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Summary

The microstructure of Nb_3Ge thin film superconductors coevaporated onto heated molybdenum foil substrates has been investigated by transmission electron microscopy (TEM) using a 200 kV HITACHI 700H electron microscope. Specimens for a large area TEM inspection were prepared by applying a new chemical etching technique. Various kinds of defects could be indentified in high T_c films. for example, a large part of grain boundaries is shown to consist of dislocation networks. Two kinds of Nb_5Ge_3 second phase precipitates have been revealed by dark field imaging: a lamellar and a granular structure. Several other types of imperfections like twins and stacking faults have been seen. Occasionally observed striations in high resolution TEM photographs of high T_c Nb_3Ge films are similar in appearance to the martensitic lamellae seen in V_3Si samples below the transformation temperature.

Transmissionselektronen-Mikroskopie von Nb_3Ge Aufdampfschichten

Zusammenfassung

Die Mikrostruktur von Nb_3Ge Dünnschicht-Supraleitern wurde mittels Transmissions-Elektronenmikroskopie (TEM) an einem 200 kV HITACHI 700H Elektronenmikroskop untersucht. Die Schichten wurden auf eine Molybdänfolie aufgedampft. Mit einem neuartigen chemischen Ätzverfahren wurden großflächige Proben für die TEM-Untersuchungen hergestellt. Verschiedene Defektarten konnten in hoch-T_c Schichten identifiziert werden. So konnte beispielsweise gezeigt werden, daß ein großer Teil der Korngrenzen aus Versetzungsnetzwerken besteht. Mittels Dunkelfeld-Abbildung wurden zwei Arten von Ausscheidungen der Nb_5Ge_3-Zweitphase nachgewiesen: eine lamellare und eine granulare Struktur. Mehrere andere Defektarten, wie Zwillinge und Stapelfehler, wurden beobachtet. Gelgentlich in TEM-Aufnahmen hoher Auflösung bei hoch-T_c Nb_3Ge Schichten sichtbare Streifenmuster sind in ihrem Erscheinungsbild den Martensit-Lamellen ähnlich, wie sie in V_3Si Proben unterhalb der Transformationstemperatur beobachtet wurden.

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I. Introduction

In recent years A15 superconductors have got remarkable attention as they are the most important candidates to meet the requirements for large scale applications, e.g. for fusion magnets operating at 12 T or even higher magnetic fields[1]. To solve the complicated problems in the conductor development concerning, for example, the superconducting critical parameters, phase formation and transformations, effects of strain and of alloying etc., thorough knowledge of the microstructure is quite necessary. Transmission electron microscopy (TEM) is an almost ideal tool for microstructural study. In particular, recent high resolution electron microscopy (HREM) has been successfully applied to characterize the atomic structure of crystalline defects, to elucidate the crystal structure in real space at an atomic scale and also to determine composition in alloys[2][3]. However, for studies of A15 materials such powerful capacities have rarely been utilized before. Besides the fact, that A15 materials like Nb_3Sn or V_3Ga have only recently been developed as technical (filamentary) conductors one important reason for this postponement is the great difficulty in specimen preparation[4]. In this basic research program of the KfK Institut für Technische Physik on A15 materials effort has been made to find suitable techniques for TEM specimen preparation and to include TEM to characterize the microstructure of superconductors[5].

A successful new method for preparing large area TEM specimens has been developed, appropriate for high resolution studies of various crystalline imperfections[6]. Some interesting observations on high T_c Nb_3Ge films have been made, using this technique described below[7].

II. Experimental

The Nb_3Ge films were prepared by electron beam coevaporation of commercial Marz-grade niobium (4N purity) and semiconductor purity germanium from two sources under ultrahigh vacuum conditions.

Evaporation rates were controled by two quadrupole mass filter detectors and kept constant to within a few percent. Films were prepared on molybdenum substrate foils 0.2 mm thick with respect to TEM specimen preparation. The substrate was heated by electron bombardement to ~ 800°C. Films were characterized by X-ray analysis with the Mo substrate resolved chemically, and Rutherford backscattering of 2 MeV α-particles. Their average thickness was 3000 Å, the Nb:Ge-ratio was close to 3:1 and the inductive T_c was about 21 K at 5.14 to 5.15 Å lattice spacing.

TEM specimens were prepared by a backprotective floating, chemical thinning procedure. The molybdenum substrate is dissolved by a $FeCl_3$ solution. Then the A15 layer, protected by a lacquer spray (Plastik 70) on the upper side and floating on the etchant ($FeCl_3$ + HF), undergoes chemical thinning down to the required average thickness of several hundreds of angstroms. Finally the lacquer layer is removed by acetone and the thin A15 specimen is submitted to TEM observation. Details of this preparation technique were described elsewhere[6].

TEM observations were made on a HITACHI 700H electron microscope in the Electron Microscopy Laboratory of the Karlsruhe University, operating at a voltage of 200 kV. For some high resolution imagings a two-beam imaging technique[8] was used.

III. Results and Discussion

Grain Boundaries

Although it is well known from studies of many authors that grain boundaries play an important role in flux line pinning and thus have decisive influence on the critical current density of A15 materials, so far very few structural information about the nature of grain boundaries in these compounds has been found. Present work shows that TEM is a very powerful tool in this direction. A large amount of moiré fringes was found at grain boundaries as can be seen from Fig. 1.

As discussed in [9], this type of pattern comes from the overlapping of two adjacent slightly misoriented crystallites and requires a well defined condition for its appearance. Therefore, one may expect from the present observation that a large part of grain boundaries are low angle boundaries with the nature of dislocation networks. An example of such dislocation boundary, a tilt boundary, can be clearly seen from high resolution electron microscopy in Fig. 2. In a two-beam imaging condition, using the (000) and (100) reflection, the edge dislocations of such a boundary with their extra half (100) planes clearly appeared at that places, where in a lower magnification photograph one can find boundary moiré fringes.

Second Phase

In high T_c stoichiometric Nb_3Ge films a small amount of second phase Nb_5Ge_3 is always present. Its influence on the critical current has been shown before[10]. Thus it is important to know the size, distribution and morphology of such additional phase precipitates. Nevertheless, as mentioned by several authors[11][12], a quantitative identification of Nb_5Ge_3 phase by TEM is not available at present time. This is due to the very fine Nb_5Ge_3 microstructure and the fact that almost all second phase reflections overlap with some A15 reflections. This is true except for the low index reflections of the tetragonal and hexagonal Nb_5Ge_3 phase.+) Thus the (110) reflection of the tetragonal Nb_5Ge_3 phase can be resolved separately, which corresponds to

+) The low indexed lattice spacing of the NbGe system are

A15 Nb_3Ge	tetrag. Nb_5Ge_3	hexagon. Nb_5Ge_3
	7.18 Å (110)	
		6.67 Å (100)
5.14 Å (100)		
	5.07 Å (200)	
	4.59 Å (101)	
		3.85 Å (110)
3.64 Å (110)		

a lattice spacing of 7.18 Å compared to 5.14 Å for the (100) reflection of A15 Nb_3Ge. Since the smallest objective aperture is 20 μm in diameter for the HITACHI 700 H electron microscope (due to a semi-angular aperture of ~ 3.3 x 10^{-3} rad), it is still difficult to separate the (110) Nb_5Ge_3 reflection distinctly from A15 reflections. However, in some special case where we have a large A15 grain with |001| orientation in the field of vision, one can by a careful small shift of the aperture (not covering the (100) A15-reflection) identify some Nb_5Ge_3 phase particles from their glaring brightness in contrast to the known |001| A15 grain. Figure 3 shows such an example, where two types of second phase arrangements with different shapes and scales can be seen, i.e., granular type Nb_5Ge_3 with diameters mostly of about 200 Å, and fine lamellae of Nb_5Ge_3 in a mixture with A15 material, as it has been reported before for some sputtered samples[13].

