0.5mA rms current was supplied at 40Hz with the voltage drop measured by a lock-in amplifier. The resistivity-temperature curve, normalized to its room temperature value, is displayed in Fig.2 and shows a sharp drop in resistivity around 115K. Based on our results from other samples (to be published elsewhere) we expect the zero resistance to be around 75K.

Since the exposed surface exhibited strong repulsion of the magnet, this region was taken up for examination by transmission electron microscopy (TEM). Samples for TEM were prepared by scraping off the top surface with a razor onto a holey carbon coated nickel grid. The samples cleave parallel to the a-b plane. The particles on the grid were

subsequently coated with a thin layer (about 100Å) of carbon to reduce damage to the sample. The TEM experiments were carried out in a Philips 400T TEM/STEM at room temperature as well as at liquid nitrogen temperature and a JEOL 200CX which is equipped with an ultra-thin window Energy Dispersive Xray (EDX) detector, capable of detecting oxygen. Quantification was carried out using the Kevex 8000 software. The usual precautions were taken in acquiring and analysing the EDX data.

Fig.3(a) shows a bright field image of a typical platelet of the superconducting phase, while the SAD pattern in the [001] zone axis is shown in Fig.3(b) (inset in Fig.3(a)) and is in agreement with those already published[5-12]. It yields two of the lattice parameters, i.e., a=5.63Å and b=5.4Å with a superstructure of 27Å (5 x 5.4Å). As in Fig.3(a), several dislocations can be observed in all the platelets. Although it is possible that these defects are introduced by the sample preparation method, subsequent experiments with ion-milled samples have shown that they are inherent to the material. These are typical of interface dislocations between faulted layers (in this case the a-b plane), indicating weak bonding along the c-axis similar to the well known structure of graphite. A detailed analysis of the dislocations is in progress.

Convergent beam electron diffraction (CBED) was carried out at liquid nitrogen temperature to determine the symmetry and the c-parameter. The diffraction patterns have been analysed using Tables 1-4 of ref.(14). The overall [001] zone axis convergent beam diffraction pattern from the platelet in Fig.3(a) is shown in Fig.4(a). This pattern shows a symmetry of 2mm. The bright field pattern, shown in Fig.4(b) also shows 2mm symmetry. The Zero Order Laue Zone (ZOLZ) shown in Fig.4(c) also shows 2mm symmetry. The symmetry of the general dark field order is "1", while the special dark field orders (those reflections parallel to the mirror planes) the symmetry is "m". In Fig.4(d) the +g and -g dark field patterns for the general dark field reflection[14], obtained by displacing the condenser aperture, are shown. It can be seen that the symmetry relation between them is a two-fold rotation. Similarly, the +g and -g dark field patterns for the special dark field reflection[14] are shown in Fig.4(e). The symmetry relation between them is also a two-fold rotation. Using the results in Figs.4(a-e) and the information in Table 2 of ref.(14), it can be directly inferred that the diffraction group of this zone axis pattern is 2mm. In Table 3 of ref. (14) the relation between the diffraction groups and the point groups is given. Corresponding to the diffraction group of 2mm, only two point groups can exist, namely, mm2

and 6m2. The latter can be eliminated since it is a hexagonal point group. Thus the point group is determined to be mm2.

The higher order Laue zone (HOLZ) rings that are observed in a CBED pattern can be used to measure the periodicity along the beam direction. Thus, the [001] zone axis pattern was also used to measure the periodicity along the c-axis. In the [001] zone axis CBED pattern in Fig.4(a), the first and second order Laue zones are marked. The analysis of the HOLZ rings to obtain the periodicity along the beam direction is available in ref. (15) and will not be repeated here. Upon carrying out the analysis the periodicity along the beam direction, within a probe of diameter 400Å, was calculated to be 38.22Å. This is at variance with the results presented by other workers who have shown that the c-parameter of the orthorhombic unit cell is 30.4Å (8 x a_p, where a_p is the fundamental perovskite unit of 3.82Å)[4-12]. It appears that in our case the c-parameter is 10 x a_p. This suggests that two more perovskite units have been introduced into the unit cell along the c-direction. This has also been observed by high resolution electron microscopy of ion milled samples with the c-axis in-plane and will be reported separately. The inference that two more perovskite unit cells have been introduced was also supported by the EDX microanalysis results. Fig.5 is a typical EDX spectrum from one of the particles obtained using the ultra-thin window detector. Since a nickel grid was used , and Ni K_β has an overlap with the Cu K_α xray peak, Ni was also included in the quantification and was subsequently deducted. One significant feature of the microanalysis results is the fact that the ratios of Ca:Sr:Bi:Cu are different from those reported by other workers for the composition of the superconducting phase. The composition of this phase (without oxygen) is presented in Table I and is compared to that reported by other workers. The composition is richer in Cu compared to that proposed by other workers , although Zandbergen et. al[12] have reported a phase with a similar composition. At the bottom of Table I the overall composition of this phase is given. This was determined as an average of 10 data points obtained from different regions. It must be pointed out that care was taken to ensure that the foil thickness for each of the ten data points was similar, by monitoring the count rate to be close to 1000 counts per second for the same probe size.

