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ON THE NATURE OF THE "SHORT RANGE ORDER" IN $1\frac{1}{2}$ O ALLOYS

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ON THE NATURE OF THE "SHORT RANGE ORDER" IN $1^{1/2}0$ ALLOYS¹

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ABSTRACT

High resolution electron microscope images of the $\langle 1^{1/2}0 \rangle$ special point short range ordering alloys, Ni₄Mo, Au₄Cr, Au₄V and Au₄Fe are compared, and the extent to which optical diffractograms from local regions of such micrographs can be interpreted is discussed. For Au₄Cr and Ni₄Mo, the observed state of order can be interpreted as being due to the presence of microdomains of the DO₂₂ structure and elements of the D1a structure, extending sometimes several unit cells along the c-direction, but being quite often only one or a small number of unit cells wide. For Au₄V and Au₄Fe, the observed diffuse intensity is probably too weak to allow decisive conclusions.

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1. INTRODUCTION

It is expected that short-range order (SRO) in alloys will manifest itself by broad diffuse intensity maxima in reciprocal space in the vicinity of points where the second derivative F'' of the free energy will have a minimum value. Of particular interest are these points at which extrema of F'' must exist for symmetry reasons alone: these are the so-called Special Points (SP) which satisfy the Lifshitz criterion requiring that two or more symmetry elements intersect at a point (de Fontaine, 1979). The relative local site occupation of the constituents of such alloys in this state can differ markedly from those characteristic of long range order (LRO) at the same compositions, however. Indeed, the LRO state results from the minimization of the internal energy, whereas the SRO state results from the minimization of F'' . The distinction between LRO and SRO is particularly apparent in solid solutions belonging to the $1^{1/2}0$ family, i.e. for which F'' has a minimum at that particular SP. That is because, for those systems, the corresponding LRO states have superlattice peaks at positions other than the $1^{1/2}0$ SP. Rather than attempting to study SRO directly at temperatures above ordering, it is simpler, from an experimental viewpoint, to quench such alloys rapidly to low temperatures so as to avoid nucleation of the equilibrium LRO state. In so doing, the ordering spinodal may be crossed in a temperature range where atomic mobility is still appreciable, thereby leading to amplification of the associated SP concentration wave (de Fontaine, 1975).

It is tempting to try to interpret these SRO effects in direct (or "real") space, noting that the SRO state should probably be a prefiguration of the LRO state. Ruedl et al. (1968) were the first to observe "bright speckles" in dark-field transmission electron microscopy, and interpreted

these as ordered microdomains having the LRO structure. Although a random distribution of very small microdomains belonging to all possible orientation variants may produce diffuse maxima at the $1^{1/2}0$ positions, it is now thought that the size of the observed speckles was presumably too large to allow their interpretation as images of single microdomains. For this system, Okamoto and Thomas (1971) therefore proposed a more elaborate microdomain interpretation based upon the presence of non-conservative antiphase boundaries (APB) along the (420) fcc planes in the ordered structure.

After crossing the spinodal, a pure SRO fluctuation state surely cannot be maintained, and the system will spontaneously begin to evolve towards the expected LRO state along paths which are very difficult to predict theoretically as they will evolve non-linearities in the free energy function. Hence, an interpretation based on an intermediate state between SRO and LRO is perhaps to be preferred. Such an interpretation was suggested by De Ridder et al. (1976) who characterised the state of order by clusters of a specific type, the type of cluster(s) being determined from the geometry of the diffuse intensity pattern.

In the present paper, we shall reexamine, by means of high resolution electron microscopy, SRO in various $1^{1/2}0$ family alloys, namely Ni₄Mo, Au₄V, Au₄Cr and Au₄Fe, and we shall try to determine what may be the most appropriate qualitative description.

It will turn out that the two competing concepts "concentration waves" (de Fontaine, 1975) versus "microdomains" (Ruedl et al., 1968) are in fact two aspects of the same physical reality or two languages to describe the same phenomenon. A wave with a wavelength equal to interatomic distances in a discrete medium, consisting of atoms on a lattice, can in fact only be

materialized as a configuration of atoms on an appropriate geometrical pattern. It will be shown furthermore that the present results are also compatible with the conclusions of the cluster model as described by De Ridder et al. (1976).

2. EXPERIMENTAL EVIDENCE; PREVIOUS OBSERVATIONS

An interesting point is that, while all three materials, in the as-quenched, state scatter electrons to the $1^{1/2}0$ reciprocal lattice positions, the diffuse scattering shows characteristic differences between the different alloys which should be of help in choosing descriptions for the SRO state. Diffraction patterns obtained along [001] for the four alloys are shown in Fig. 1. The first point to note is that we find the $1^{1/2}0$ scattering most intense for Ni₄Mo and least intense for Au₄Fe. Given the different atomic scattering factors involved, this is the inverse of what would be expected for the same degree of order. We can also see from Fig. 1, that while the $1^{1/2}0$ scattering is relatively symmetrically distributed about this position for Ni₄Mo, it tends to be somewhat elongated towards the fcc matrix reflections for Au₄V or for Au₄Fe but in each case in a somewhat different way. Whereas, for Au₄Fe, this linking intensity tends to be curved in towards $\langle 100 \rangle$ positions, the curvature has the opposite tendency for Au₄V. During this discussion, it is assumed that these observations reflect the SRO state and that no nuclei for LRO have formed. The conditions for retaining the SRO state are different for the alloys used. Au₄Fe can be aged for several days at temperatures in the range 720-920 K without showing any development of LRO. For Ni₄Mo, a fast quench rate is required to retain the SRO state. Other alloys such as Au₄Mn (another member of the $1^{1/2}0$ family) can only be retained in the SRO state

by splat cooling. The usual fast water quench produces a long range ordered transition state (Van Tendeloo et al., 1978).

The development of long range order in Ni₄Mo has been studied in detail by electron diffraction and electron microscopy (Ruedl, Delavignette and Amelinckx, 1968; Okamoto and Thomas, 1971; Van Tendeloo, 1976; De Ridder, Van Tendeloo and Amelinckx, 1976; Chevalier and Stobbs, 1976; Thomas and Sinclair, 1977; Van Tendeloo 1981b). On slight annealing, first diffuse "circles" are formed in reciprocal space just outside the $1^{1/2}0$ positions, i.e. different from the diffuse intensity observed for Au₄V or Au₄Fe (Fig. 1c,d). The ordering process in Au₄Cr was studied by Dutkiewicz and Thomas (1975). Using electron diffraction and lattice imaging, they concluded that the transformation from SRO to LRO occurs with the formation of a transitional ordered phase (similar to DO₂₂) which can be described in terms of composition modulations along [001] (with a wavelength equal to the c-parameter of the DO₂₂ structure). Au₄V has only been studied to a limited extent using electron diffraction by De Ridder et al. (1976), but a much more thorough study has been performed using x-ray diffraction by Furnrohr (1976). For Au₄Fe, x-ray diffraction studies by Dartyge et al. (1982) have shown the existence of diffuse intensity streaks with maxima at the $1^{1/2}0$. The present observations are the first ones obtained by electron diffraction (W. M. Stobbs, 1983).

Until now, the most convincing technique to prove (or disprove) the presence of microdomains was to make dark field images using the $1^{1/2}0$ diffuse intensity in the manner of Ruedl et al. (1968); see e.g. Chevalier (1980). When doing so, for the four alloys, one observes speckles of the order of 0.5-1 nm depending on the degree of order. The interpretation however, is not clear since the size of the speckles is such that they could

be produced by microdomains as well as by the presence of the objective aperture. Moreover, it has been observed in the case of Ni₄Mo that the speckles grow more intense and larger during long observations (Van Tendeloo, 1980). This may be due to contamination of the specimen surface and/or formation of a Mo₂C film at the surface which, in dark field, also produces speckles of the same type as the possible Ni₄Mo microdomains (Kesternich et al., 1982). Possibly, the early dark field observations by Ruedl et al. (1968) showing larger (2-3 nm) dark field speckles have to be attributed, at least in part, to contamination in the microscope.

3. EXPERIMENTAL EVIDENCE: NEW OBSERVATIONS AND THEIR INTERPRETATION

3.1 Reciprocal Space: Diffraction Patterns

The diffraction vectors corresponding with the positions of the SRO spots are $k_1 = 1/a [1\frac{1}{2}0]$; $k_2 = 1/a [1\frac{1}{2} 1 0]$ and the crystallographically related ones $\pm k_1$, $\pm k_2$; $\pm k_3$ and $\pm k_4$ shown in Fig. 2a, where a is the lattice parameter of the basic fcc structure. These vectors are also the first order diffraction vectors corresponding with the {101} type planes of the DO₂₂ structure based on the same cubic lattice.

It is therefore suggestive to use atom configurations derived from the DO₂₂ structure as the ingredients of a possible model of the SRO state. The DO₂₂ as well as the D1a structure are represented schematically in Fig. 3. The first order spots 101 of the two variants of the DO₂₂ structure which have their c-axis perpendicular to the viewing direction, lead to the four observed SRO diffraction spots (Fig. 2b). The second order spots, 202, which are present in the DO₂₂ structure, are absent in the diffraction pattern of the SRO state. This suggests that the disorder affects the d_{202} .

spacings in such a way that the second-order spots are suppressed. The insertion of a slab of D1a type atom configurations (Fig. 4) causes a shift of $1/4$ of the $\{101\}$ planes, but a shift of $1/2$ of the $\{202\}$ planes (represented as dotted lines in Fig. 4). The second-order spots will thus be much more suppressed by the introduction of this type of defect than the first-order spot.

During the first stages of LRO ordering, one observes in the diffraction pattern that intensity is "transferred" from the $1^{1/2}0$ type spots to the $2/5, 2/5, 0$ spots (Fig. 2c). This corresponds to a reduction in length of the diffraction vector, without a change in its direction. In direct space, this means an increase in average spacing, i.e. that possibly slabs of D1a structure are introduced between the $\{101\}$ planes of DO_{22} structure (Fig. 4). Depending on the proportion of DO_{22} and D1a slabs, the average spacing will vary, and hence, also the position of the intensity maximum will shift from the SRO position to the D1a position. The "wings" of diffuse intensity, connecting the D1a spots with the SRO spots, can be attributed to disorder in the arrangement of DO_{22} and D1a slabs in the two families of $\{101\}$ planes of a given variant of DO_{22} . As the long range ordering proceeds, more slabs of the D1a type are introduced, and the eight D1a spots will finally appear clearly.

Since the three orientation variants of the DO_{22} structure are a priori equally probable, one would expect to find in the diffraction pattern evidence also for the variant which has its c-axis parallel to the viewing direction. As yet, there is no reference in the literature to the presence of the 110 reflection (in the centre of the square of $1^{1/2}0$ reflections), which would indicate the presence of this third DO_{22} variant. In an attempt to find such evidence, we have deliberately overexposed the

diffraction pattern of a small selected area of Au₄Cr, which was briefly annealed at 270°C, such that the SRO spots remain prominently present; it is reproduced in Fig. 5. It is quite clear that a surprisingly sharp 110 reflection is present. The second order reflections of the type 120, on the other hand, are not observed. Tilting experiments show that the 110 reflection is streaked along the viewing direction, but very sharp along the lateral directions. This seems to indicate that the c-domains are small along the viewing direction and larger along the lateral dimensions. This is consistent with the presence of linear arrangements of several square bipyramids (5-point clusters) along the [010] DO₂₂ and [100] DO₂₂ directions, but not along the [001] direction (De Ridder et al., 1976). Along the latter direction, there is apparently some planar disorder. Moreover, the diffracted amplitudes, due to the sets of {110} planes in the different translation variants, are either in phase or in anti-phase. This means that the d_{110} spacing in c-domains is well defined even in the presence of domain fragmentation, and the 110 reflection consequently remains sharp. If all translation variants are present in equal volumes of the crystal, the resultant amplitude will be zero; only if the selected area contains unequal volumes of the different translation variants will a nonvanishing 110 reflection result. This is presumably the reason why the 110 reflection is often weak and sometimes absent, and remained unobserved until now.