In the samples with high T_c, no such identification could be made because the A15 grain size is so small (≲ 1000 Å) that we always observe polycrystalline diffraction patterns even with the smallest select area aperture. However, similar lamellar striations can be found frequently (Fig. 4a,b). By high resolution imaging we can also see some Nb_5Ge_3 grains of about 200 Å diameter as in Fig. 4c.

In some places in the high T_c samples where such lamellar striations are absent some very small precipitates of second phase were found. By high resolution imaging (Fig. 5a, b) a spot of sharp contrast change could be seen in an A15 grain with a diameter of about 900 Å, caused by a small volume structural difference. Similar pictures with lower magnification are shown in Fig. 5c and 5d.

Coexistence of second phase particles with different shape and size in the same sample might give some reasonable explanation to the complicated influence of second phase content on current-carrying-capacity as it has been mentioned in[12]. However, the microstructural study of second phase in A15 superconducting materials is still at a very early stage. One may expect much interesting and instructive findings in the future especially by means of HREM.

Other Imperfections

Several other types of imperfections can also be found in the high T_c Nb_3Ge samples. Twins and stacking faults with their characteristic parallel boundaries and contrast fringes as discussed in[14] are often seen. Figure 6 shows a large twin and in Fig. 7 one can see the imaging of a stacking fault. Thorough study on these types of defects in high resolution images is going on.

It is an interesting question whether some structural ('martensitic') transformation similar to that in Nb_3Sn and V_3Si could also occur in Nb_3Ge. As mentioned before, striations are often found and some of them have been recognized as lamellae of Nb_5Ge_3. However, since the identification is sometimes far from beeing unequivocal one can still doubt whether some of the others could not have a different origin. In Fig. 8 we see some wider contrast striations on the background of faint fine periodic fringes. Obviously, this kind of striations can be hardly attributed to some second phase. In some high resolution pictures a gradual transition of atomic arrangements between two parts of the same grain with and without striations can also be found. One possible explanation of this kind of striations might be that some lattice defects and residual strains are introduced to the sample caused by some back and forth structural transitions during the cooling down and warming up of the specimen when it has been submitted to superconducting critical temperature measurement before TEM examination. A low temperature structural transformation from the cubic A15 to a tetragonal distorted lattice has been observed by TEM for V_3Si[15] and V_3Ga[16]. Lamellar striations were observed below the'martensitic' transformation temperature. The question, whether some of the striations in our Nb_3Ge films found at room temperature TEM are of the same origin, can probably be answered by a TEM and X-ray analysis at varying temperature, using homogeneous, stoichiometric high T_c samples. Both, a transformation temperature above room temperature or a frozen remainder of the lamellar structure from a low temperature transformation could be envisaged.

Conclusions

An encouraging new approach for HREM specimen preparation from A15 material is now available. Preliminary studies on coevaporated Nb_3Ge films show several interesting structural features of grain boundaries, second phase particles and other types of imperfections. Further thorough structural study might be very helpful to advance A15 superconductors, as it has been shown in the developement of other materials.

Acknowledgments

This study was encouraged by H. Wühl. The authors are very grateful to him as well as to R. Flükiger, H. Küpfer and M. Kutschera for helpful discussions. The TEM examination has been performed at the "Labor für Elektronenmikroskopie" of the Karlsruhe University. The helpful assistance of Mrs. Kasperek and H. Wagner is gratefully acknowledged.

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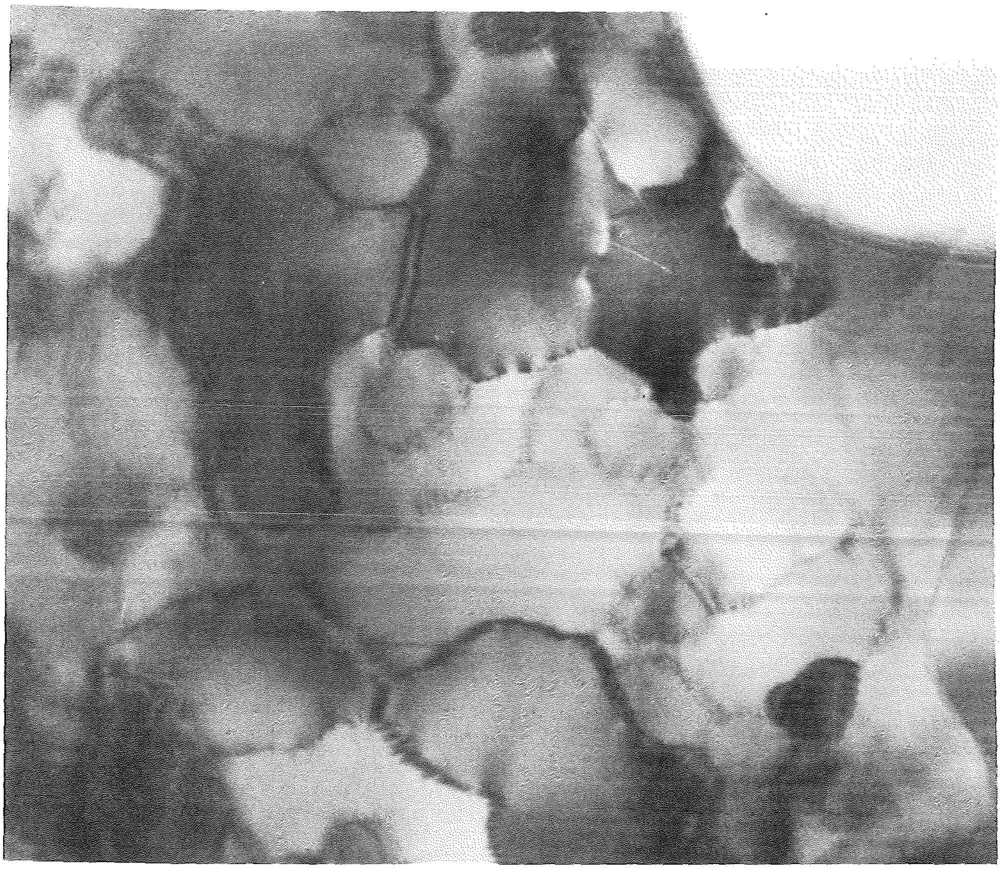