DISCUSSION AND CONCLUSIONS

The structure of the superconducting phase, which also repelled the magnet strongly, has been determined to be orthorhombic with a point group of mm2. This inference is in agreement with the results of other

workers. However, the lattice parameters of the orthorhombic unit cell are different from those generally reported. The "a" and "b" parameters are the same as reported by earlier workers but the c-parameter is 38.22Å and not 30.4Å. This difference in c-parameter is exactly equal to 2 x a_p , where a_p is the fundamental perovskite unit of dimension 3.82Å. This result along with that of microanalysis and the observation that this region of the bulk sample repels a magnet very strongly, suggests that this phase may be responsible for the transition at 115K and may be a better superconductor compared to the sample which has the c-parameter of 30.4Å. This result is consistent with the predictions of Grant[16] in that intercalation of increased number of copper oxide layers is expected to increase T_c. High resolution imaging allows such structures to be imaged directly although these alkaline earth oxides suffer displacement damage at high voltages where resolution is optimized. More details of the structure imaging and defect analyses will be reported shortly.

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TABLE I

REFERENCE NO.	ATOMIC% Ca	ATOMIC%Sr	ATOMIC%Bi	ATOMIC%Cu
This work	14.3	23.47	27.09	35.11
Ref.(11)	12.0	26.9	32.0	28.9
Ref.(12)	15.8	18.4	26.3	39.5
Ref.(7)	14.2	28.6	28.6	28.6
Ref.(6)	(Ca + Sr = balance)		28.6	28.6
Ref.(10)	15.0	25.0	30.0	30.0

REFERENCE	At.% O	At.% Ca	At.% Sr	At.% Bi	At.%Cu
This work*	58.27	6.97	9.39	9.20	16.27

* This composition is the average of ten EDX spectra obtained from different regions and is corrected for absorption.

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FIGURE CAPTIONS

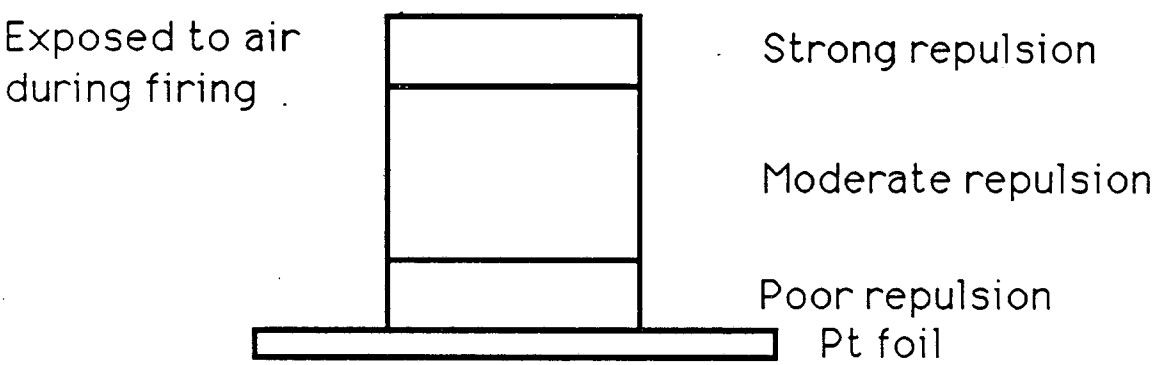
Figure 1: A Schematic representation of the cross-section of the fired sample showing three regions. The region exposed to air during firing exhibited the strongest repulsion of the magnet.

