

## New Orientationally Ordered Low-Temperature Superstructure in High-Purity C<sub>60</sub>

G. Van Tendeloo,<sup>(1)</sup> S. Amelinckx,<sup>(1)</sup> M. A. Verheijen,<sup>(2)</sup> P. H. M. van Loosdrecht,<sup>(2)</sup>  
and G. Meijer<sup>(2)</sup>

<sup>(1)</sup>*University of Antwerp (RUCA), B2020 Antwerpen, Belgium*

<sup>(2)</sup>*Research Institute of Materials, University of Nijmegen, 6525 ED Nijmegen, The Netherlands*

(Received 4 February 1992)

Evidence is provided for a new low-temperature superstructure in pure C<sub>60</sub>; its structure can be described as face-centered cubic with a lattice parameter  $2a_0$ . The superstructure is most probably the result of rotations alternatingly over  $+\varphi_1$  and  $-\varphi_2$  about one of the  $\langle 111 \rangle$  axes of neighboring molecules along the cube directions. The experimental evidence is based on low-temperature electron diffraction.

PACS numbers: 61.55.-x, 61.14.Hg

Recently methods to prepare significant quantities of well separated high-purity fullerenes C<sub>60</sub> and C<sub>70</sub> have become available and it has become possible to grow mm-size single crystals [1,2]. This has allowed detailed study of the crystal structures and the phase transitions occurring in these phases [3-6]. The room-temperature structure of C<sub>60</sub> had been a matter of some controversy [7] until it was shown that solution-grown crystals may retain a significant concentration of solvent molecules, which apparently stabilizes the hcp structure [8,9]. On observing the hcp-stacked solution-grown crystals in the microscope vacuum, they transform under electron irradiation, by a shear transformation, into faulted fcc crystals [10]. It is now well established that the stable room-temperature phase of C<sub>60</sub> is fcc [11].

The kinematical diffraction pattern exhibits a remarkable feature: The  $h00$  reflections have zero intensity even for  $h = \text{even}$  [4]. It was shown that this is due to the fact that the diffracting power is localized in a spherically symmetric shell of which the average radius is  $\frac{1}{4}$  of the fcc lattice parameter [12]. This observation is a strong argument in support of the assumption of free rotation of the molecules at room temperature, leading to time-averaged spherical symmetry [6]. High-resolution electron microscopy and electron diffraction have shown that the fcc-stacked crystals of C<sub>60</sub> are often multiply twinned on (111) planes and may contain a high density of stacking faults, both intrinsic and extrinsic, the stacking fault energy being very small [13].

The material studied was high-purity C<sub>60</sub> produced in the conventional manner in a dc arc discharge between two high-purity graphite electrodes in a 0.2-atm helium environment [1]. Extraction in cold toluene of the soot so obtained allows us to separate mainly the mixture C<sub>60</sub> and C<sub>70</sub> from the other products. Repeated liquid column chromatography is used to obtain C<sub>60</sub> with a purity better than 99.9% as measured by mass spectrometry, NMR, and Raman spectroscopy [14]. All possibly residual solvent is removed by heating the material to 250°C for several hours in an evacuated quartz tube ( $< 10^{-5}$  Torr). During further heat treatments the quartz tube is kept at low pressure by continuous pumping. The materi-

al is then repeatedly sublimated in a segmented quartz tube; hereby C<sub>60</sub> is transported from one segment to the next one. The last segment is sealed off on both ends. This capsule is then placed in a furnace to perform the crystal growth by slow cooling of the vapor to room temperature in about 4 h. Crystals having sizes of the order of 0.5 mm are obtained in this way [2].

Small single crystals are crushed and the fragments are mounted on microscope grids. The adherence of the crystal fragments to the grid was ensured by using grids which had previously been covered with a thin layer of glue, by dipping them in a dilute solution of glue in chloroform, followed by drying. Other specimens were prepared by depositing crystal fragments on a holey carbon film. No difference in behavior was noted. The electron diffraction patterns were obtained from electron transparent edges of wedge-shaped crystal fragments. Typical areas from which electron-diffraction patterns were recorded are  $1 \mu\text{m}^2$ . The thickness of the sample is variable but never so small as to give rise to shape transforms which are a significant fraction of the interlevel spacing in reciprocal space.