Fig. 1a

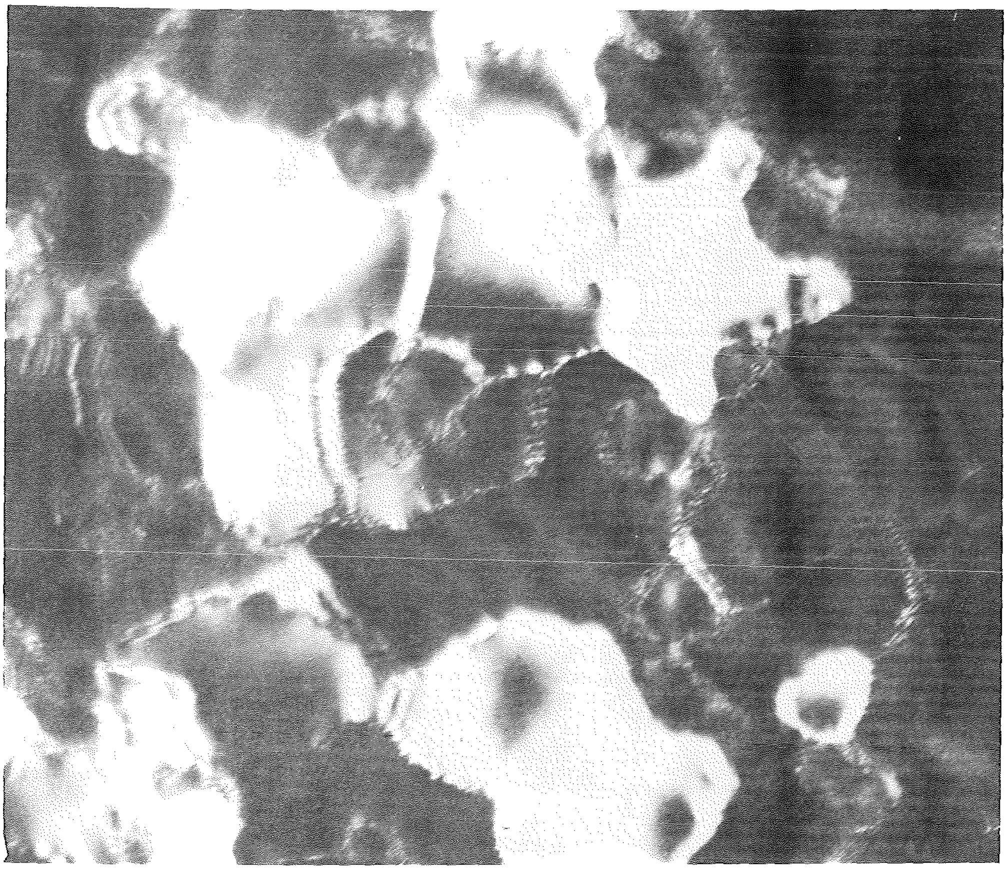

Fig. 1b

Fig. 1: Moiré fringes at grain boundaries of high T_c Nb_3Ge
(# 836-3); 460 000 x
(a) and (c) bright field imaging
(b) and (d) dark field imaging