3.2 Direct Space

3.1.1. High Resolution Images; Dot patterns

Recent improvements in the resolution of modern electron microscopes have led us to reexamine whether or not useful information

can be obtained on the structure of the SRO-state in $1^{1/2}0$ alloys, using axial high-resolution observations. Similar observations in Cu_3Pd have led to positive conclusions and have illustrated the importance of choosing the right objective diaphragm. Images made using a large aperture (including fcc reflections up to 220) show lattice details, but obscure the ordering effects, while images obtained with an aperture just excluding the first 200 fcc-reflections show the ordered microdomains very clearly (Van Tendeloo and Amelinckx, 1983).

Fig. 6a and b show axial illumination high-resolution images of Au_4Cr , using a large enough aperture to include 200 as well as 220 FCC reflections; Fig. 6a refers to a thin area and Fig. 6b to a thicker region. The first micrograph only shows a regular square arrangement of bright dots separated by 0.2 nm characteristic of the fcc lattice, but the second one illustrates that there is something more than just the lattice. Some of the bright dots have an increased intensity and, in certain areas, they form very locally a square arrangement corresponding in spacing and orientation with the projected D1a type superstructure. In other areas, triangular configurations are observed similar to the ones formed by the minority atoms in the DO_{22} structure projected along one of the cubic fcc axes (see Fig. 3c).

However, the bright field image, obtained using a smaller objective diaphragm only including the central beam and the nearest 8 SRO reflections (Fig. 7,8), rejecting the redundant information from the fcc lattice, shows a reduced resolution but clearly exhibits bright dots aligned in small clusters (encircled areas). In almost all clusters, the arrangement characteristic of one of the three DO_{22}

variants can be recognized. The borders of such clusters (where the periodicity breaks down) often consist of an arrangement of the D1a type.

The optical diffraction patterns of the high resolution images under the two imaging modes are shown as insets in Fig. 6, 7 and 8. The diffuse $1^{1/2}0$ intensity is quite visible, indicating that information on the SRO state is recorded in the HREM pictures. The optical diffraction pattern of Fig. 8 shows remarkably well the objective aperture used for imaging as a sharp cutoff in the diffuse intensity. When Au₄Cr is annealed for 3 hours at 270°C, no changes are observed in the electron diffraction pattern apart from the appearance of an occasional weak 110 reflection. However, on the high resolution image, using a limited aperture (Fig. 8), the effect of ordering is observed. The number of bright (or dark) dots forming a coherent microdomain is larger than in the as-quenched state observed in Fig. 7.

Very similar observations are made for Ni₄Mo (Fig. 9a, b). Again, we recognize limited areas where square or triangular arrangements of bright dots are observed in a configuration and spacing such that they resemble the projected minority atom configurations in DO₂₂ or D1a structure.

For Au₄V and Au₄Fe however, where the diffuse intensity is remarkably weaker, no clear cluster or microdomain formation has been observed in any of the high resolution images (see Fig. 10). Optical diffraction patterns from the area having an intermediate thickness show a very weak and hardly interpretable diffuse intensity (W. M. Stobbs, private communication).

We shall now examine to the direct space evidence in relation to

the diffraction patterns. In this respect, it is of interest to compare the annealing behavior of Au₄Mn, Au₄Cr and Ni₄Mo. Fully ordered Au₄Mn has the D1a structure; however, after a mild quench, this alloy exhibits a structure consisting of parallelogram shaped islands of DO₂₂ structure of varying size (Van Tendeloo et al, 1978) separated by antiphase boundaries containing structural elements of the D1a phase. In stoichiometric Au₄Mn, this constitutes a metastable transition structure which disappears on annealing; in non-stoichiometric alloys Au_{4-x}Mn this structure is stable and can be observed in symbiosis with the D1a structure and with a one and two-dimensional long period superstructure of the latter (Van Tendeloo and Amelinckx, 1981). It is thus not unrealistic to assume that in quenched Ni₄Mo a similar DO₂₂ based type "texture" occurs as in Au₄Mn, in a certain temperature range. This texture would only appear in the embryonic stage, i.e. as very small microdomains, which, on further annealing at high enough temperature, but still below the critical temperature for D1a ordering, would not grow very much, but develop into the D1a structure instead. The SRO state of Ni₄Mo would thus be derived in the first place from structural elements of DO₂₂-type configuration of the minority atoms (A-atoms). Since under suitable imaging conditions, a bright (or dark) dot can be associated with a projected column of atoms, an "average DO₂₂" structure as proposed by de Fontaine (1975) cannot be excluded (see Fig. 3c). This structure is an average structure, because one introduces "grey atoms," i.e. a mixture along the viewing direction of A and B atoms. Of course, on an atomic scale, grey atoms do not exist (they are either A or B), but HREM only images a projected structure where small composition differences

between neighboring columns cannot be detected. In Figs. 7, 8 and 9, we are imaging the minority atom configurations but no decisive conclusions can be drawn about the exact occupation of the other atom columns. Pure B-columns would be impossible to discern from B-columns containing a number of A-atoms as well. In the rest of the text, we will continue talking about DO_{22} , keeping in mind that a concentration wave type DO_{22} arrangement (as in Fig. 3c) would be possible as well.

The dot patterns in quenched Ni_4Mo and Au_4Cr suggest the occurrence of such elements of DO_{22} structure, in different orientation variants next to elements of the $D1a$ structure. The fact that well defined dot patterns are not systematically observed is a consequence of the stringent requirements that have to be fulfilled for them to be visible (see par. 4).

However, when viewing the photographs of Au_4Cr or Ni_4Mo at grazing incidence (e.g. in Fig. 8 or 9 along the indicated arrows), patches containing slightly wavy rows of somewhat brighter dots can be observed along the four directions indicated by arrows k_1 , k_2 , k_3 and k_4 in Fig. 9 and which are perpendicular to the vector $\bar{k}_1$, $\bar{k}_2$, $\bar{k}_3$ and $\bar{k}_4$ in Fig. 2a; their spacing is roughly $d_{101}(DO_{22})$. In this way, information of a more statistical nature is recorded. These rows can be considered as images of the "concentration" waves that result from "spinodal ordering." Their direction and spacing suggest that the underlying structure would be the DO_{22} structure. The bright dots, representing the cluster configurations, are situated on the observed rows or waves; the microdomain (or cluster) model and the concentration wave model are in this respect two aspects of the same phenomenon.

3.2.2 High Resolution Images of Concentration Waves

Instead of looking at high resolution images under grazing incidence in order to observe concentration waves, we have attempted to visualize such waves directly by making two-beam images using a single $1^{1/2}0$ spot and the 000 spot. Unfortunately, this was not feasible with the circular selector aperture of the microscope. We have instead used the following combination of beams: the 200 beam, and two neighboring $1^{1/2}0$ spots. This imaging mode allows the observation of fringes in one cube direction of the underlying fcc lattice, as well as two of the concentration waves (Fig. 11). The concentration waves appear in patches of short segments of parallel fringes with a spacing equal to $(d_{101})DO_{22}$ and of course oriented along the $\langle 101 \rangle$ atom rows in DO_{22} . In different patches, the waves are out of phase, their general direction being quite variable. The wave images again reflect the presence of microdomains, and they are consistent with DO_{22} structural elements.

3.2.3 Dark Field Images in $1^{1/2}0$ Spots

In order to make the link with the original observations, using the diffraction contrast mode (Ruedl et al., 1968, Okamoto and Thomas 1971), and which started the controversy on the nature of the $1^{1/2}0$ state in Ni₄Mo and in structurally similar alloys, we have produced dark field images in single $1^{1/2}0$ spots in Au₄Cr (Fig. 12). As in the original observations in Ni₄Mo, we found also in this case the same type of small bright patches with irregular shapes, but now with better defined boundaries, and hence with the possibility to have a better estimate of their sizes than was possible hitherto. It was verified that very similar configurations of bright patches are found when using

diffraction vectors such as k_1 and k_2 (Fig. 12a, b) belonging to two different variants of DO_{22} , both having their c-axis perpendicular to the viewing direction.

The visibility and shape of the microdomains depend on the exact foil orientation. Therefore, there are slight differences in the images of Fig. 12a and Fig. 12c. These photographs were made in the four SRO reflections in succession; at the end, the first SRO reflection was used once again in order to check the reproducibility and to rule out orientation changes during these operations. The dislocation image in Fig. 12 is a convenient reference mark. We have also attempted to identify corresponding configurations of bright patches in the DF images and in the H.R. images of microdomains of the same area. Due to the lack of adequate reference marks, we have not been able to find unambiguous conclusions in this manner. However, it is found that the size distribution of the bright patches is in qualitative agreement with that of the images of microdomains in the H.R. images. Also, the fraction of the surface area covered by bright patches is compatible with that giving rise to observable resolved dot patterns, taking into account that only $1/3$ of the microdomains produce a bright patch in the DF image and only $2/3$ of the DO_{22} microdomains are visible as lozenge shaped dot patterns in the H. R. image. The conditions that must be fulfilled in order to produce a visible bright patch in a dark field image are probably very similar to the requirements for the formation of a dot pattern in an H.R. image, i.e. coherency in a certain minimum volume of crystal, especially along the viewing direction.

We conclude from this that the majority of the observed bright

patches are presumably produced by microdomains of DO_{22} structure of a sufficient size. The dark areas are presumably due to other variants than those reflecting in the considered spot, or to regions where the coherency is not good enough to produce a reasonably sharp intensity maximum in the $1^{1/2}$ direction.

Whereas in the original paper, the bright patches were attributed to different variants of the D1a structure, it now seems clear that different DO_{22} variants are mainly responsible for their presence.

3.3 Optical Simulations

In order to test the proposed models, it is convenient to construct optical gratings representing the projected atomic configurations in a one unit cell thick slab. Representative parts of such optical gratings are reproduced in Figs. 13 and 14, whereas the corresponding optical diffraction patterns are shown below each diagram.

In Fig. 13a, the diffraction gratings contain exclusively sub unit cell elements of the D1a structure in two variants, whereas in Fig. 13b only sub-unit cell atom configurations of the DO_{22} structure are used. The corresponding optical diffraction patterns exhibit maxima which are much broader than those which are actually observed in most electron diffraction patterns. A combination of elements of D1a and DO_{22} (Fig. 13c) leads to a result (Fig. 13f) which resembles somewhat more closely the electron diffraction pattern. However, the spots in the electron diffraction pattern are still much sharper than those produced by the optical diffraction gratings. This suggests that somewhat larger domains, containing one or a few unit cells, must be assumed.