Figure 2: Resistivity versus temperature plot for the sample used in this study.

Figure 3: (a) A bright field TEM image of a typical platelet extracted from the top part of the sample (see Fig.1) ; (b) the [001] zone axis SAD pattern corresponding to the platelet in (a).

Figure 4: (a) [001] zone axis CBED pattern from a platelet showing 2mm whole pattern symmetry ; (b) bright field CBED pattern corresponding to the pattern in (a), showing the presence of 2mm symmetry ; (c) Zero Order laue Zone (ZOLZ) pattern showing the 2mm symmetry ; (d) ±G dark field images for the general reflection showing the presence of a two-fold rotation symmetry relation between them ; (e) ±G dark field images for the special reflection, showing the presence of a two-fold rotation symmetry between them.

Figure 5: A typical EDX spectrum from the platelet phase obtained using an ultra-thin window detector. The quantified data is summarized in Table I.



XBL 884-1249

Figure 1

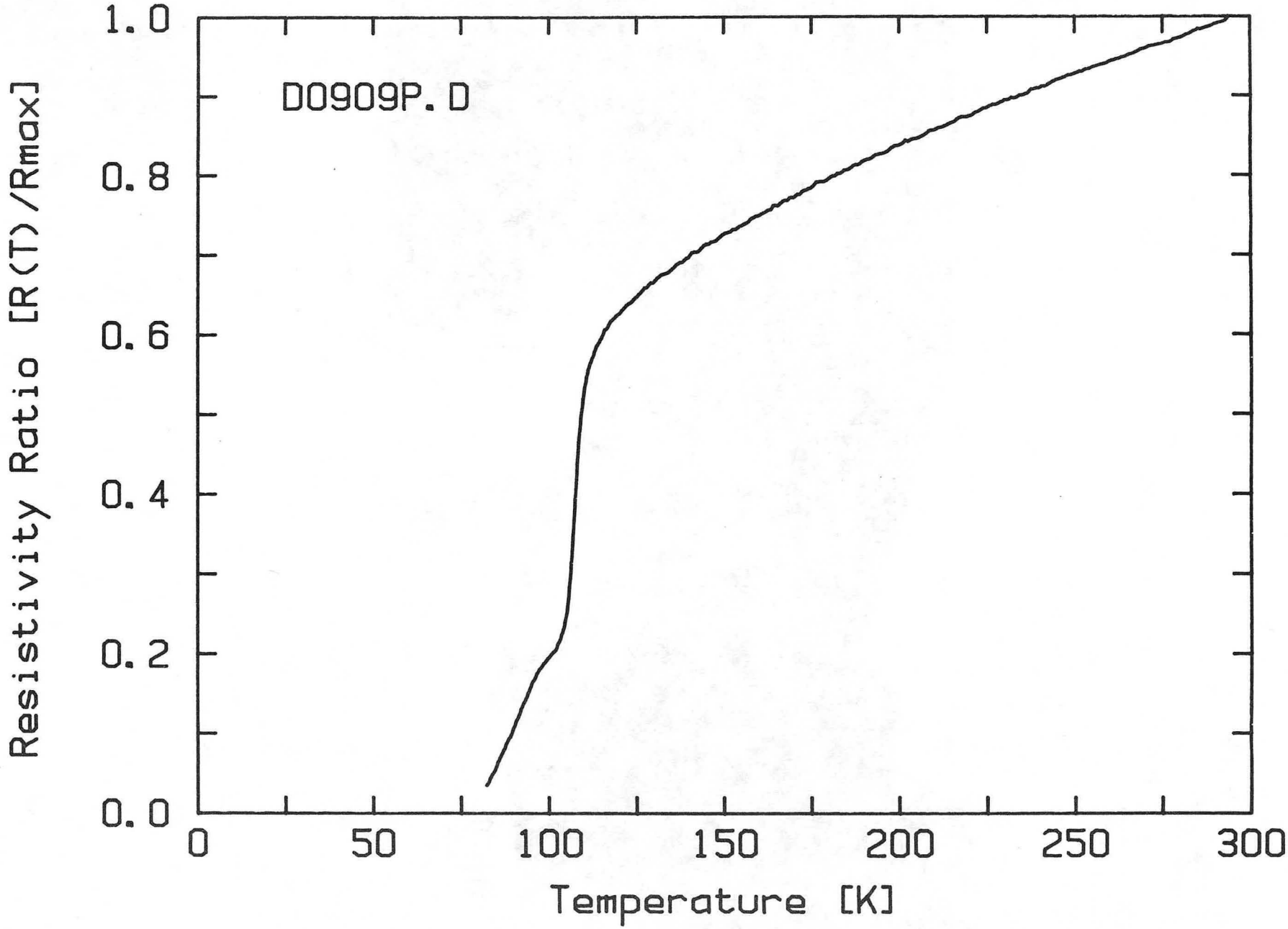


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Figure 2

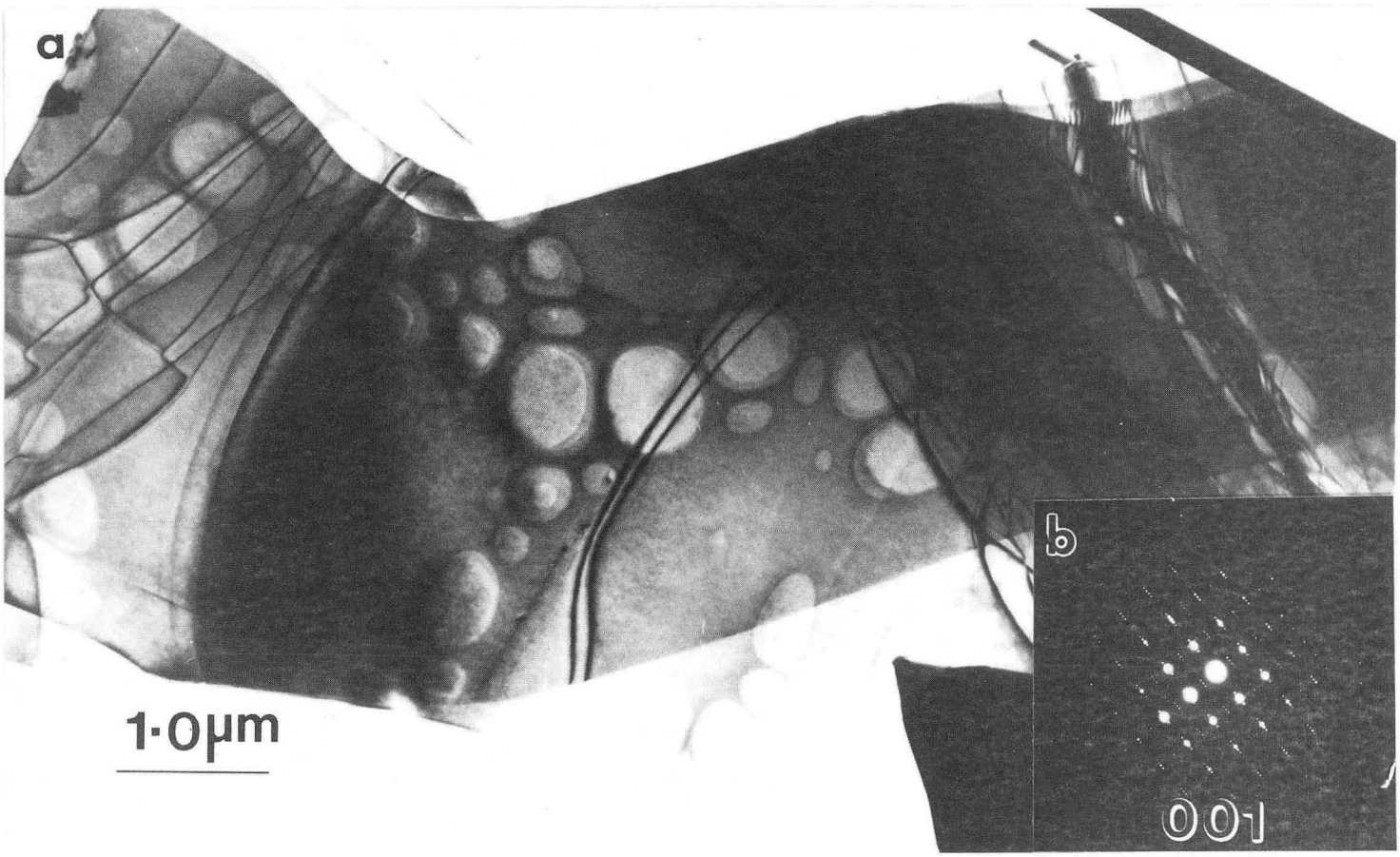

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Figure 3

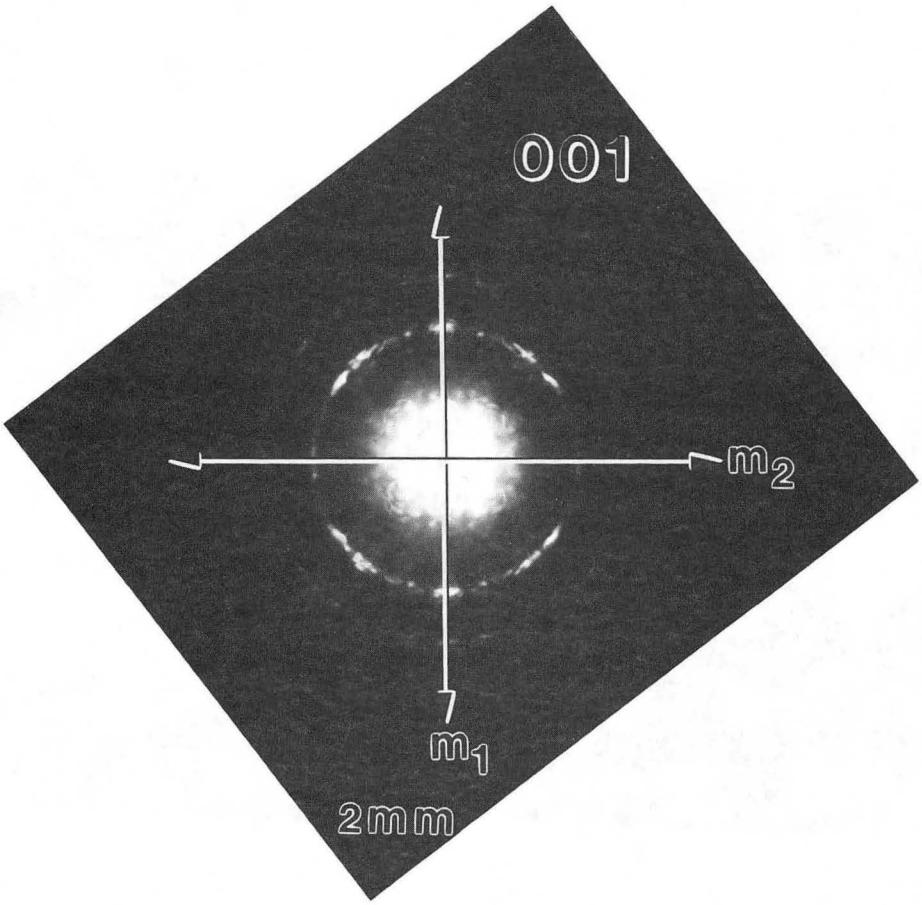

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Fig.4(a)