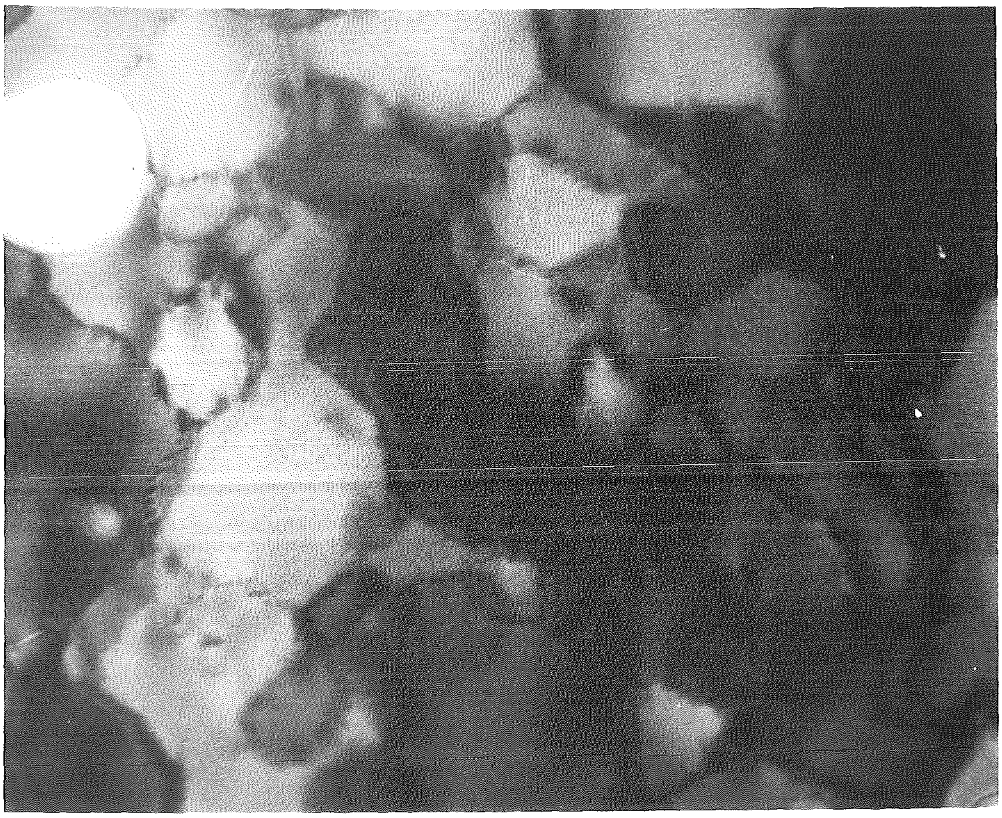

Fig. 1c

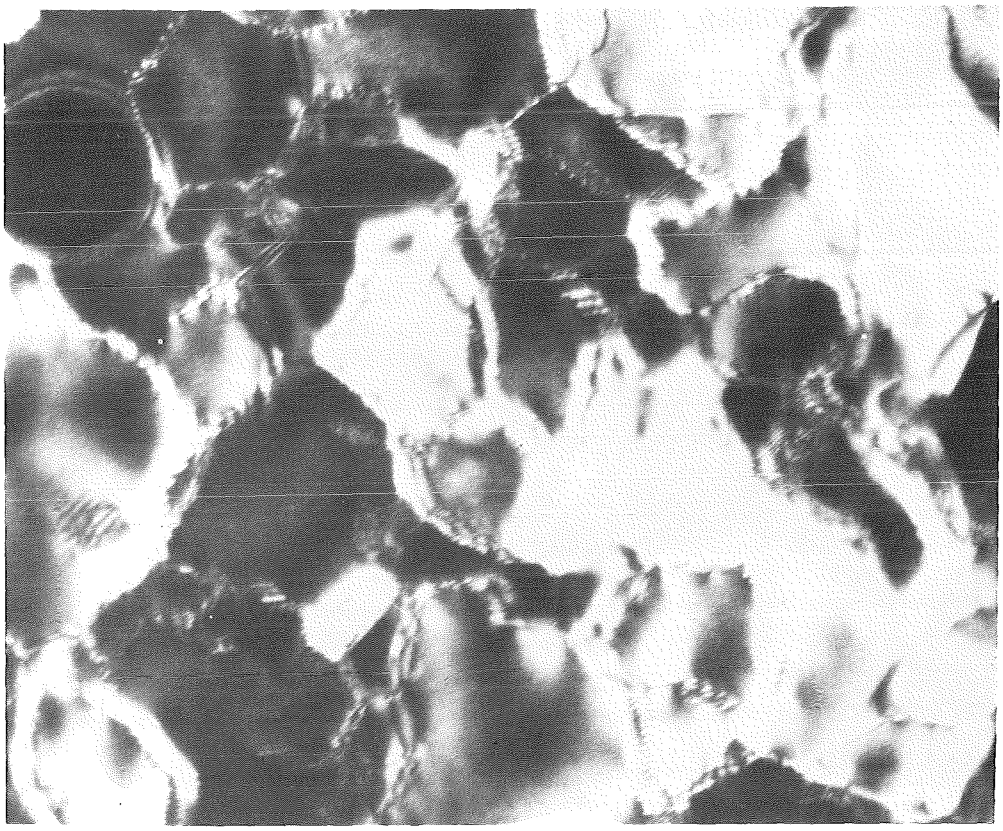

Fig. 1d

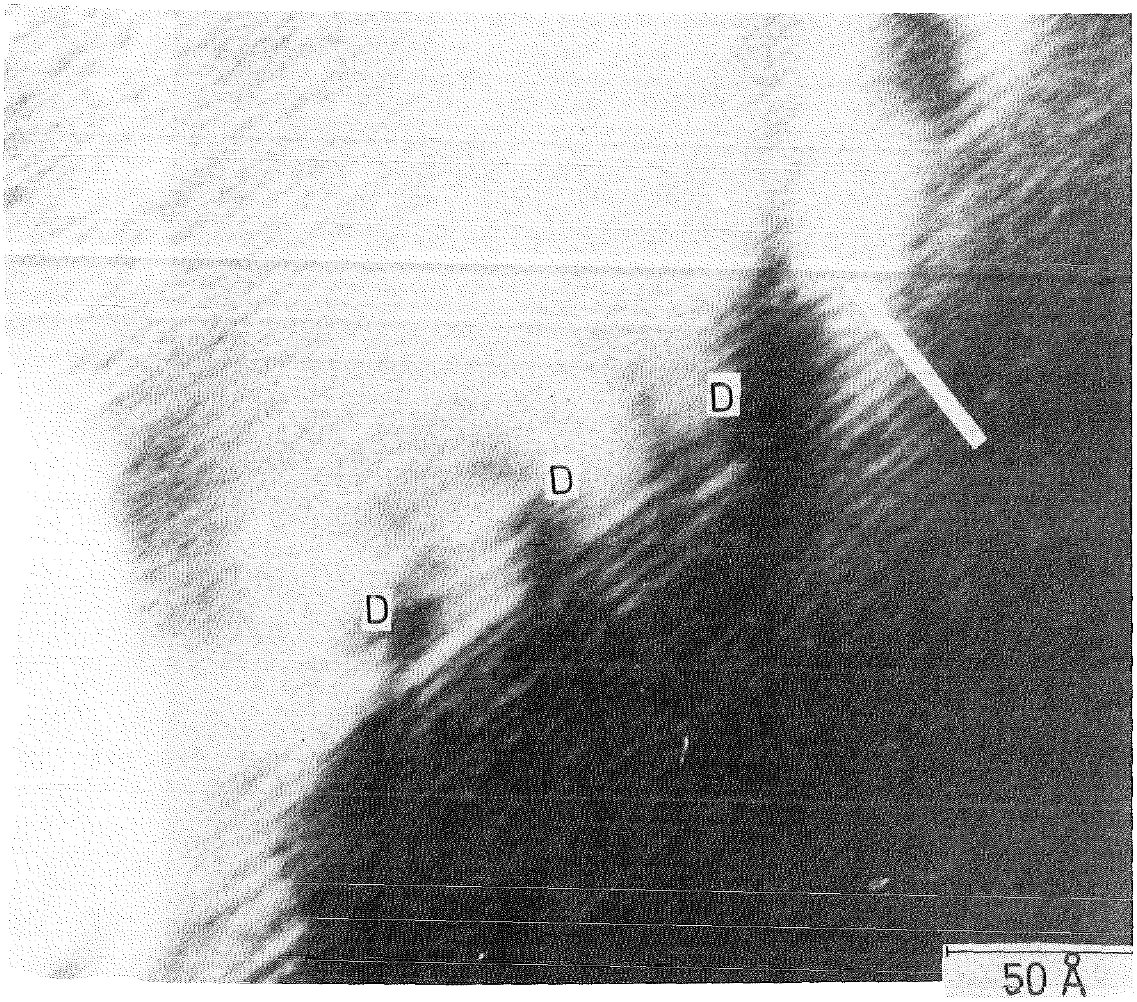

Fig. 2: High resolution imaging of (100) planes in high T_c Nb_3Ge (#836)[7]. Edge dislocation imaging with extra half plane marked by "D" can be seen at the boundary between two grains. Lattice spacing of about 5.10 Å (A15 (100) planes) can be extracted (the white diagonal bar corresponds to 56 Å containing 11 lattice spacings); scale given in the figure.