Fig. 14a represents an optical grating which contains microdomains of

DO₂₂ structure of the two orientation variants which have their c-axis perpendicular to the viewing directions. The atom columns of the third variant all have the same chemical composition and project on fcc sites; they do not contribute to the SRO spots, except for the 110 spots. We have therefore omitted this variant from the model. It is clear that the optical diffraction pattern closely resembles the $1\frac{1}{2}0$ intensity distribution, suggesting that the SRO state consists primarily of microdomains of the DO₂₂ structure. In Fig. 14b, APB's having the D1a configuration have been inserted; the optical diffraction pattern is found to develop "wings" towards the D1a spots. In Fig. 14c finally, more slabs of D1a structure have been inserted in the (101) rows of the DO₂₂ structure. The D1a spots become already weakly visible, next to the SRO spots in the diffraction pattern of Fig. 14f.

These optical simulation experiments confirm the conclusions derived from the diffraction patterns and from the high resolution images.

Viewing the optical gratings under grazing incidence also reveals the atom rows or "concentration waves" along {101} directions. As in the images, the concentration wave in different "patches" or "domains" have different "phases" corresponding to different translations variants of the DO₂₂ microdomains.

3.4 SRO Coefficients

Careful measurements of the SRO coefficients for Ni₃Mo, using the diffuse x-ray intensity distribution around the $1\frac{1}{2}0$ positions, have been performed by several authors (Spruiell and Stansbury, 1965; Chakravarti et al., 1974). Computer generated models based on such measurements have been presented by Chakravarti et al. (1974). We shall now show that the

resulting measured SRO coefficients are compatible with our model. Furthermore, we shall demonstrate also that their computer generated model is in agreement with our domain models.

The measured SRO coefficients in the alloy, ordered for 5 min. at 650°C, obey the following inequalities as to their magnitudes: (Spruiell and Stansbury, 1965, Chakravarti et al., 1974)

$$\alpha_{400} > \alpha_{211} > \alpha_{200};$$

we have only considered the three largest positive SRO coefficients α , which describe the essential features of the structure. The same succession of magnitudes for the largest SRO coefficients is found in all of our models. The measured values are, of course, somewhat different for the different models of Fig. 14, but in all cases, the order of the sequence is the same. On measuring the SRO coefficients on our projected models, we have assumed that the gratings represent a slab of one fcc unit cell thick and that the values obtained from such a slab are representative of the whole specimen.

Chakravarti et al. (1974) have presented 5 successive (001) layers of two computer generated models, based on the experimentally determined SRO coefficients, in the "as quenched" state and after a short anneal at 650°C. The authors concluded from these to the predominant occurrence of rod-like arrangements of molybdenum atoms along $\langle 100 \rangle$ directions. As the alloy is slightly annealed and becomes more ordered, still remaining in the $1^{1/2}0$ state, the rods appear to become longer. This is also consistent with our observations; unfortunately, the authors failed to represent their results in space. On doing this for layers 1 and 2 of their model (Fig. 15), we find that their molybdenum arrangements consist, in fact, predominantly of elements of the DO_{22} structure and some elements of the $D1a$ structure. We

have constructed an optical grating based on this computer generated model by considering again atoms in a slab of one fcc unit cell thick. The grating was obtained by superposing layers (1) and (2) and layers (3) and (4) of their figure 8 and layers (1) and (2) and layers (3) and (4) of their Fig. 9. The four so-obtained projections were juxtaposed so as to obtain a single sufficiently large grating, which contains a mixture of regions representative of the "as quenched" and of the very briefly annealed state (5 min. at 650°C). This grating produces an optical diffraction pattern which is similar to the ones produced by our model gratings. It is thus clear that our results are in fact compatible with those obtained by Chakravarti et al. (1974), although the authors interpret them quite differently.

3.5 Radiation Behavior: Equilibrium SRO State

It is of some interest to discuss the implications of our results to the observations of the radiation behavior of Ni₃Mo. The ordering and disordering of this material under irradiation with 1 MeV electrons was studied by Van Tendeloo et al. (1981) and by Banerjee et al. (1984). It was found that, when irradiating in the temperature range 200K to 450K, an initially long-range-ordered specimen becomes first disordered and subsequently the short range ordered state is formed. Irradiation above 450K always leads to the formation of LRO, unless LRO was destroyed previously by pre-irradiation at a temperature below 200K; in that case SRO can be developed also by irradiation at 450K. A surprising conclusion from these observations is that a direct transition from "SRO" (i.e. 1¹/₂0 disorder) to LRO or from LRO to SRO seems to be forbidden on irradiation in the temperature range 220 to 550K. The fully disordered state must first

be formed before the transition is possible. This remarkable result is difficult to understand if the SRO state is merely a prefiguration of the LRO state. However, if the SRO state is a microdomain state based on a different structure (in this case DO_{22}) from the LRO state (D1a), it becomes quite understandable that one structure must first be sufficiently disordered before another one can start to form.

On thermal treatment, the behavior is quite different. On annealing at temperatures below the critical temperature for LRO (T_C), a SRO specimen, obtained by quenching from above T_C , transforms into the long-range-ordered state, and it remains in that state on prolonged annealing at that or at a lower temperature. We have also verified whether or not the $1^{1/2}0$ state is the equilibrium SRO state in A₄B alloys. We have performed an experiment on Au₄Cr, where T_C is as low as 330°C: we have annealed an initially SRO specimen of Au₄Cr at 270°C during 75h; after this treatment, it exhibits the LRO state. On heating this specimen in the electron microscope to just above T_C , the LRO spots rapidly disappear at $(340 \pm 10)^\circ\text{C}$ and the typical SRO pattern of Fig. 16 appears above this temperature. This is in agreement with the results of a similar experiment on Au₃Cr (Das et al., 1973). It is thus clear that the $1^{1/2}0$ state is an equilibrium state, just above T_C . At this temperature, $1^{1/2}0$ spots are more diffuse and weaker than in the room temperature quenched specimens; this is undoubtedly, at least in part, due to the Debye-Waller factor, but it is also a consequence of spinodal ordering which sharpens and intensifies the $1^{1/2}0$ spots as the specimen is cooled below the instability temperature.

On cooling down to room temperature in the microscope, this specimen remains in the SRO state, diffusion being apparently too slow at these temperatures to generate the LRO state in times of the order of minutes.

These experiments seem to confirm that the quenched-in $1\frac{1}{2}0$ state in Au_4Cr , and presumably also in the other A_4B alloys (except perhaps Au_4Mn), represents the equilibrium SRO state, apart from a possible difference in microdomain size.

4. DISCUSSION

In discussing short range order, it is important to specify exactly what is meant by that term. Consider first equilibrium states: above the transition temperature, the stable solid solution will contain dynamic equilibrium fluctuations, which may, in fact, be rather intense as a second order transition or ordering instability is approached. The state just described is that of equilibrium SRO proper. The ground state of order at very low temperature is that of equilibrium LRO. As explained in the introduction, the former state is that which minimizes the second derivative F'' ; the latter is that which minimizes the internal energy E . Between those two equilibria lies, in principle, a non-denumerable infinity of non-equilibrium states of partial order. For these transition states, it is not really meaningful to ask at what point SRO gives way to LRO, simple descriptions of such states are not available, theories are virtually non-existent. Indeed, there exists no universal minimization procedures which will yield correct evolutionary paths that a system must follow on its way from equilibrium SRO to LRO.

It is precisely those transition states which are really observed by the type of experiments described above; small wonder that clear structural understanding is still lacking. High-temperature equilibrium SRO is best described in reciprocal space, for instance by the Krivoglaz-Clapp-Moss formula. Low temperature LRO is, of course, most conveniently described in

direct space by specifying the unit cell of the ordered structure. In between, it is a matter of taste whether one adopts a reciprocal or a direct space formulation.

At best, we can try to understand qualitatively the evolution from SRO to LRO: when the solid solution is quenched rapidly from a high temperature, we expect the equilibrium fluctuations to be retained, thereby producing broad, diffuse intensity maxima about the special point characteristic of that "family," in the present case, the $1^{1/2}0$ SP. As the ordering spinodal, or the stability limit of the very same SP concentration wave is crossed, the diffuse intensity maxima should intensify, initially in a manner quite independent of the actual average concentration, i.e. independent of the final LRO state towards which the system is tending. The reason for this initial independence is that, in the spirit of simple spinodal theory (Cahn, 1961), the early stages of evolution are governed approximately by a linear kinetic equation which "knows about" F'' only, the latter second derivative containing little information about the final ground state. Soon, however, non-linearities should make their presence felt, and the symmetric diffuse SRO intensity maxima should begin to distort, in a way which will depend on the average concentration, on the type of equilibrium LRO state appropriate for that concentration, on the particular alloy system considered, i.e. on the relationship between the various phases present in the phase diagram, and also, as shown for example by Martin (1982), on the type of impurity or third element present. Thus, in the examples considered here, we expect to see different shapes of diffuse intensity patterns in Ni₄Mo, Au₄Cr, Au₄V and Au₄Fe after some amount of "spinodal ordering" has taken place, although in all four cases both the SP family and the stoichiometry are the same. At present, it is

impossible to predict theoretically how the "intensity transfer" from SRO to LRO will take place.

All we know is that, in intermediate states of order, information about final states must be present in some embryonic way. It is, therefore, tempting to construct simple models combining clusters of atoms in the correct LRO relationship (the D1a structure in the present case), in various allowed orientations, along with clusters characteristic of the ordered structure closest to the disappearing SRO state (the DO₂₂ in the present case). Such "cluster" models have been constructed in the form of two-dimensional mixtures of "Ni₄Mo," "Ni₃Mo" and "Ni₂Mo" - type domains have recently been proposed to explain diffuse neutron intensity patterns obtained from PdH and PdD samples at very low temperatures (Blashko et al., 1981). Apparently, this hydride system also belongs to the 1¹/₂0 family.

The transition state between SRO and LRO, and in general any state of local order, but of long range disorder on a lattice, can be described by means of a "cluster relation" which has to be satisfied at each lattice point, i.e. by specifying which clusters are predominant. De Ridder et al. (1976) have shown that the geometrical locus of diffuse intensity in Ni₄Mo and Ni₃Mo suggests that the predominant clusters in the 1¹/₂0 state should be the five point cluster consisting of one molybdenum atom forming the apex of a square pyramid of nickel atoms. With respect to the basic fcc lattice, we can specify the clusters as follows: Mo at 000, Ni at $\pm \frac{1}{2} \frac{1}{2} 0$ and $\frac{1}{2} 0 \pm \frac{1}{2}$. It can easily be verified that this cluster relation is satisfied at all lattice sites of the DO₂₂ structure as well as in the D1a structure. The linear arrangement of such clusters in bipyramids along cube directions is a predominant feature of the ideal DO₂₂ structure. It thus also turns out that the results of the clusters theory are compatible

with the present model, whereby a dominant role is attributed to the D0_{22} structure.

One central question in this discussion, is "do we see microdomains and clusters or not?" In other words, can the bright dots observed in Fig. 7, 8 and 9 be interpreted as minority atom strings lined up along the electron beam, i.e. along one of the cubic axes?

When talking about microdomains with respect to ordering, one usually refers to domains the size of a few unit cells having the long range ordered structure. The ordered clusters we possibly observe here by HREM quite often consist only of a small number of bright dots (i.e. sometimes less than one unit cell) but extend probably over a few nm along the cube direction perpendicular to it. This conviction is substantiated by the following arguments: if certain atom columns, having the configuration of the minority atom columns in the LRO structure, are clearly differentiated from the surrounding ones, this can only mean that they also contain almost exclusively minority atoms. Moreover, these columns have to be extended over a sufficient length in order to be sufficiently different from columns containing both types of atoms in the macroscopic proportion.