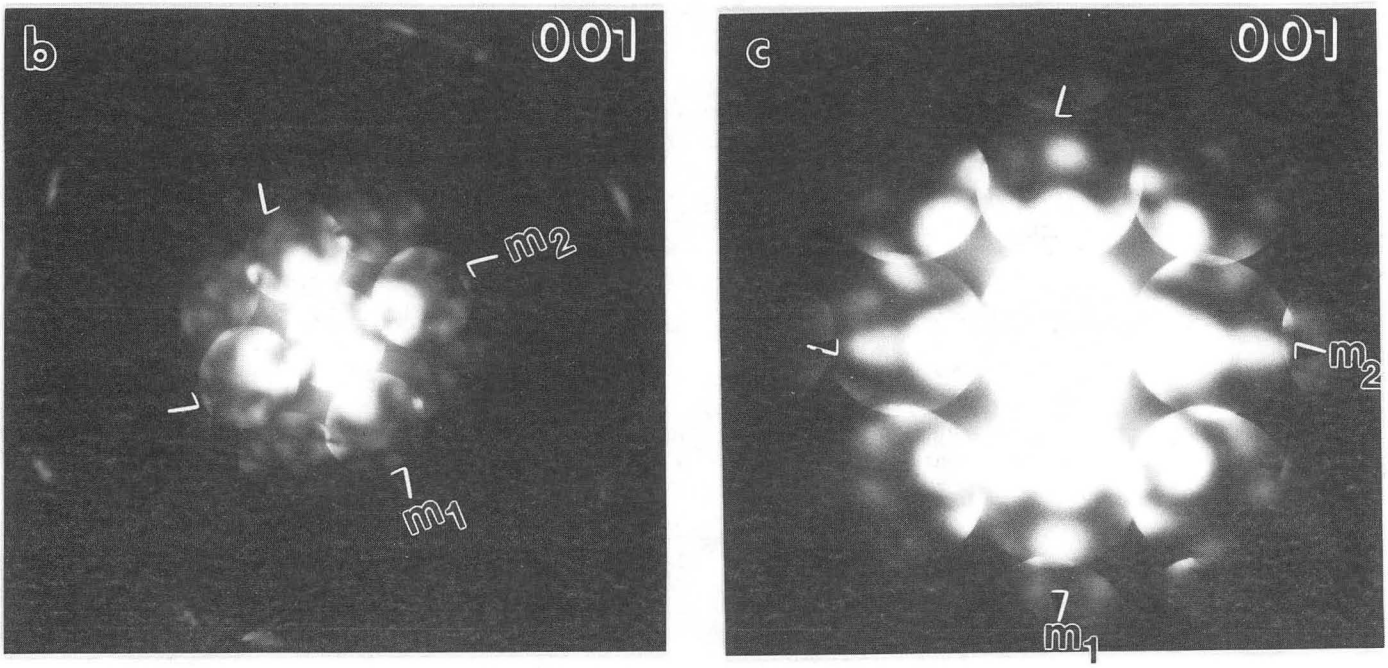

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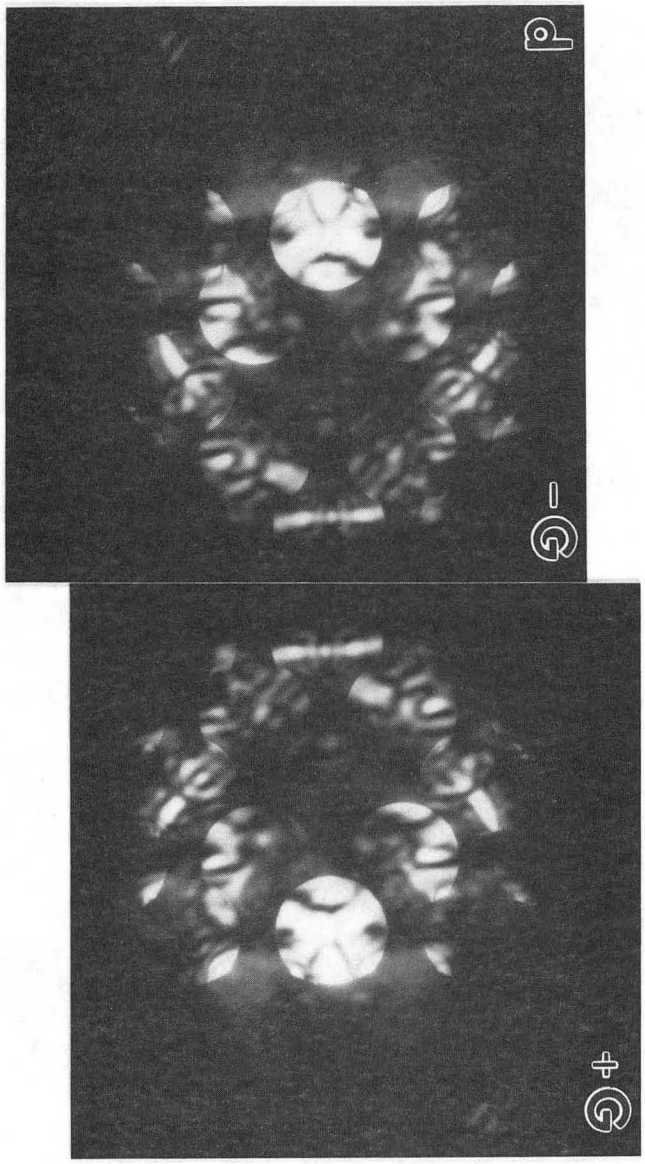
Fig.4(b,c)