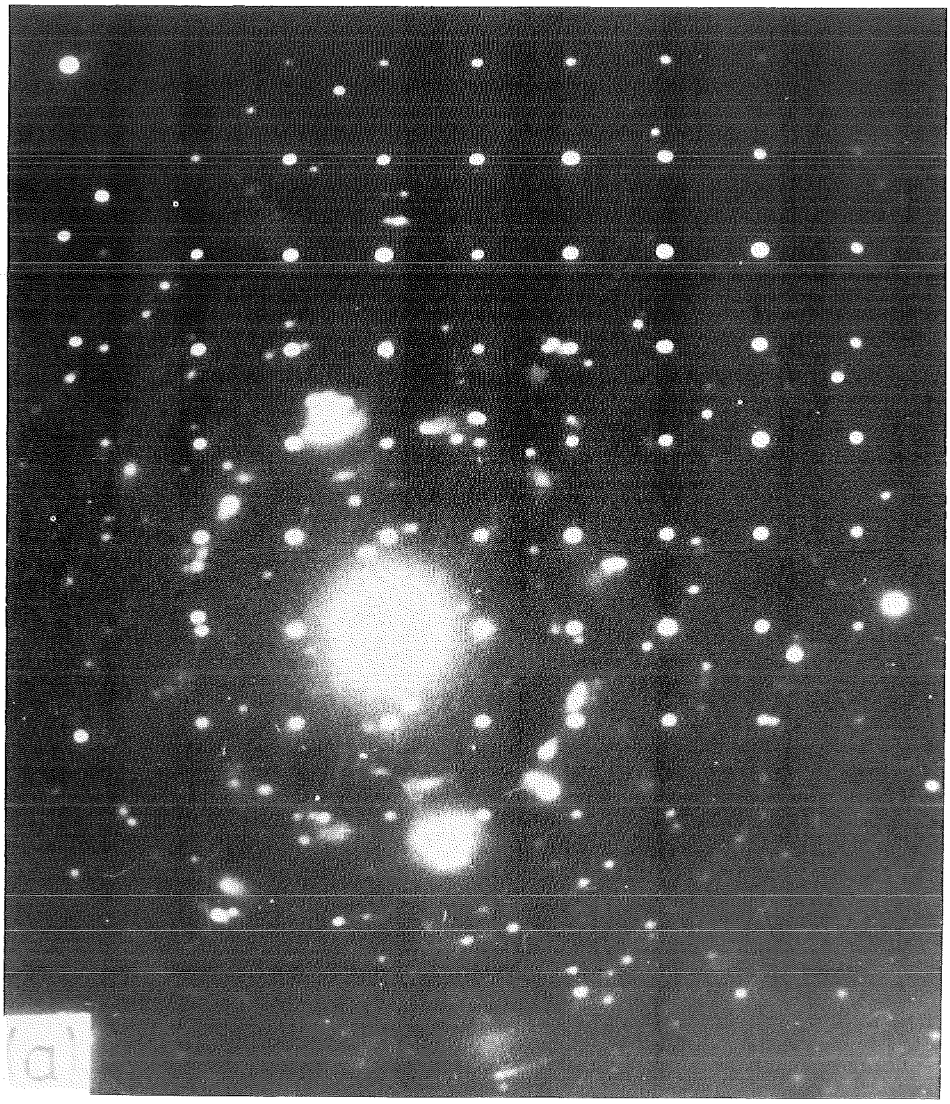

Fig. 3a: Selected area diffraction of a large A15 grain (Fig. 3b,c) with [001] orientation.

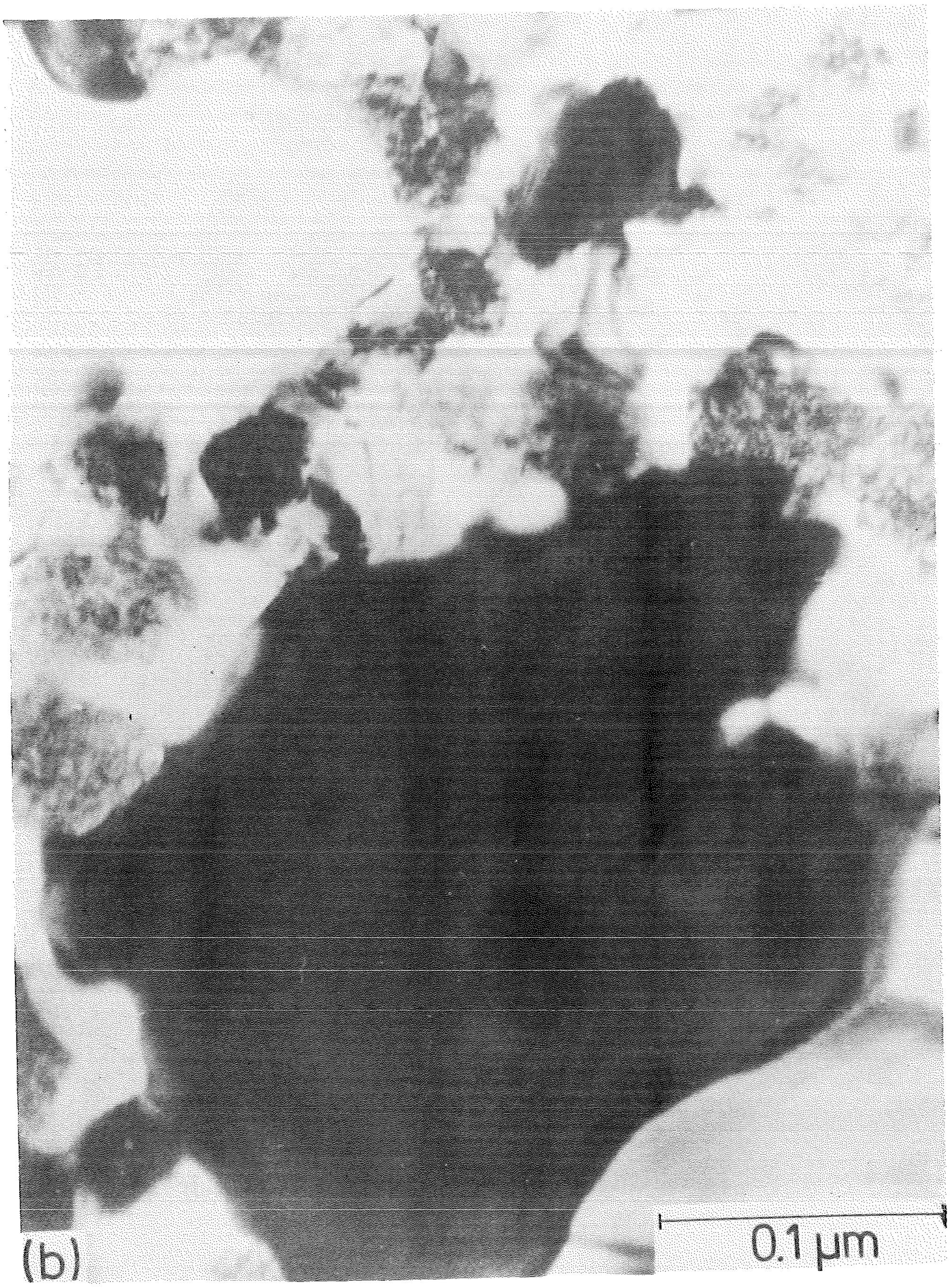

Fig. 3b: Example of Nb_5Ge_3 phase identification in Nb_3Ge film with [001] A15 grain as reference[7], bright field imaging; scale given in the figure.