We will now try to rule out the presence of possible artifacts. One might argue that electropolishing introduces a surface layer which gives rise to moire-type artifacts or that oxides may be formed at the surface. However, in that case, one would have to assume that Au_4Cr forms a surface layer and, with the same electropolishing solution, Au_4V will not; Ni_4Mo and Au_4Cr would both suffer from it although prepared with a different solution. Moreover, a possible surface layer, which has a constant thickness, would be better observable in thinner areas, which is not the case.

Another argument is that one might actually be looking at the initial stages of LRO rather than at the SRO state. This would be quite possible for Ni₄Mo where fast water quench has been used and a slight anneal of a few seconds at 800°C already produces long range ordering effects observable in the diffraction pattern. However, for Au₄Cr, where the ordering temperature is only about 330°C, the kinetics are very slow and anneals up to 3 hours at 270°C did not produce any further ordering effects. Only after anneals of more than 10 hours, long range order reflections appear weakly (Dutkiewicz and Thomas, 1975), which denies the probability that any long range ordering would have taken place during quench in this material.

A striking and interesting feature is that "microdomains" are not visible close to the edge of the specimen when imaging with the larger objective diaphragm (Fig. 6a), while the same area imaged with only the transmitted beam and the eight SRO reflections does show microdomain contrast up to the edge of the specimen (Fig. 8). However, this is not so surprising since similar effects have been observed for long range ordered alloys. In the thinnest areas, only the matrix is imaged and, in order to see the ordering effects, one needs a minimum thickness since the structure factor for the ordering reflections is much smaller than the structure factor for the basic reflections. This has been pointed out by Shindo (1982) for ordering in Au-Cd alloys and by Van Dyck et al. (1982) for the Au-Mn system.

In our model, we have to assume that, at least for some microdomains, the coherency is rather good along the electron beam; i.e. the microdomains extend several unit cells along this cube orientation. If this were not the case, one would fail to observe the clusters or dot patterns for two reasons:

- a) If the microdomains only extend over 1 or 2 fcc unit cells for a specimen thickness of at least 10 unit cells (i.e. 4nm), one would not observe such pronounced effects.
- b) For thin microdomains, one would, of course, have overlapping domains along the imaging direction and, even for a microdomain thick enough to produce a contrast effect, the overall effect would be partly cancelled out due to overlap. The observed dot patterns will then underestimate the order present.

In some cases, one might still observe "coincidence patterns" under these conditions; these would consist of dot patterns with a geometry that differs from that of the projected structure of a single domain (Van Tendeloo and Amelinckx, 1978).

Assuming extended elongated microclusters along one of the cube orientations, we must have three orientation variants having their c-axis along all three cube axes. However, with the present HREM techniques, we can only image a fraction of these clusters, namely those having good coherency along the electron beam. This idea agrees well with the x-ray results of Chakravarti et al. (1974) who proposed for Ni₃Mo that the first ordering effect is to form extended Mo-Mo chains along the cube axes. We have shown here that these are in fact due to microdomains of DO₂₂ structure elongated along these directions. It is also consistent with the further ordering data obtained by electron diffraction by De Ridder et al. (1976), where the diffuse circles observed around the SRO reflections are interpreted as being due to pyramidal clusters, which also imply ordering along the cube directions.

Optical diffraction from the observed high resolution images clearly shows the presence of the diffuse SRO reflections and no presence of any

LRO intensity, indicating that at least some information on the SRO state has been recorded in the images. In order to find out the validity of a microdomain model partly consisting of DO_{22} (lozenge) configurations and partly consisting of $D1a$ configurations (squares), we produced two dimensional optical masks for different types of domains (Fig. 13, 14).

It might seem unrealistic to include DO_{22} fragments (AB_3 composition) in the ordering process of AB_4 alloys, however, the DO_{22} structure is the only one, apart from the AABBB phase with composition AB (Khatchaturyan, 1973), having superstructure reflections at the $\langle 1^{1/2}0 \rangle$ special points. Moreover, in similar systems (e.g. Au-Mn), the DO_{22} structure plays an important role in the ordering process of Au_4Mo (Van Tendeloo et al., 1978) as well as in equilibrium $Au_{4-x}Mn$ phases (Van Tendeloo and Amelinckx, 1981; Terasaki et al., 1980; Hiraga et al., 1980, 1982). This is summarized in Fig. 17 where the three Au-Mn equilibrium phases between 20 and 23% Mn are reproduced under high resolution conditions (upper part) and in a schematic representation (lower part), where only the Mn configurations are indicated. Close to Au_4Mn one forms a one dimensional (Fig. 17a) and a two dimensional long period superstructure (Fig. 17b) of Au_4Mn . Along the boundaries, a DO_{22} configuration (triangular arrangement of bright dots) results. At 23% Mn, the basic structure is DO_{22} but with two dimensional periodic antiphase boundaries along which the $D1a$ configuration (square arrangement) is retained. This phase, although ideally not having the A_4B composition, occurs invariably as a high temperature transition structure during the ordering process of perfectly stoichiometric Au_4Mn (Van Tendeloo et al., 1978).

A transmission electron microscopy foil, though very thin, is a three dimensional object. Enlarging somewhat on the proposed model, we may then

regard the thin foil as made up of several stacked layers of two-dimensional patterns, similar to the ones described above, bearing a certain degree of positional or orientational relationship to one another. Because of this partially random stacking, the projection of the resulting structure will only occasionally reveal the original D1a or DO₂₂ clusters. Hence, the projected image will tend to exhibit islands of ordered domains in a sea of disordered material, as may be seen, for instance, in the micrograph of Fig. 8 and 9. Such an artificial interpretation would result from the fact that, in an electron micrograph, one does not see three-dimensional space, but a two-dimensional projection thereof; it would underestimate the order present.

To the question "does high resolution TEM reveal microdomains?", one may tentatively answer: "One sees apparently ordered microdomains wherever clusters, characteristic of transition states intermediate between equilibrium SRO and LRO, happen to project coherently." It is quite clear that there is more order than revealed in this way by the H.R. images due to the overlap effects.

5. CONCLUSIONS

The experimental evidence relative to the 1¹/₂0 state in a number of A₄B alloys is critically reviewed.

- a) The most likely model for the 1¹/₂0 state of these alloys consists of different variants, based on a common fcc lattice, of microdomains of DO₂₂ structure, containing one or a small number of unit cells, separated by boundaries containing structural elements of the D1a structure. Depending on the annealing treatment, the ratio of the number of D1a elements to the number of DO₂₂ elements is different.

This model is consistent with the results obtained using a number of different electron optical observation modes, as well as optical simulation and diffraction and computer simulation.

- b) It is argued that the "microdomain" model and the "concentration wave" model are two descriptions of the same physical reality, which are revealed by different imaging modes. Also, the results of the cluster model are compatible with the proposed structural model.
- c) A re-interpretation of some results obtained by x-ray diffraction and based on measurement of the SRO coefficients in quenched and briefly annealed Ni₃Mo confirms the proposed model as well (Chakravarti et al., 1974).

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FIGURE CAPTIONS

Fig. 1 Electron diffraction patterns along [001] for four different alloys showing diffuse intensity around $1^{1/2}0$ positions.

(a) Ni₄Mo; (b) Au₄Cr; (c) Au₄V; (d) Au₄Fe.

Fig. 2 Schematic representation of three diffraction patterns relevant for the understanding of the SRO state and the evolution towards LRO in $\langle 1^{1/2}0 \rangle$ alloys.

(a) a cubic section of the SRO state with only reflections at $1^{1/2}0$ positions.

(b) a [010] section of the tetragonal DO₂₂ structure.

(c) a [001] section of the tetragonal D1a structure. Superstructure reflections of two variants, having a common c-axis, are indicated by open and closed dots.

Fig. 3 Representation of the D1a (Fig. a) and DO₂₂ structures (Fig. b) projected along one of the axes of the basic fcc structure. Different variants are represented. In Fig. c an "average projected DO₂₂" structure is represented. Black dots represent A atoms; open circles are B atoms and hatched circles represent a mixture of A and B atoms (e.g. projected along the viewing direction). The A-atoms are still in a DO₂₂ configuration but a concentration modulation is obvious along the $(^{420})_{\text{fcc}} \equiv (101)_{\text{DO}_{22}}$ planes (dotted lines) (after de Fontaine, 1975).

Fig. 4 Schematic representation of the DO₂₂ structure as projected along [010]; only the minority atoms are indicated. The introduction of a slab of D1a configuration causes a shift of $1/4$ of the (101) planes and of $1/2$ of the (202) planes.

Fig. 5 [001] diffraction pattern of Au₄Cr quenched from 550°C and annealed for three hours at 270°C. Note the presence of the weak 110 reflections in the centre of the square of four $1^{1/2}0$ spots.

Fig. 6 High resolution image of Au₄Cr quenched from above T_c, taken along [001]. All reflections up to 220_{fcc} are included in the objective aperture (aperture A in the inset of Fig. 7).

(a) thin region

(b) thicker region

The optical diffraction pattern is shown as an inset. Next to the fcc spots one notes the presence of the $1^{1/2}0$ spots. In the thin region only the fcc lattice is revealed; in the thicker part a differentiation of the atom columns is visible.

Fig. 7 High resolution image of Au₄Cr, quenched from above T_c. Only the central beam and the nearest SRO reflections are used to produce the image (aperture B in the lower inset). The optical diffraction pattern (upper right inset) exhibits the diffuse maxima at $(1^{1/2}0)$ positions.

Fig. 8 [001] image of Au₄Cr under the same conditions as in Fig. 7, but annealed for 3 hours at 270°C. The number as well as the size of the ordered domains have increased although the diffraction pattern is still the same. Note the microdomains (or clusters) in the encircled areas.

- (a) Lower magnification;
- (b) High magnification.

Fig. 9 [001] high resolution image of Ni₄Mo using a limited objective aperture similar to the one used to obtain Fig. 7 or 8.

- (a) Low magnification;
- (b) Higher magnification.

The optical diffraction pattern is reproduced as an inset.

Fig. 10 [001] high resolution image of Au₄V. Only the basic fcc lattice is revealed. The diffraction pattern together with the aperture used for imaging are shown as an inset. Note the difference in aspect with Fig. 6b which was produced under the same conditions; no differentiation between atom columns is noted.

Fig. 11 Dark field image of Au₄Cr, using the small aperture visible in the inset; clearly indicating the presence of the concentration waves along k_1 and k_2 (see Fig. 2a). The angle of $\sim 37^\circ$ between the k_1 and k_2 waves can be read off from the image.

Fig. 12 Four dark field images made in four different SRO reflections in Au₄Cr. The indicated vectors k_i refer to the schematic pattern of Fig. 2a. Note that large similarities can be found between $a(k_1)$ and $c(k_4)$ as well as between $b(k_2)$ and $d(k_3)$;

- (a) and
- (b) as well as
- (c) and
- (d) on the other hand

exhibit significant differences in the configurations of the bright patches.

Fig. 13 Three models for optical gratings consisting of:

- (a) only square (D1a) type atom configurations on a cubic lattice.
- (b) only lozenge shaped (DO₂₂) atom configurations on a cubic lattice.
- (c) a mixture of both types of configurations.

The lines on the drawings have been added to visualize the arrangements but were not present on the original gratings.

(d,e,f) Corresponding optical diffraction patterns showing, apart from the cubic lattice, different configurations of diffuse intensity contours.

Fig. 14 (a,b,c) Models for optical gratings and corresponding optical diffractograms.

- (d,e,f) Illustrating the evolution from SRO towards LRO.
- (a,d) Only DO₂₂ fragments separated by single rows of D1a are used.
- (b,e) DO₂₂ as well as D1a fragments are present.
- (c,f) Mainly D1a and occasional DO₂₂ microdomains are represented.