XBB 884 3225

Fig.4(d)

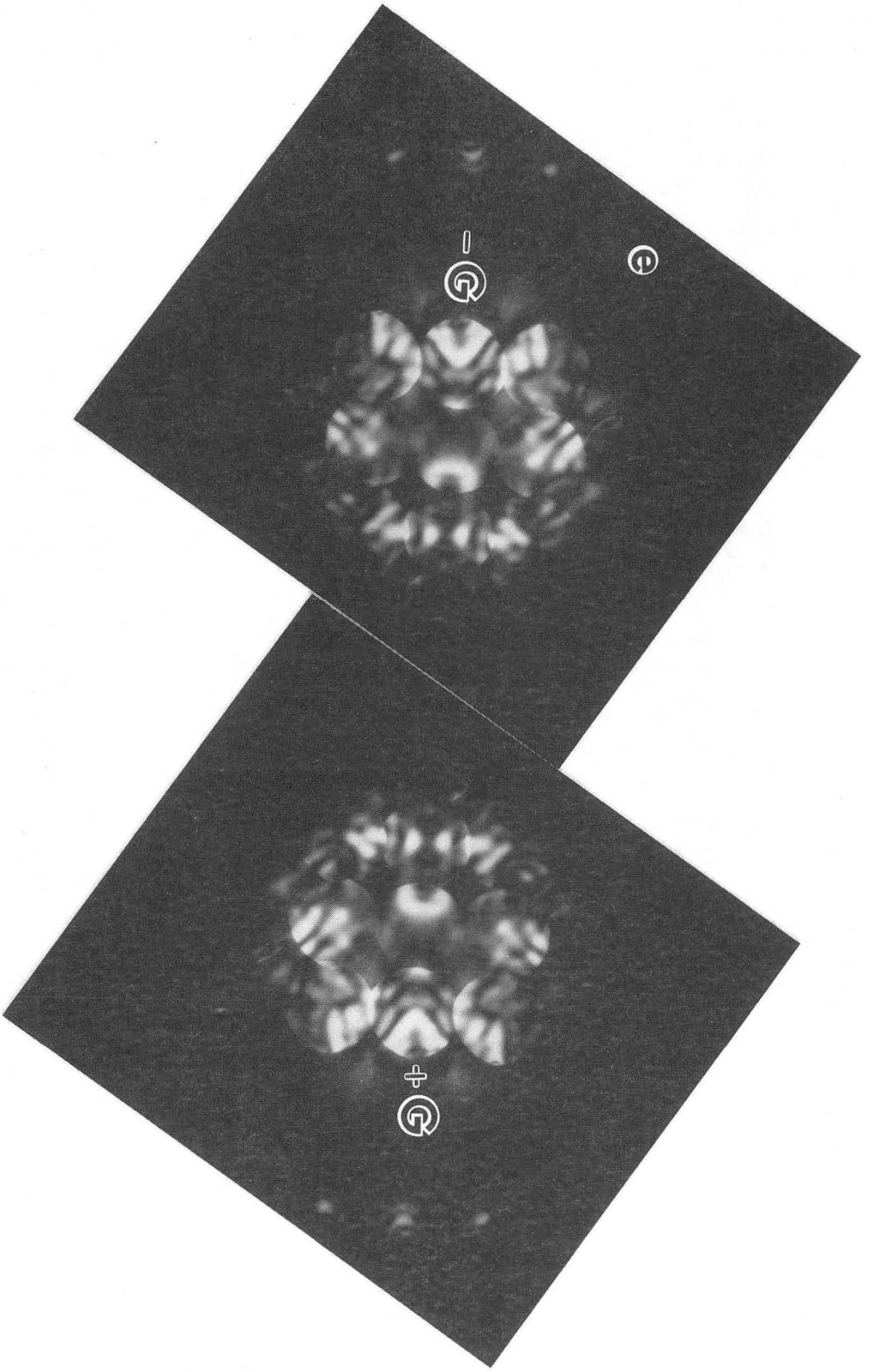


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Fig.4(e)