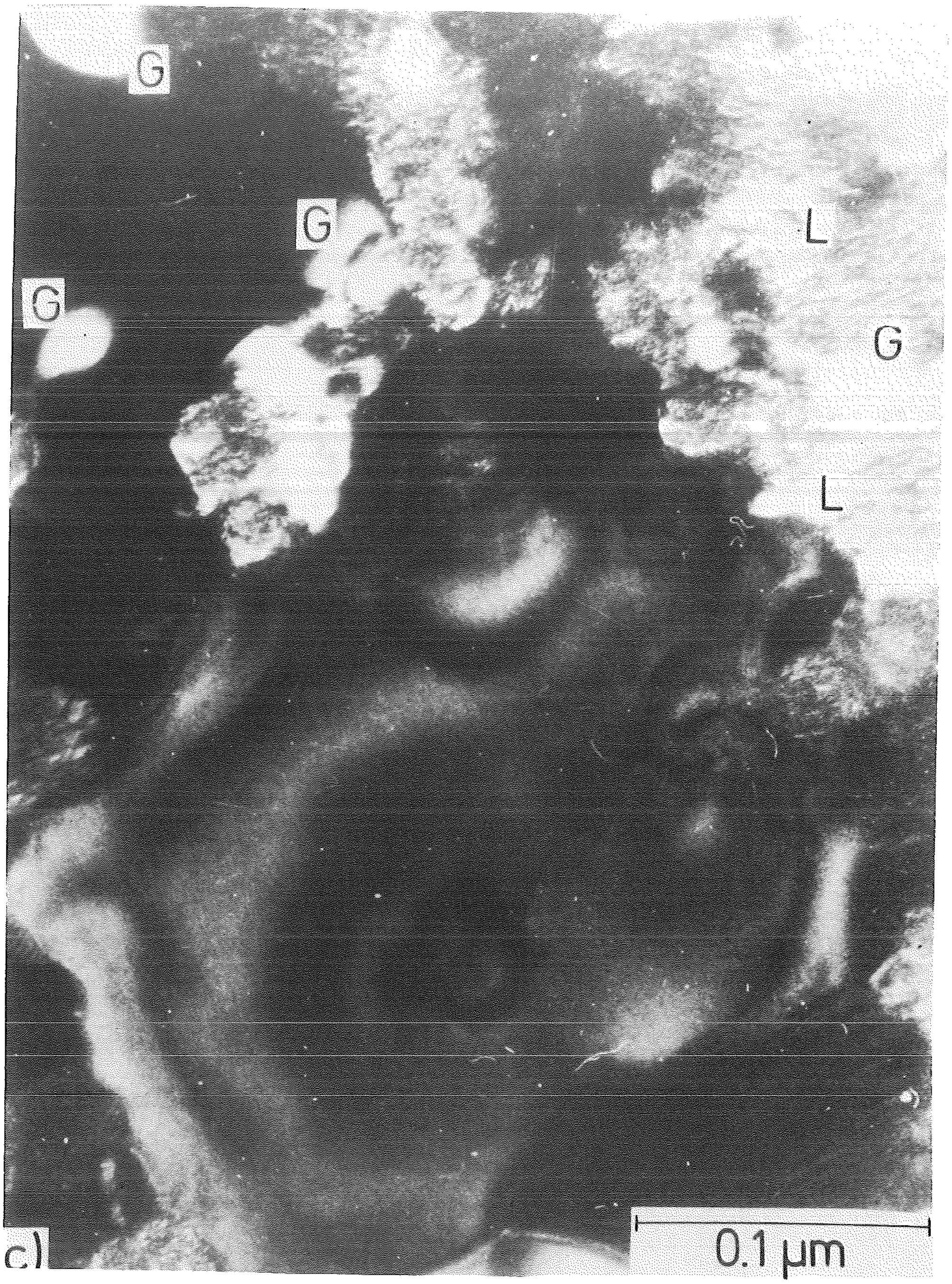

Fig. 3c: Same area as in Fig. 3b, dark field imaging using (110) Nb_5Ge_3 reflection; lamellar (L) and granular (G) Nb_5Ge_3 structure; scale given in the figure.

Fig. 4a

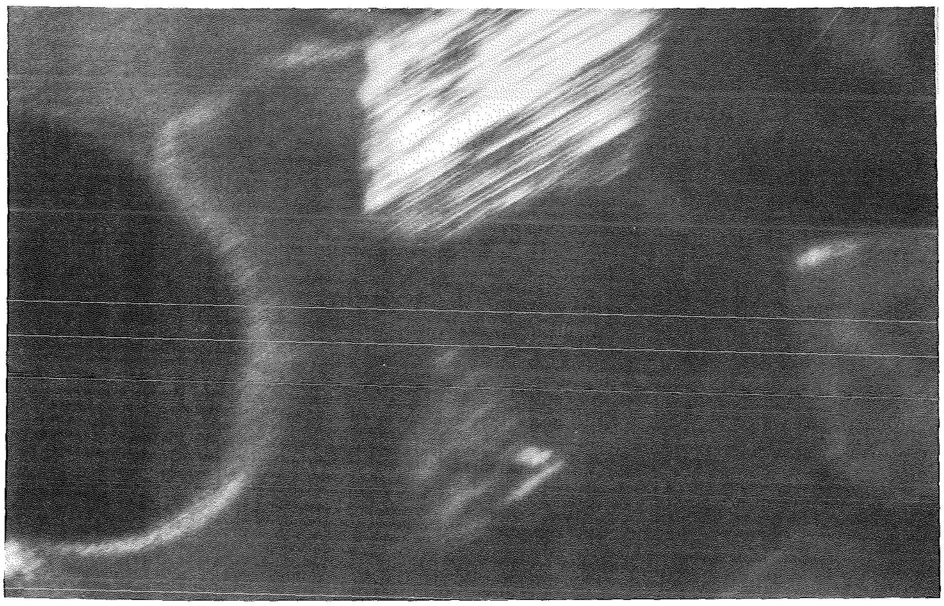

Fig. 4b

Fig. 4: Probable Nb_5Ge_3 phase in high T_c Nb_3Ge sample (# 836-3). Lamellar striations in bright field (a) and dark field (b) imaging; 460 000 x.