In all cases the c-domains were omitted; their presence would only lead to a 110 spot, as observed in Fig. 5.

Fig. 15 Structural representation of two successive (001) layers in short range ordered Ni_4Mo according to a computer generated model of Chakravarti et al. (1974). Open and closed circles represent Mo atoms at two different levels. Ni atoms have been omitted. Note the presence of fragments of DO_{22} structure and elements of D1a structure.

Fig. 16 [001] electron diffraction pattern of long range ordered Au_4Cr heated in the electron microscope just above T_C . Note the disappearance of the LRO reflections, and the presence of weak $1^{1/2}0$ spots. The pattern was recorded at $(370 \pm 10)^\circ\text{C}$.

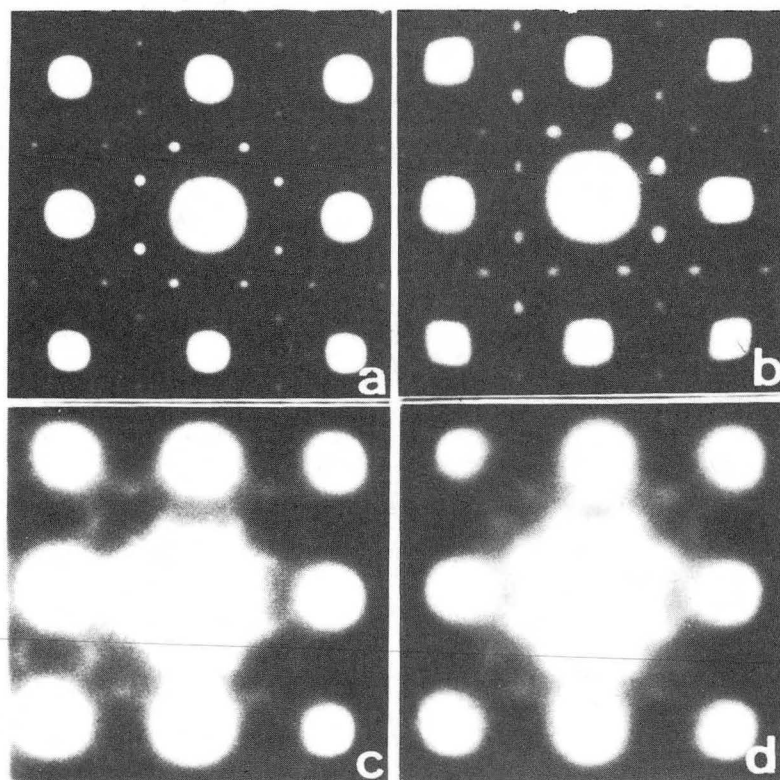
Fig. 17 High resolution images (upper part) as well schematic representations (lower part) of three structures intermediate between A_4B (D1a) and $\text{A}_3\text{B}(\text{DO}_{22})$ in the Au-Mn system.

(a) A one-dimensional long period structure of the D1a phase (1D-D1a).

(b) A two-dimensional long period structure of D1a (2D-D1a).

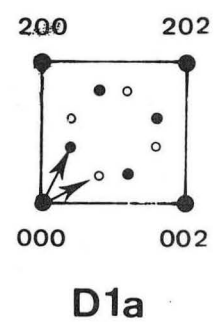
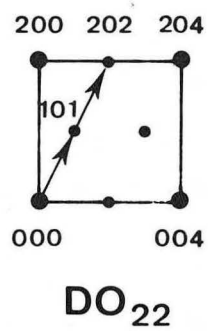
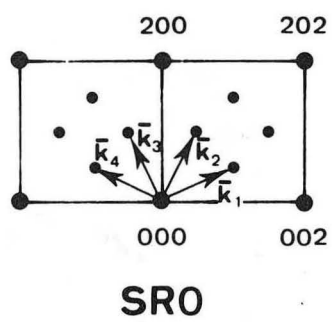
(c) A two-dimensional long period structure based on the DO_{22} structure (2D- DO_{22}).

In the D1a based phases (Fig. 17a and b) DO_{22} is locally formed along the interfaces; in DO_{22} based structures (Fig. 17c) D1a is formed along the interfaces.



XBB 848-6001

Fig. 1



XBL 848-8596

Fig. 2

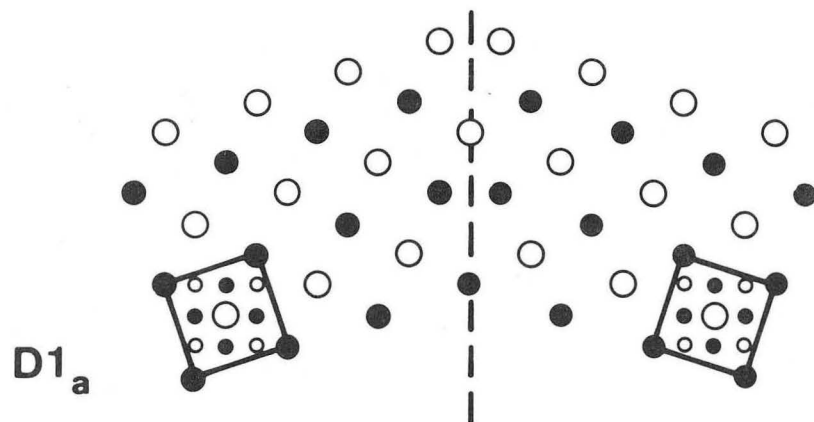


Fig. 3a

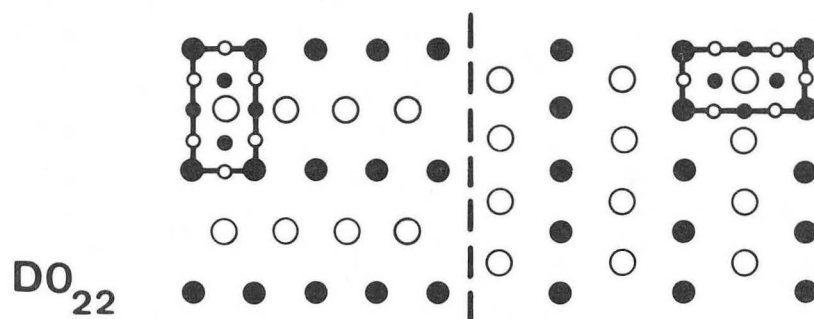


Fig. 3b

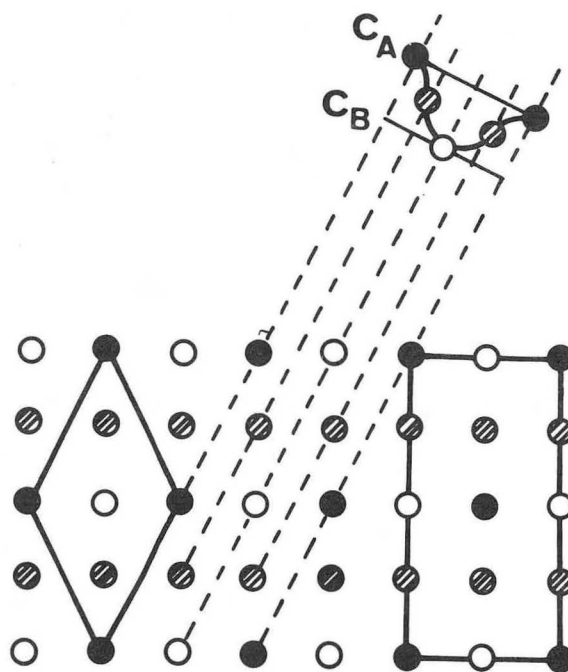
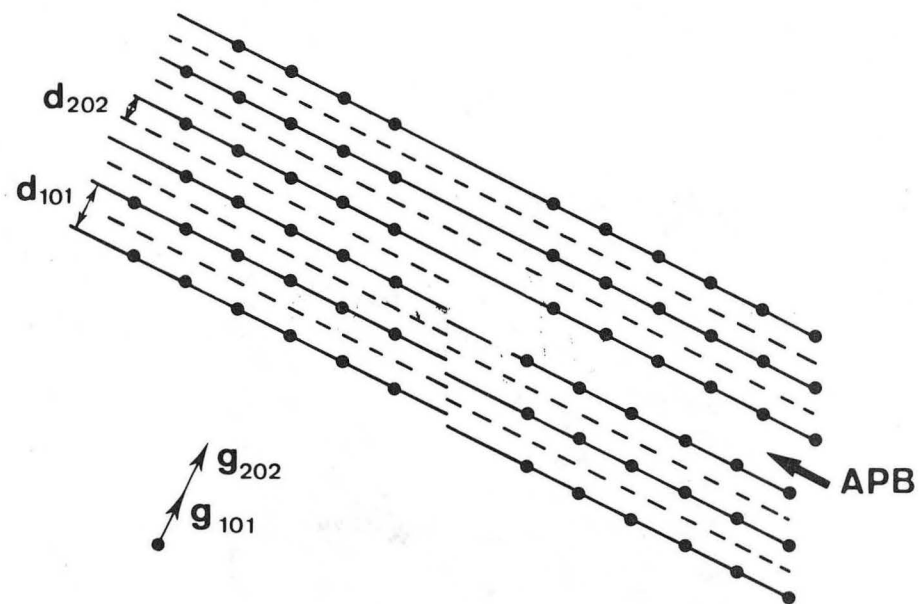