The room-temperature phase of the high-purity, solvent-free, fullerene C<sub>60</sub> has a fcc structure with lattice parameter  $a_0 = 14.2 \text{ \AA}$ , all node points being occupied by equivalent molecules. It has been shown [4] that below 250 K this face-centered phase transforms into a simple cubic structure with roughly the same lattice parameter  $a_0$ , apart from a small contraction [15].

At room temperature the four molecules per fcc unit cell are quasifreely rotating but they become distinguishable by their orientations in the simple cubic phase [4]. The structure then consists of four interpenetrating simple cubic sublattices, related by the lost symmetry translations  $\frac{1}{2}a_0\langle 110 \rangle$  of the fcc lattice, each sublattice being occupied by one type of oriented molecules *A*, *B*, *C*, or *D*. Starting from the reference configuration where all molecules have the same orientation and where the three cube axes of the fcc lattice are parallel to three mutually perpendicular binary axes of the molecule, one obtains the orientationally ordered simple cubic structure by rotating the *A*, *B*, *C*, and *D* molecules, respectively, around

the four  $\langle 111 \rangle$  directions over an angle of about  $26^\circ$  in a sense determined by the space-group symmetry  $Pa\bar{3}$  [4,16–19]. These conclusions are based on the results of x-ray and neutron powder diffraction experiments and recently also single-crystal diffraction experiments.

We have verified the occurrence of the phase transition on single-crystal fragments of highly purified  $C_{60}$  by means of low-temperature (liquid nitrogen) electron diffraction and electron microscopy. It was confirmed that below 250 K the single-crystal electron-diffraction patterns of the fcc phase develop weaker superstructure spots at spot positions which are systematically extinct in the fcc structure, in accordance with the pattern to be expected from a simple cubic lattice with space group  $Pa\bar{3}$  [Fig. 1(a)]. The occurrence of  $90^\circ$  rotation ordering twins was noted [Fig. 1(b)]. Careful examination of the electron-diffraction patterns reveals moreover very weak spots which indicate a multiple unit cell as compared to the simple cubic one. In particular in the  $[110]$  zone pattern of Figs. 1(c) and 1(d) very weak but unambiguously identifiable sharp spots appear in the centers of the rectangular meshes of the pattern of intense spots [Fig. 1(d)]. The interpretation of the diffraction pattern of Fig. 1(d) is straightforward, provided one is aware of the possible complications that certain spots might be caused

by  $\langle 111 \rangle$  streaks in reciprocal space, due to faulting or to multiple twinning on  $\{111\}$  planes. The characteristic  $2a_0$ -fcc spots, indicated by the arrows in Fig. 1(d), are crucial in this respect.

As mentioned in several papers, crystals of  $C_{60}$  are sometimes multiply twinned and moreover often contain stacking faults [13]. In such crystal fragments all reciprocal-lattice nodes, which are not common to the fcc and the hcp stackings, are streaked along the  $\langle 111 \rangle^*$  directions normal to the fault planes. The diffraction patterns then exhibit “parasitic” spots with fractional indices, already in the room-temperature phase. Therefore only crystal fragments which did not produce parasitic spots in their room-temperature diffraction pattern were considered for study of the low-temperature phase. The room-temperature pattern of the same crystal fragment viewed in the same orientation as that which produced Fig. 1(d) is shown in Fig. 2(a); there is no indication of parasitic reflections due to faulting, and in particular not at sites where supplementary spots appear in Figs. 1(d) or 2(b). The diffraction pattern of Fig. 2(c) is made again from the same crystal fragment, in the low-temperature phase, but after reorientation along the  $[111]$  zone. Spots due to faulting, if present, would appear in the centers of triangles of basic spots. No such spots are visible. The particular crystal fragment that