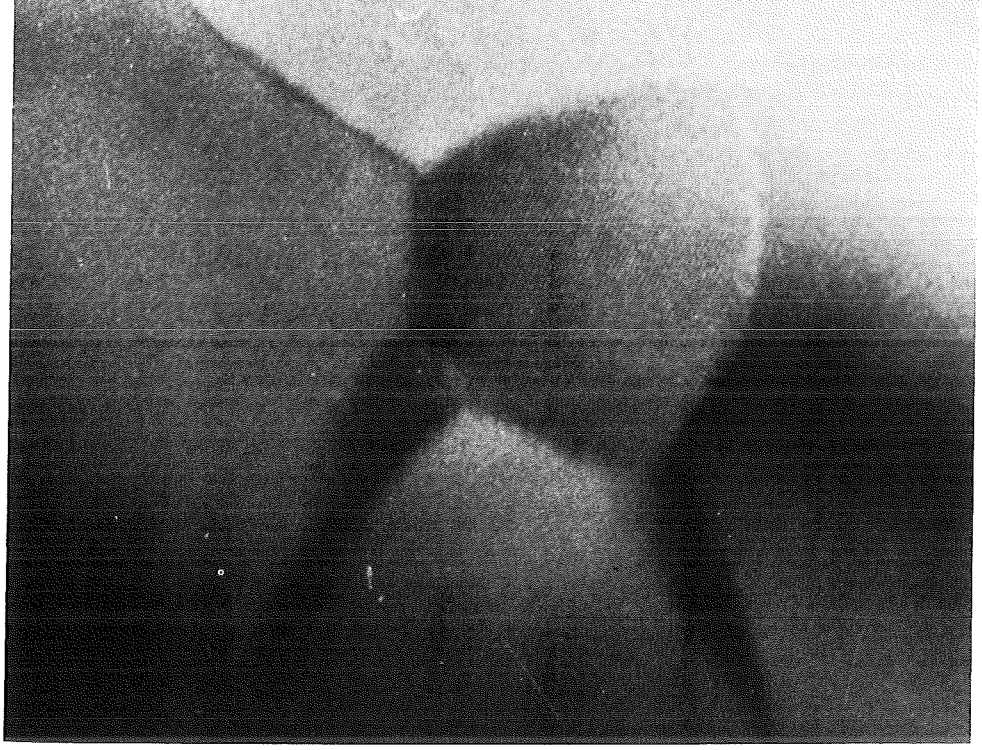

Fig. 4c: High resolution TEM of small Nb_5Ge_3 grain. Interplanar spacing of about 4.55 Å corresponding to the (101) planes in Nb_5Ge_3; $1.6 \cdot 10^6$ x.

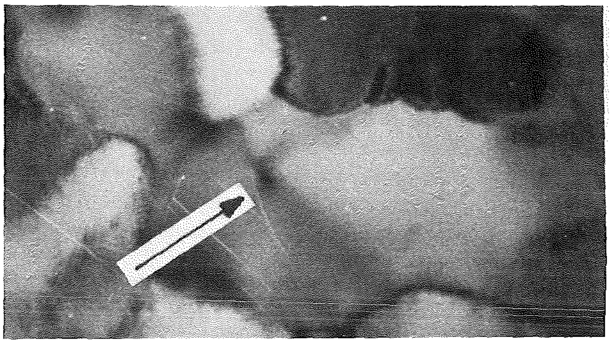

Fig. 5a

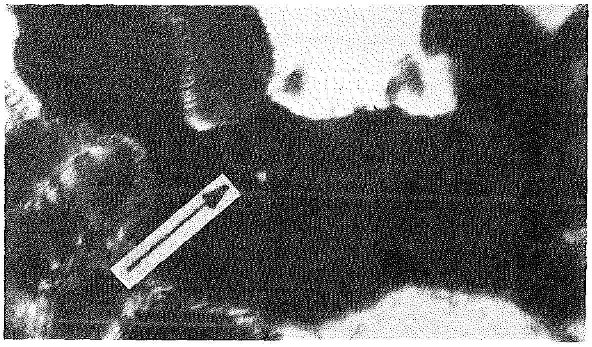

Fig. 5b

Fig. 5: Small Nb_5Ge_3 precipitates in high T_c Nb_3Ge samples,
bright field (a) and dark field (b) imaging of # 836-3; 460 000 x,
bright field (c) and dark field (d) imaging of # 785-3; 360 000 x,
singularities due to precipitates are indicated by arrows.