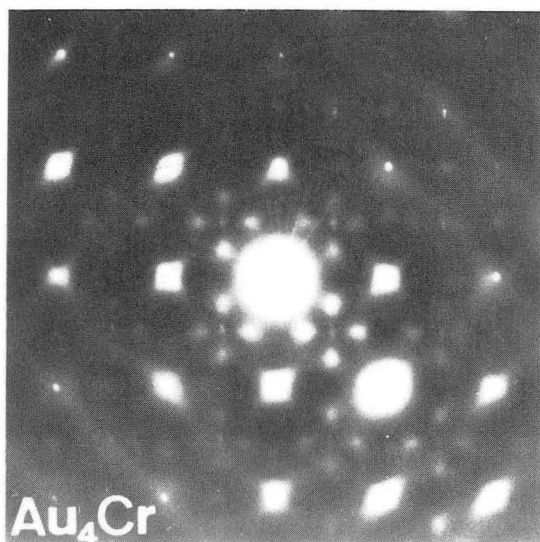
Fig. 3c

XBL 848-8597



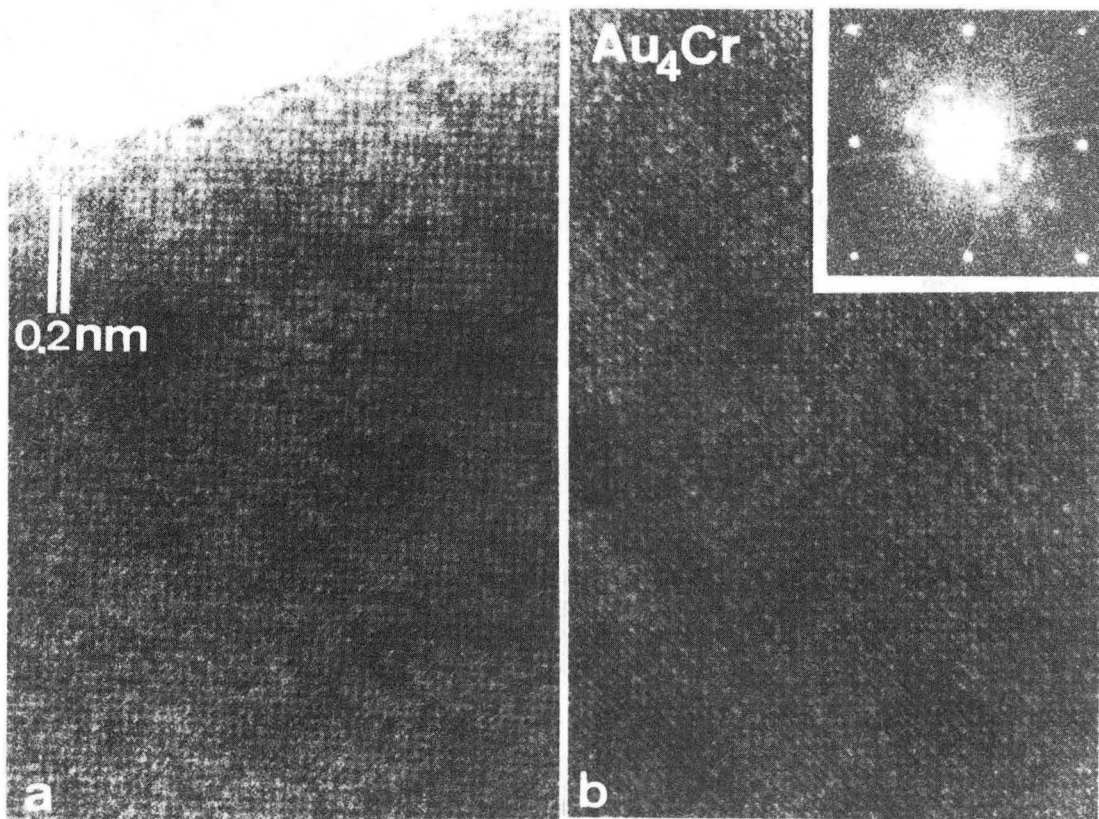
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Fig. 4