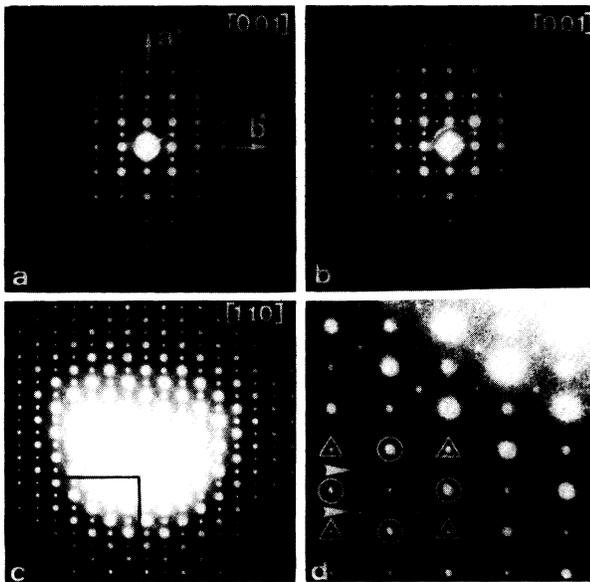


FIG. 1. Electron-diffraction patterns produced by the low-temperature phase of  $C_{60}$  at liquid-nitrogen temperature. (a) Monodomain pattern along  $[001]$ ; note the absence of the spot rows with  $k = \text{odd}$  in accordance with the space group  $Pa\bar{3}$ . (b)  $[001]$  zone pattern of an area containing two  $90^\circ$  orientation variants of the structure. (c)  $[110]$  zone diffraction pattern exhibiting supplementary spots due to the fcc ( $2a_0$ ) structure. (d) Magnified part of the pattern in (c);  $a_0$ -fcc reflections are indicated by circles;  $Pa\bar{3}$  simple cubic reflections are surrounded by triangles; weak  $2a_0$ -fcc reflections are indicated by arrows.

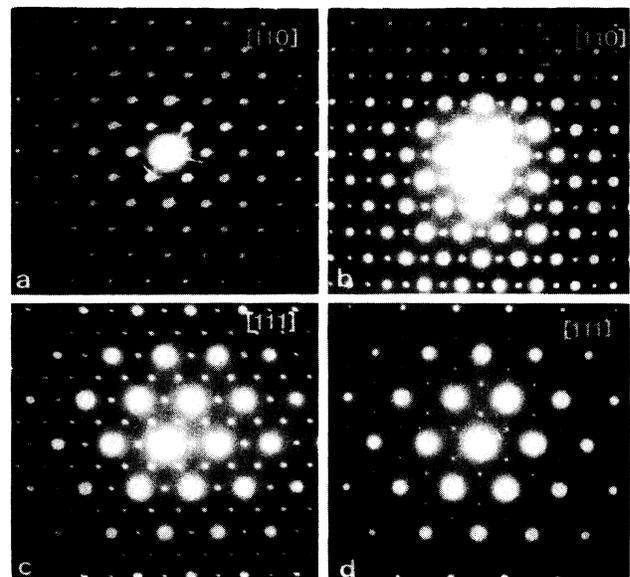


FIG. 2. (a) Electron-diffraction pattern of the fcc phase; no “parasitic” spots due to faulting are visible. (b) Electron-diffraction pattern under the same diffraction conditions as (a) but after cooling to liquid-nitrogen temperature. Note the sc and the  $2a_0$  spots. (c) Electron-diffraction pattern along  $[111]$  of the same sample as in (a); note the absence of parasitic spots; low-temperature phase. (d) Room-temperature diffraction pattern along  $[111]$  of a different sample exhibiting parasitic spots due to faulting.

produced the diffraction pattern of Fig. 1(d) is thus sufficiently free of stacking faults to allow an unambiguous conclusion as to the absence of parasitic spots due to "positional" faulting. For comparison purposes Fig. 2(d) shows a crystal fragment, in the room-temperature phase, also viewed along the  $[111]$  zone, and which did exhibit parasitic spots.