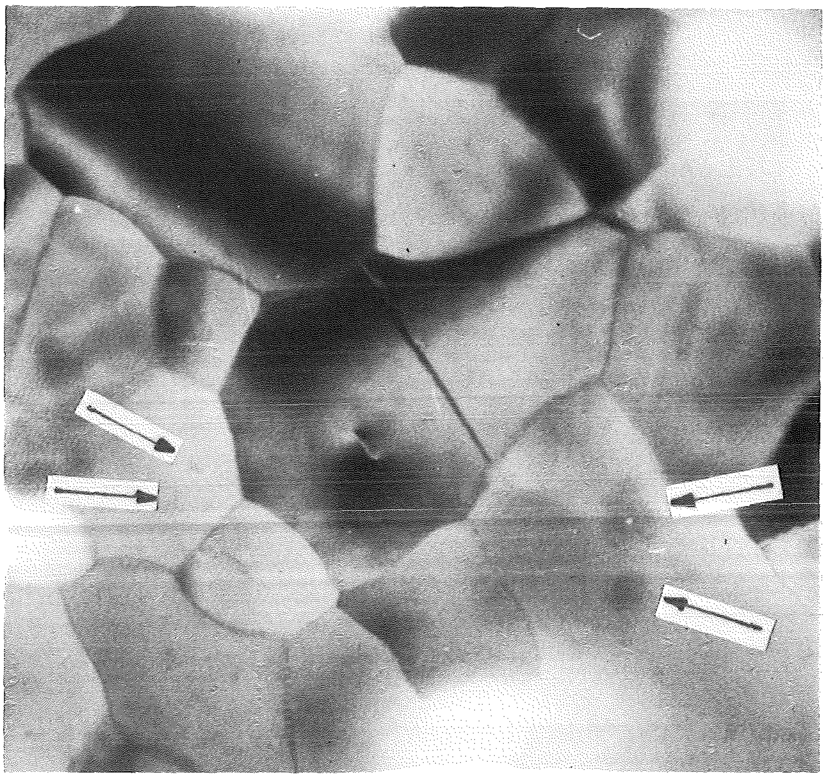

Fig. 5c

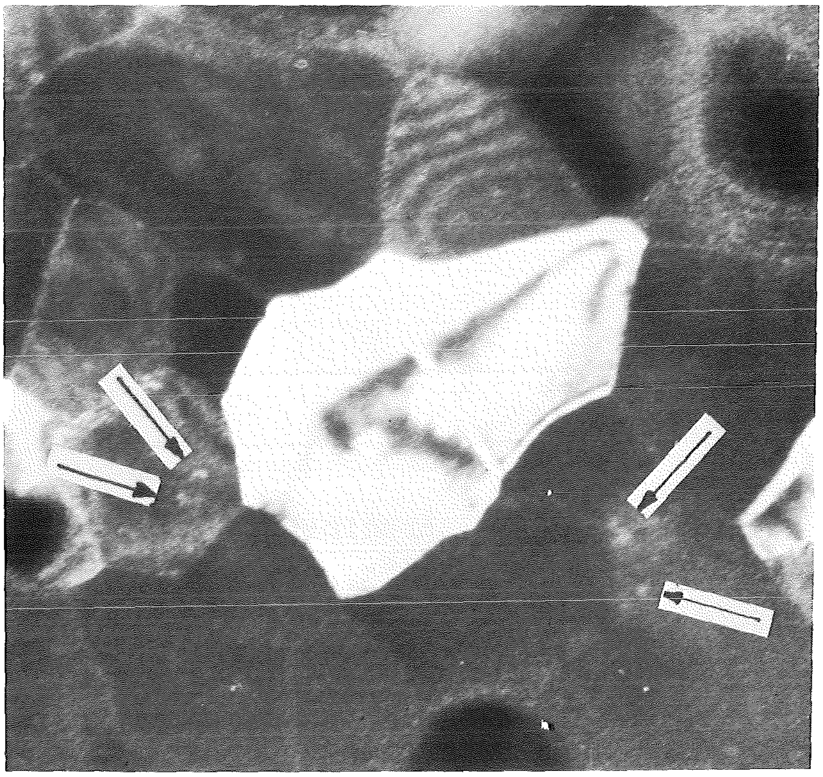

Fig. 5d

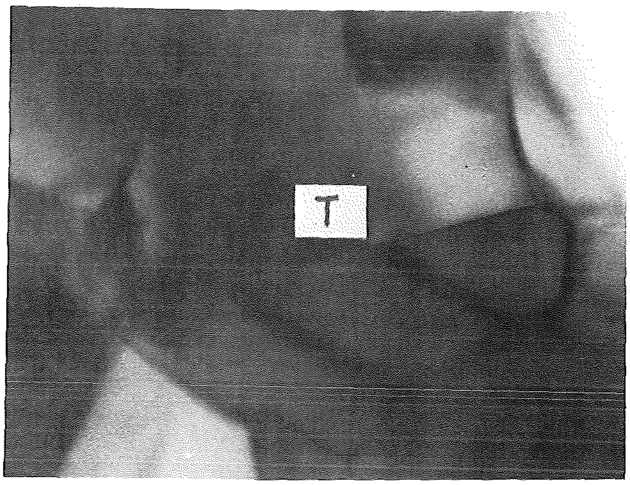

Fig. 6a

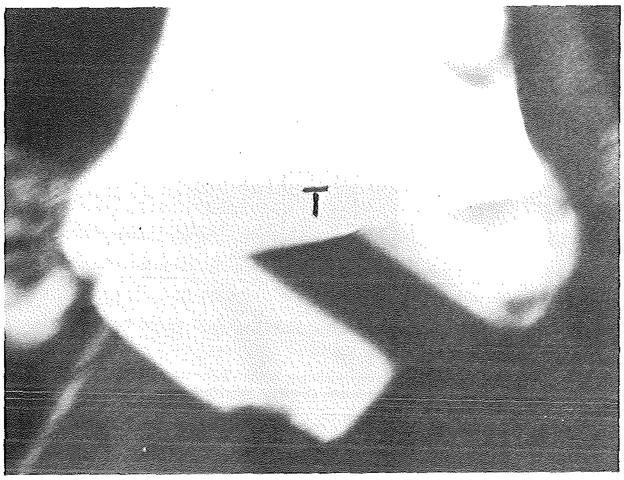

Fig. 6b

Fig. 6: Twin marked with T in high T_c Nb_3Ge (#836-3), (a) bright field, (b) dark field imaging; 460 000 x

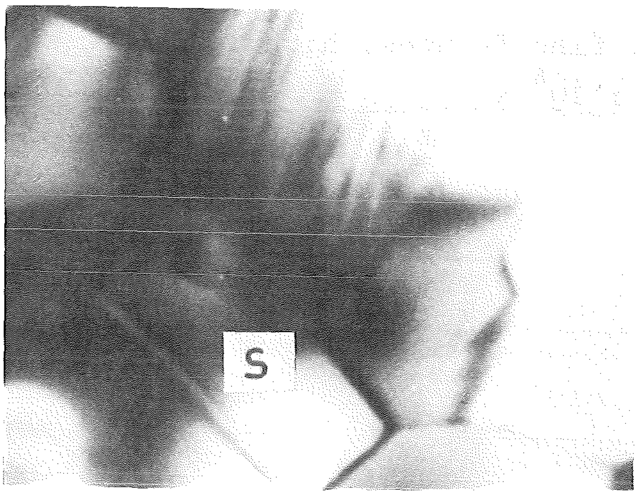

Fig. 7a

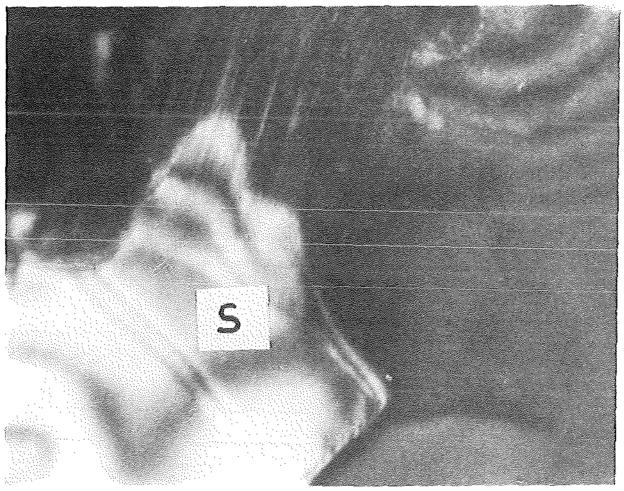

Fig. 7b

Fig. 7: Stacking fault fringes marked with S in high T_c Nb_3Ge (#836-3), (a) bright field (b) dark field imaging; 460 000 x

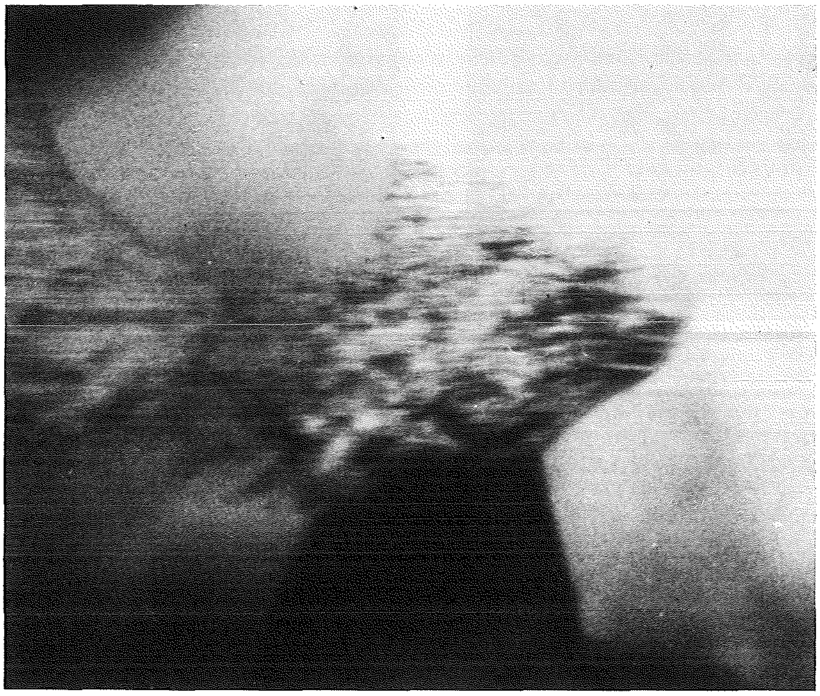

Fig. 8: Wide contrast striations on the back ground of faint fine fringes, high T_c Nb_3Ge (# 836-3); 10^6 x