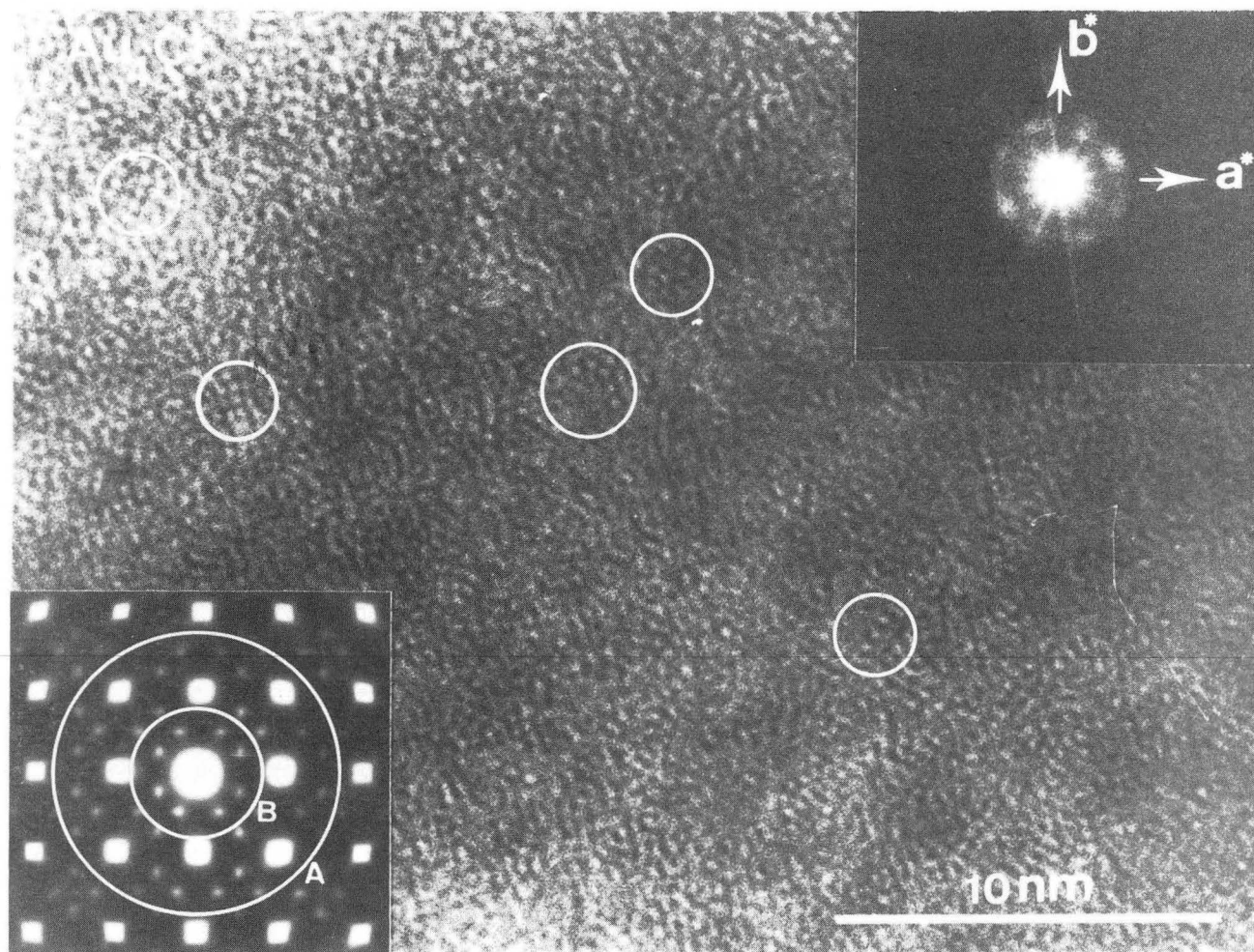
XBB 848-6002

Fig. 5



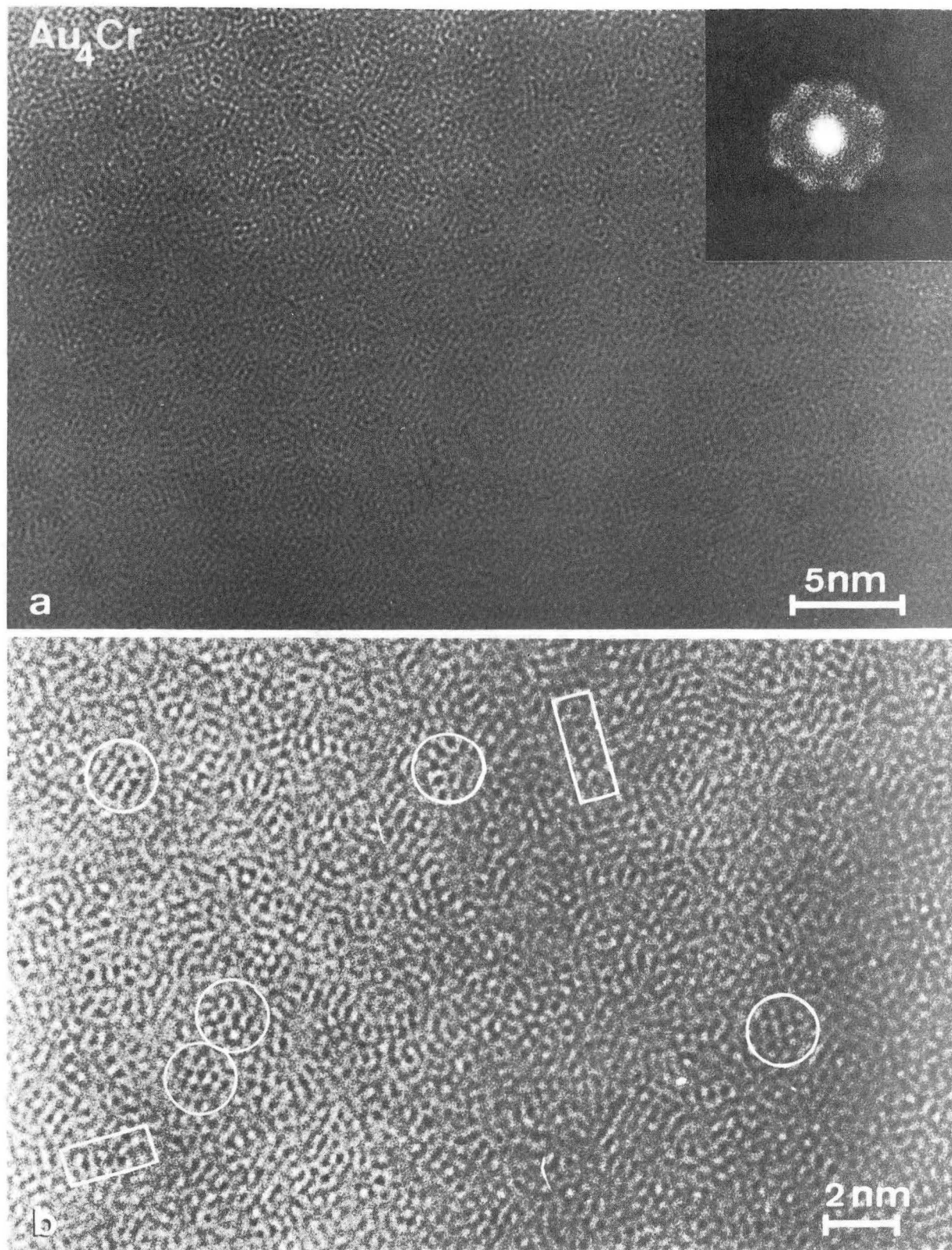
XBB 848-6003

Fig. 6



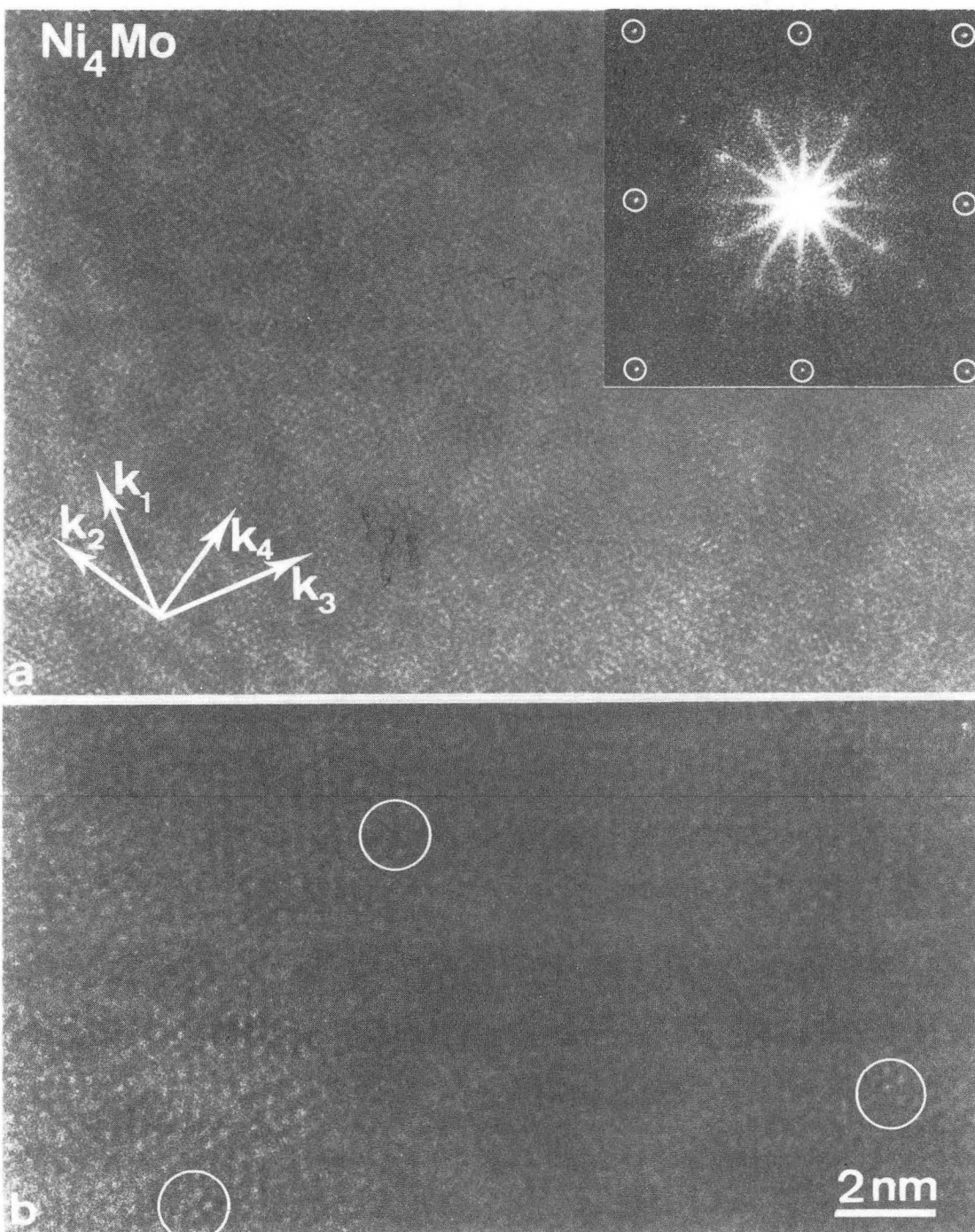
XBB 848-6004

Fig. 7



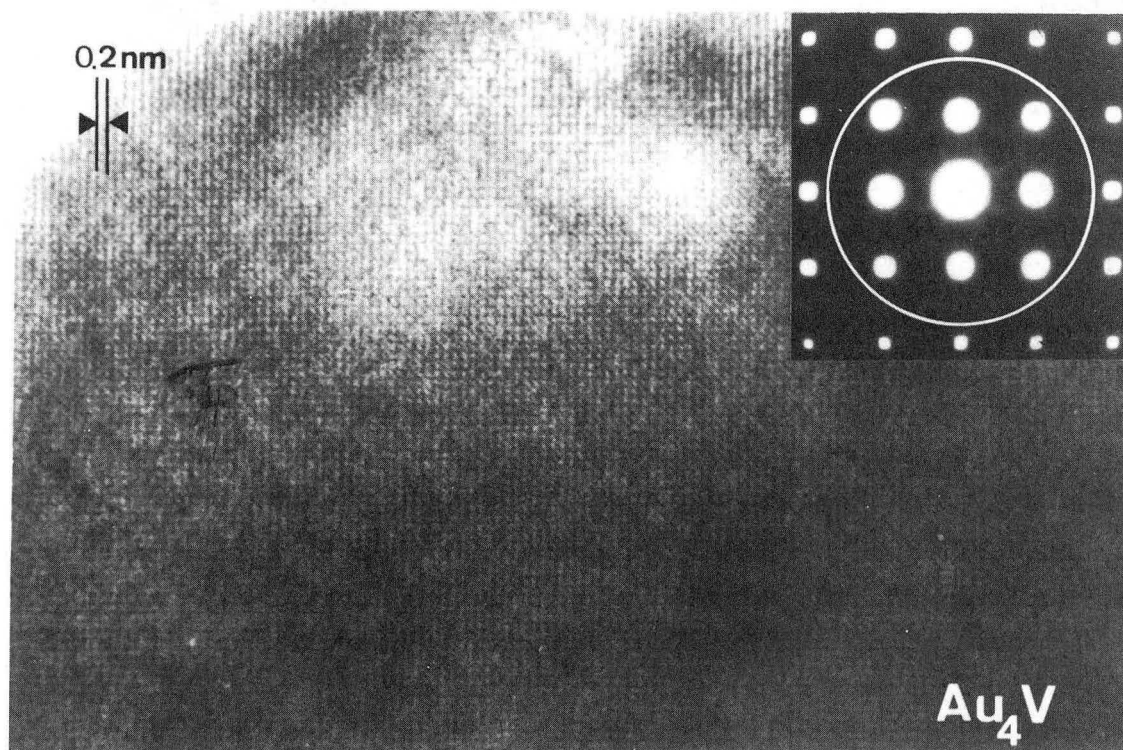
XBB 848-6005

Fig. 8



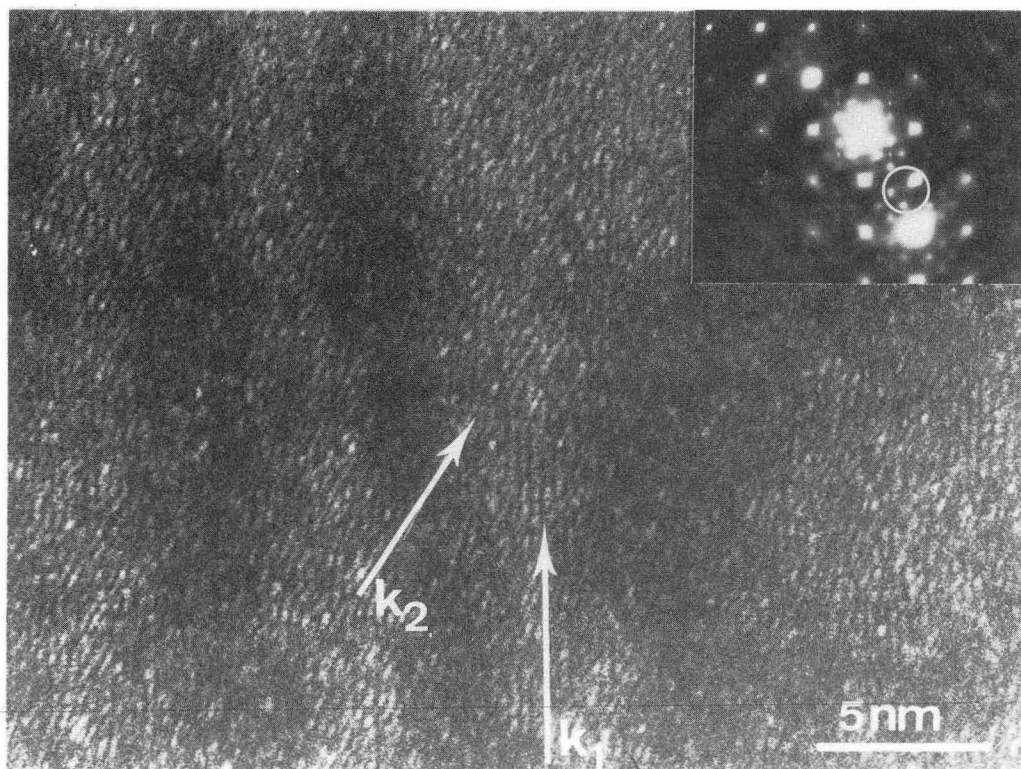
XBB 848-6006

Fig. 9



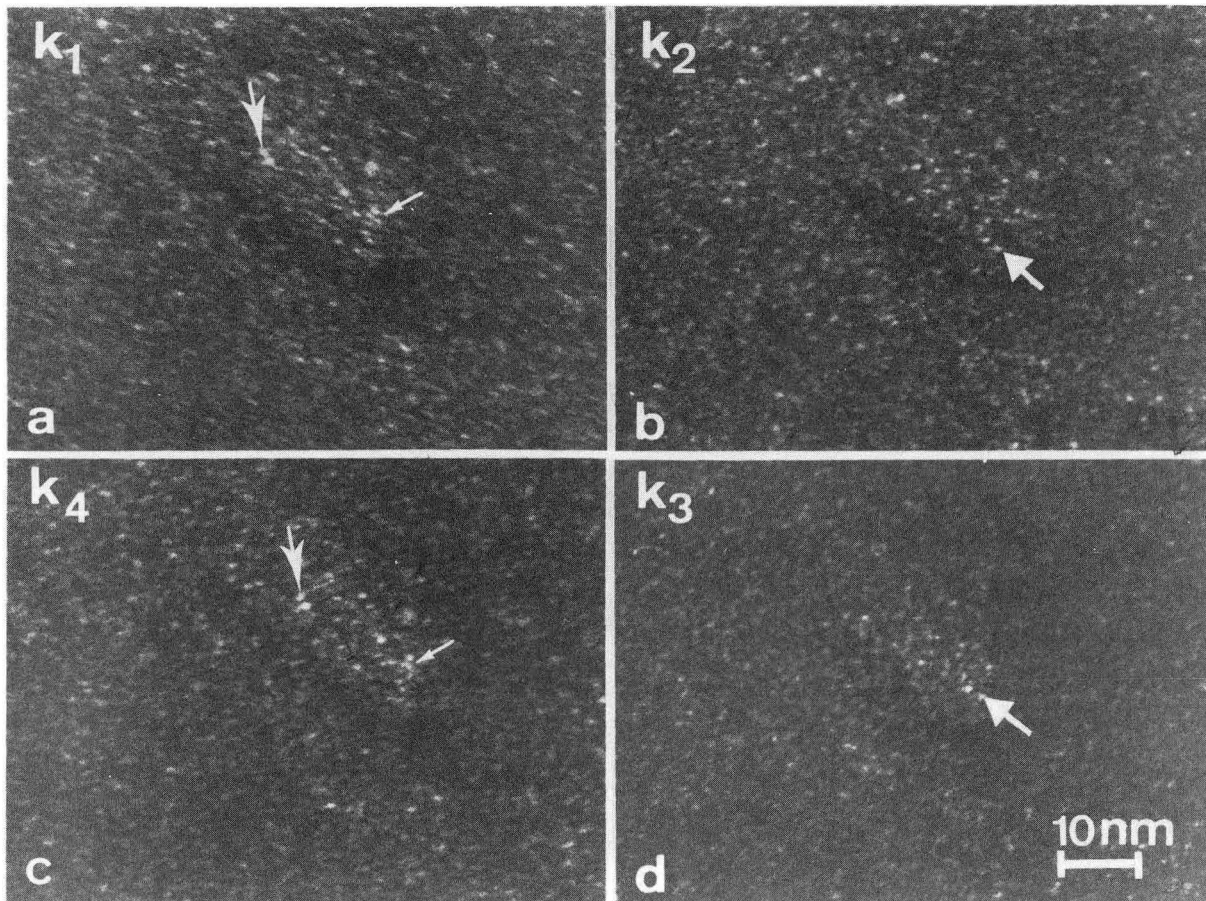
XBB 848-6007

Fig. 10



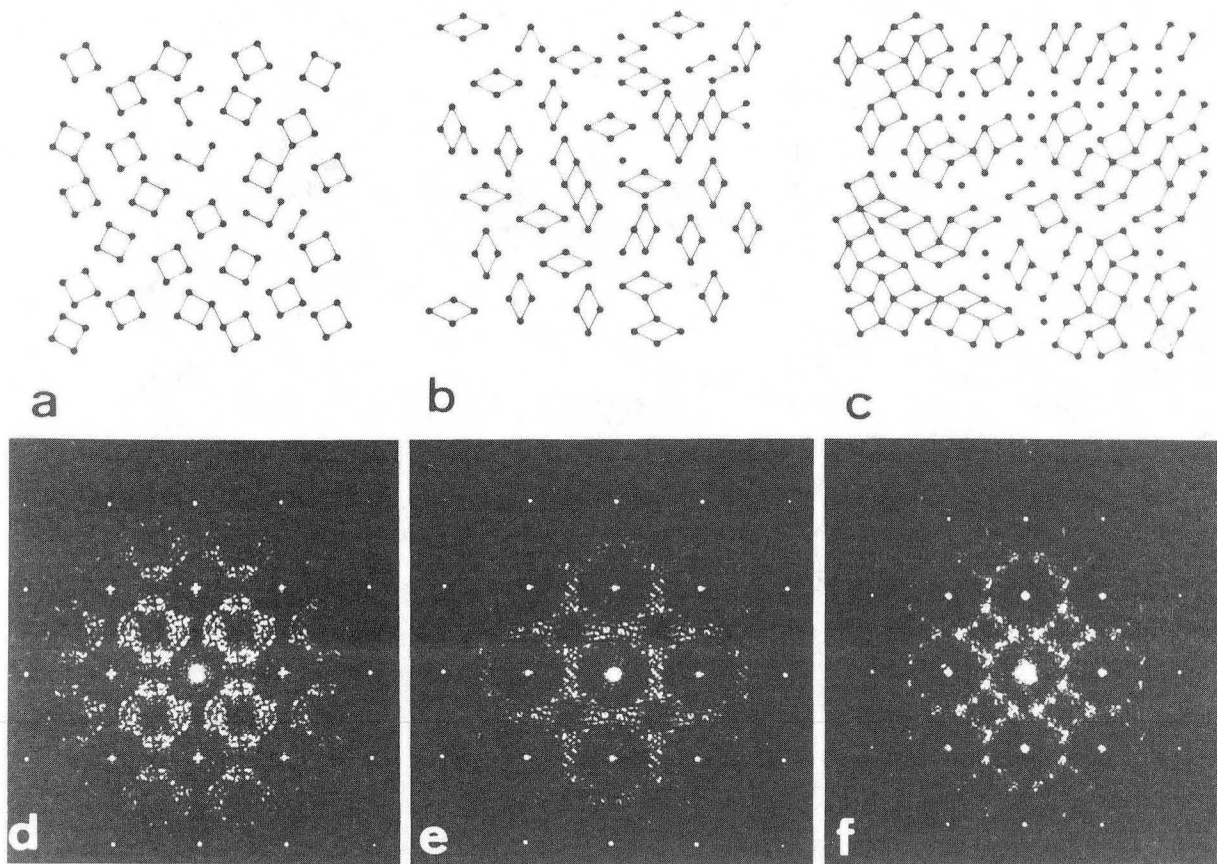
XBB 848-6008

Fig. 11