One might argue that even in a crystal free of positional faulting, "orientational" faults might develop in the low-temperature phase and give rise to streaking as well. This would require such faults to be planar and to be confined to well-defined crystallographic planes, perpendicular to the streaks. In fact two types of orientational faults can be distinguished in the simple cubic phase. Orientation variants differing by a  $90^\circ$  rotation about a cube axis usually occur [Fig. 1(b)]; the coherent interface between such domains would be a  $\{110\}$  twin plane. Moreover "translation" variants, related by the lost symmetry translations of the fcc structure are separated by translation interfaces. Dark-field imaging in superstructure reflections has revealed that these interfaces are far from planar, except where inherited from preexisting twin interfaces of the fcc structure, but in this case the streaks would anyway already be present at room temperature [13].

We further note that the spots due to the streaking result in general from nodes situated at some distance from the reciprocal-lattice plane which is being excited (i.e., which is tangent to Ewald's sphere). Unless the excited zone is perpendicular to the streaks, which is not the case in Fig. 1(d), the parasitic spots will in general be produced in eccentric positions with respect to the meshes of the reciprocal-lattice plane. Within the experimental error all supplementary spots in Fig. 1(d) are in centers of the rectangular meshes of sc spots. We conclude that all reasonable precautions were taken to avoid spurious effect due to faulting.

The only obvious possibility is that the reciprocal lattice is actually body centered and hence that the lattice is again face-centered cubic but with a doubled lattice parameter  $2a_0$ . Although the superstructure reflections are weak close to the origin, they become relatively more intense compared to the basic spots for large diffraction angles [see Fig. 1(d)]. This suggests that these spots are associated with a superstructure caused by periodic atom displacements, i.e., by commensurate displacement modulation.

The relative weakness of the reflections indicates that the superstructure does not deviate strongly from the described simple cubic orientationally ordered structure. In view of the purity of the sample, it seems excluded that an admixture of other fullerenes such as  $C_{70}$  or residual solvent might be responsible by forming an ordered  $C_{60}$ - $C_{70}$  "alloy." A more plausible and simpler model consists of molecules in eight different orientations, differing either by their  $\langle 111 \rangle$  rotation axis, or by the magnitude or—more probably—by the sense of the rotation angle

about a given  $\langle 111 \rangle$  axis. The  $2a_0$  face-centered structure would then consist of eight interpenetrating  $2a_0$  face-centered sublattices, related by the lost symmetry translations  $a_0\langle 100 \rangle$  of the simple cubic lattice, each occupied by molecules of a single orientation. In this way molecules in the same orientation are as uniformly dispersed as possible over the available lattice sites.

Let us designate molecules rotated over an angle  $\varphi$  about the  $[111]$ ,  $[\bar{1}\bar{1}1]$ ,  $[1\bar{1}\bar{1}]$ , and  $[\bar{1}1\bar{1}]$  axis, respectively, by  $A$ ,  $B$ ,  $C$ , and  $D$ , and the molecules rotated about the same axis, but over another angle (for instance,  $-\varphi$ ) by the same primed letters  $A'$ ,  $B'$ ,  $C'$ , and  $D'$ . The structure we propose is represented in Fig. 3 and does not—apart from the new superstructure spots—diffract very differently from the structure described in [4], which was found to be consistent with the observed x-ray pattern. However,  $A$  and  $A'$  being different now, a  $2a_0$  superstructure results. A similar relettering of the other sublattices results in the postulated new  $2a_0$  superstructure. A simple, somewhat speculative, possibility would be that in the simple cubic phase the libration axis of the molecules is already defined but that a rotational degree of freedom (e.g., libration between  $+\varphi$  and  $-\varphi$ ) still remains. This degree of freedom is then frozen in the  $2a_0$  structure. Because of the weakness of the characteristic fcc ( $2a_0$ ) spots, it is not excluded that such reflections have been overlooked in the x-ray and neutron diffraction studies made so far.