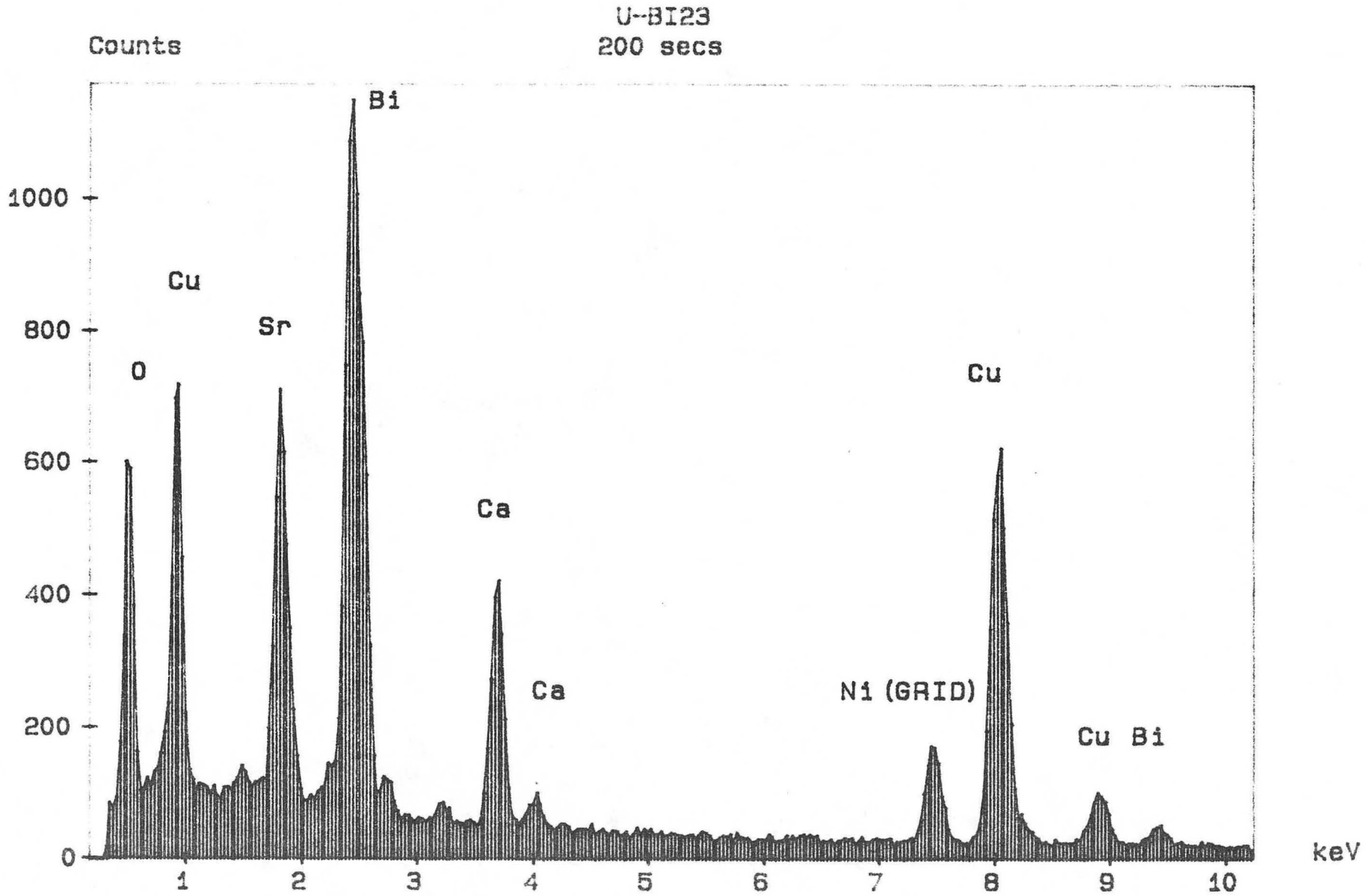
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Figure 5

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