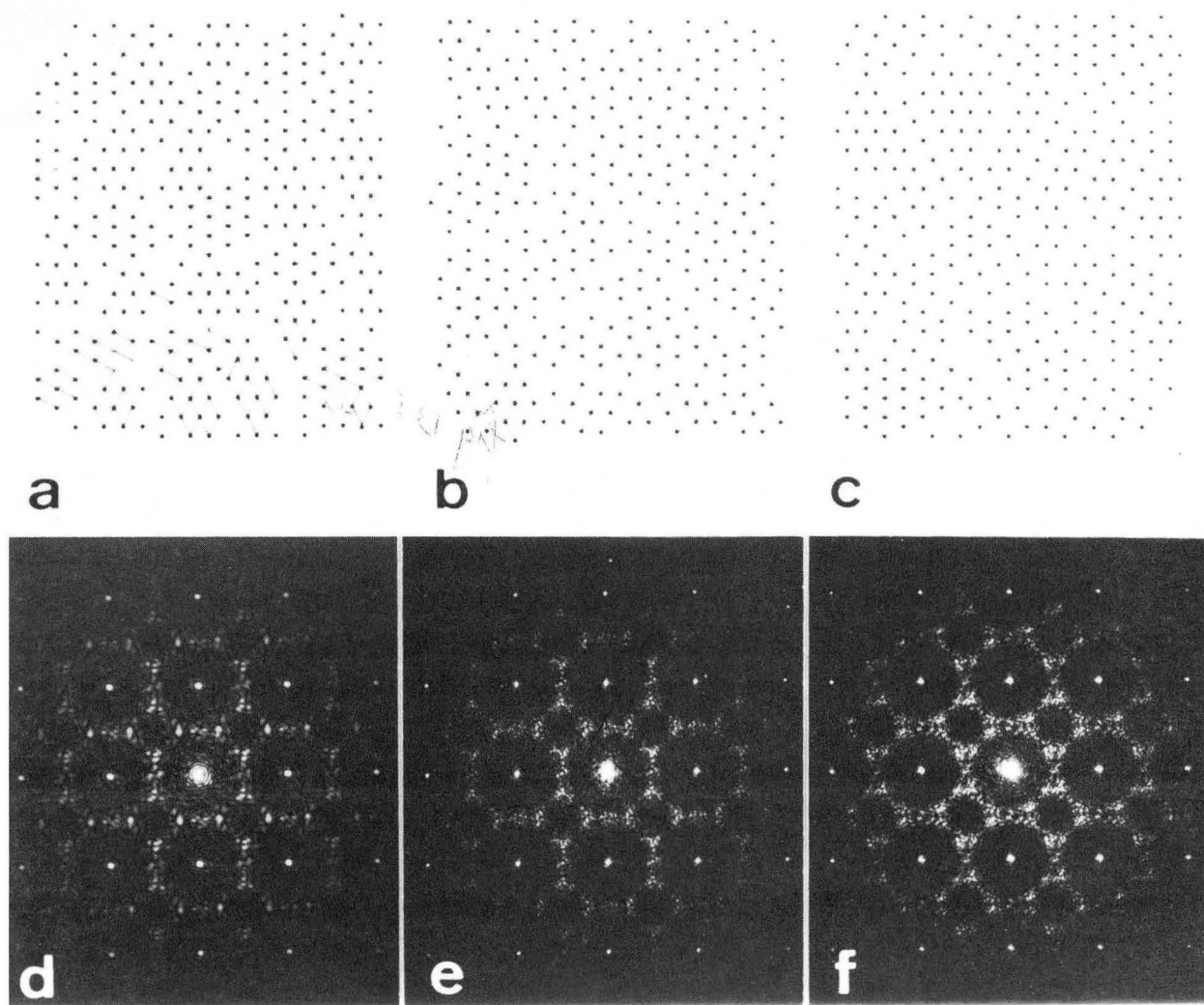
XBB 848-6009

Fig. 12



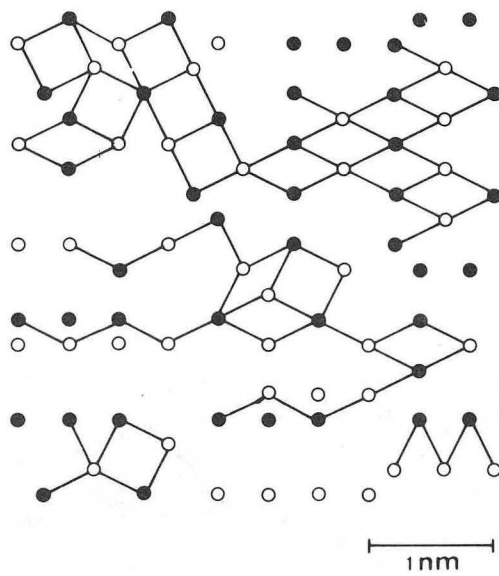
XBB 848-6010

Fig. 13



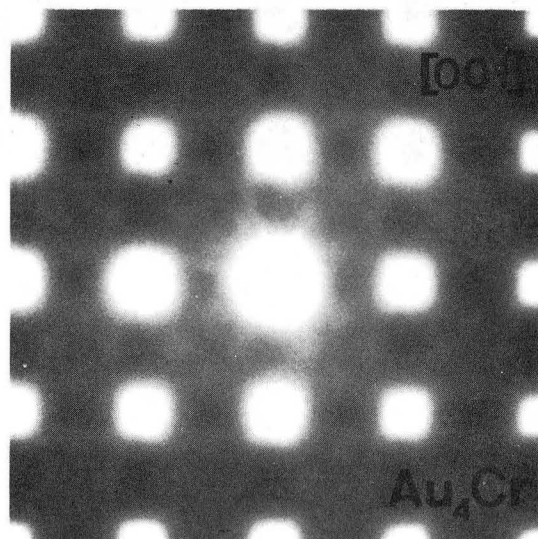
XBB 848-6011

Fig. 14



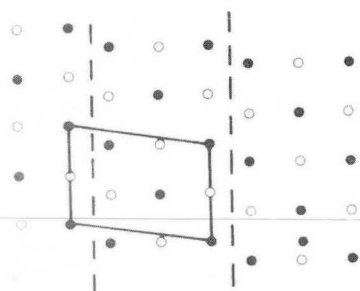
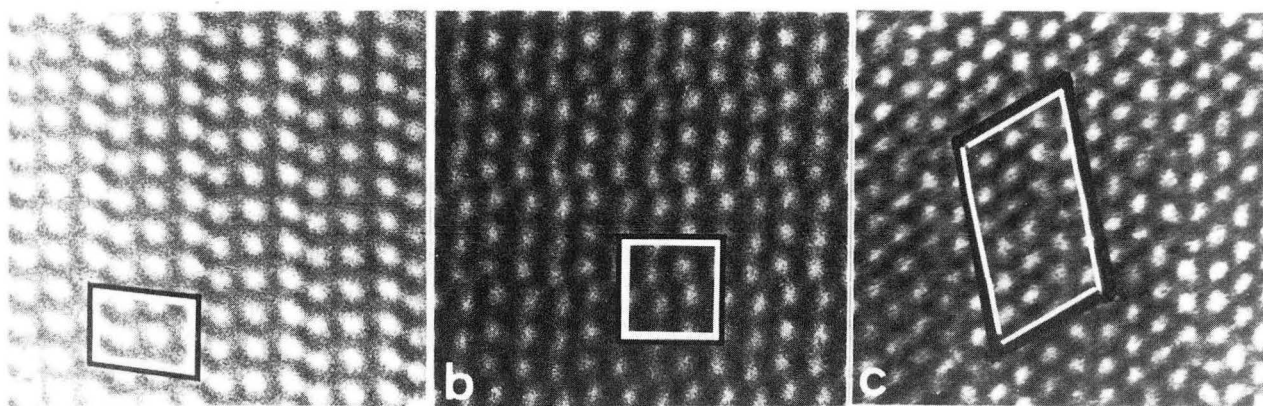
XBL 848-8599

Fig. 15



XBB 848-6012

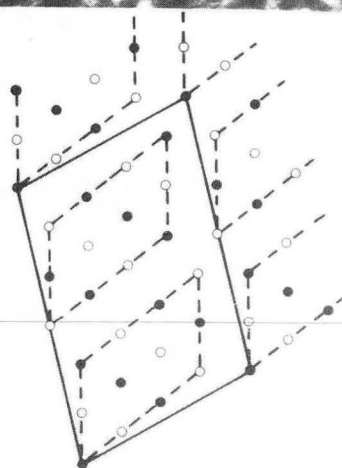
Fig. 16



1D-D1_a



2D-D1_a



2D-D0₂₂

XBB 848-6013

Fig. 17

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