As a result of the uncertainty of the sample temperature in electron microscopy, it is highly speculative to make a quantitative statement on the temperature at which the  $2a_0$ -fcc phase appears, especially since the weak superstructure reflections are not directly observed. They are only revealed on photographically recorded diffraction patterns. It is nevertheless safe to say that the  $2a_0$ -fcc phase appears at a lower temperature than the sc phase, but we cannot exclude that this occurs over a certain temperature range. For the pattern of Fig. 1(d) the grid temperature was 113 K, as indicated on the thermo-

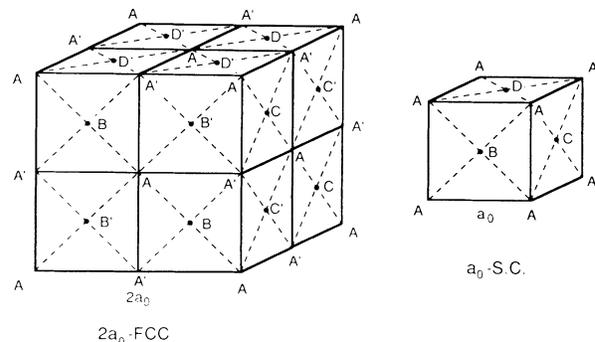


FIG. 3. Comparison of the superstructure model for the simple cubic  $a_0$  structure, according to [4], and the proposed  $2a_0$ -fcc structure. The same letters designate molecules rotated about the same  $[111]$  axis; primed and unprimed letters denote rotations over  $+\varphi$  and  $-\varphi$ , respectively.

couple; the specimen temperature was certainly above that.

The present observations may possibly have some bearing on the neutron powder diffraction experiments by David *et al.* [15], which were published after submission of this paper. These authors found evidence for the occurrence of two sets of molecules in the sc structure, corresponding to two different values of the angle  $\varphi_I = 98^\circ$  and  $\varphi_{II} = 38^\circ$ , which differ by a  $60^\circ$  rotation between energetically quasiequivalent configurations. They find that at 5 K the occupancies of both configurations are in the ratio  $I/II = 0.835:0.165$ , i.e., 5:1. With increasing temperature the two occupancies become more equal, the ratio reaching a value of 1.7:1 just below the 250-K transition. It is interesting to note that these authors mentioned the possibility of a short-range ordered superstructure, but did not find any evidence in their data.

In the literature some experimental results suggest that next to the fcc-simple-cubic transition other phase transitions might occur [15,20]. In particular differential-thermal-analysis measurements indicate the presence of a weak "shoulder" on the low-temperature side of the main peak. In a recent paper the occurrence of a sequence of phase transitions in  $C_{60}$  is predicted on the basis of group-theoretical considerations [21]. We present here evidence that the low-temperature phase of  $C_{60}$  is more complicated than hitherto assumed.

While this paper was being revised we received a preprint confirming the occurrence of a  $2a_0$ -fcc structure, based on electron spin echo measurements at 1.2 K [22].

This work was supported by the National Fund for Scientific Research (Belgium) and IUAP 11. Part of the work has been made possible by the Dutch Organization for Fundamental Research of Matter (FOM) and the Netherlands Organization for Scientific Research (NWO/SOON).

- 
- [1] W. Krätschmer, L. D. Lamb, F. Fostiropoulos, and D. R. Huffman, *Nature (London)* **347**, 354 (1990).
- [2] M. A. Verheijen, H. Meekes, G. Meijer, E. Raas, and P. Bennema, *Chem. Phys. Lett.* **191**, 339 (1992).
- [3] A. Dworkin *et al.*, *C.R. Acad. Sci. Paris* **312**, Sér. II, 665 (1991).
- [4] P. A. Heiney, J. E. Fisher, A. R. McGhie, W. J. Romanow, A. M. Denenstein, J. P. McCauley, Jr., A. B. Smith, III, and D. E. Cox, *Phys. Rev. Lett.* **66**, 2911 (1991).
- [5] D. A. Neumann, J. R. D. Copley, R. L. Cappellitti, W. A. Kamitakakara, R. M. Lindstrom, K. M. Creegan, D. M. Cox, W. J. Romanow, N. Coustel, J. P. McCauley, Jr., N. C. Maliszewski, J. E. Fisher, and A. B. Smith, III, *Phys. Rev. Lett.* **67**, 3808 (1991).
- [6] W. I. F. David, R. M. Ibberson, J. C. Matthewman, K. Prassides, T. J. S. Dennis, J. P. Hare, H. W. Kroto, R. Taylor, and D. R. M. Walton, *Nature (London)* **353**, 147 (1991).
- [7] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, *Nature (London)* **347**, 354 (1990).
- [8] R. M. Fleming, B. Hessen, T. Siegrist, A. R. Kortan, P. Marsh, R. Tycko, G. Dabbagh, and R. C. Haddon, in *Fullerenes: Synthesis, Properties and Chemistry of Large Carbon Clusters*, edited by G. S. Hammond and V. J. Kuck, American Chemical Society Symposium Series 481 (American Chemical Society, Washington, DC, 1991), p. 25.
- [9] R. M. Flemming, T. Siegrist, P. M. Marsh, B. Hessen, A. R. Kortan, D. W. Murphy, R. C. Haddon, R. Tycko, G. Dabbagh, A. M. Muijsce, M. L. Kaplan, and S. M. Zahurak, in *Clusters and Cluster-Assembled Materials*, edited by R. S. Averback, D. L. Nelson, and J. Bernholc, MRS Symposia Proceedings No. 206 (Materials Research Society, Pittsburgh, 1991).
- [10] G. Van Tendeloo, M. Op de Beeck, S. Amelinckx, J. Bohr, and W. Krätschmer, *Europhys. Lett.* **15**, 295 (1991).
- [11] J. E. Fisher, P. A. Heiney, A. R. McGhie, W. J. Romanow, A. M. Denenstein, J. P. McCauley, Jr., and A. B. Smith, III, *Science* **252**, 1288 (1991).
- [12] S. Amelinckx, C. Van Heurck, D. Van Dyck, and G. Van Tendeloo, *Phys. Status Solidi* (to be published).
- [13] G. Van Tendeloo, C. Van Heurck, J. Van Landuyt, S. Amelinckx, M. A. Verheijen, P. H. M. van Loosdrecht, and G. Meijer (to be published).
- [14] Measurements of P. H. M. van Loosdrecht at Nijmegen University.
- [15] W. I. F. David, R. M. Ibberson, T. J. S. Dennis, J. P. Hare, and K. Prassides, *Europhys. Lett.* **18**, 219 (1992).
- [16] R. Tycko, G. Dabbagh, R. M. Flemming, R. C. Haddon, A. V. Makhija, and S. M. Zahurak, *Phys. Rev. Lett.* **67**, 1886 (1991).
- [17] R. Sachidanandam and A. B. Harris, *Phys. Rev. Lett.* **67**, 1468 (1991).
- [18] W. I. F. David, R. M. Ibberson, J. C. Matthewman, K. Prassides, T. J. S. Dennis, J. P. Hare, H. W. Kroto, R. Taylor, and D. R. M. Walton, *Nature (London)* **353**, 147 (1991).
- [19] S. Liu, Y. Lu, M. M. Kappes, and J. A. Ibers, *Science* **254**, 408 (1991).
- [20] G. A. Samara, J. E. Schirber, B. Morosin, L. V. Hansen, D. Loy, and A. P. Sylwester, *Phys. Rev. Lett.* **67**, 3136 (1991).
- [21] K. Michel (to be published).
- [22] E. J. J. Groenen, O. G. Poluektov, M. Matsushita, J. Schmidt, and J. H. Van der Waals (to be published).

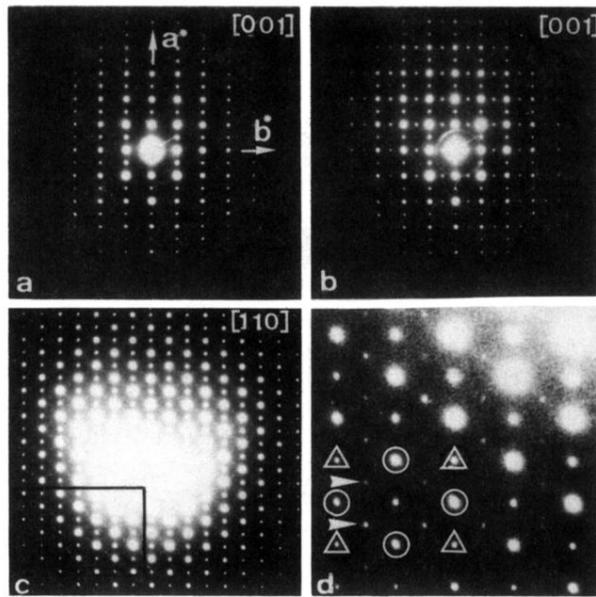


FIG. 1. Electron-diffraction patterns produced by the low-temperature phase of  $C_{60}$  at liquid-nitrogen temperature. (a) Monodomain pattern along  $[001]$ ; note the absence of the spot rows with  $k = \text{odd}$  in accordance with the space group  $Pa\bar{3}$ . (b)  $[001]$  zone pattern of an area containing two  $90^\circ$  orientation variants of the structure. (c)  $[110]$  zone diffraction pattern exhibiting supplementary spots due to the fcc ( $2a_0$ ) structure. (d) Magnified part of the pattern in (c);  $a_0$ -fcc reflections are indicated by circles;  $Pa\bar{3}$  simple cubic reflections are surrounded by triangles; weak  $2a_0$ -fcc reflections are indicated by arrows.

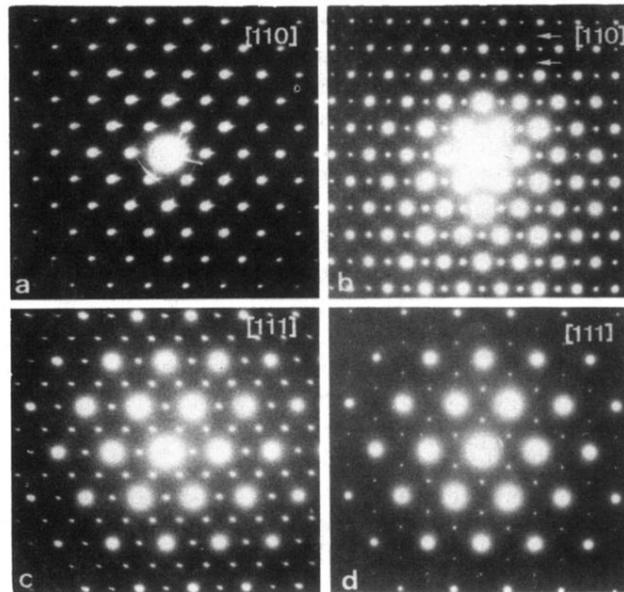


FIG. 2. (a) Electron-diffraction pattern of the fcc phase; no “parasitic” spots due to faulting are visible. (b) Electron-diffraction pattern under the same diffraction conditions as (a) but after cooling to liquid-nitrogen temperature. Note the  $sc$  and the  $2a_0$  spots. (c) Electron-diffraction pattern along  $[111]$  of the same sample as in (a); note the absence of parasitic spots; low-temperature phase. (d) Room-temperature diffraction pattern along  $[111]$  of a different sample exhibiting parasitic spots due to faulting.