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Author

Ashbee, K.H.G.

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K. H. G. Ashbee*

Inorganic Materials Research Division, Lawrence Radiation Laboratory,
Department of Mineral Technology, College of Engineering,
University of California, Berkeley, California

ABSTRACT

Single crystal foils of lanthanum trifluoride have been examined by an electron microscope. Catastrophic decomposition occurs when the microscope is operated under normal conditions at 80 kV or 100 kV. This decomposition involves both molecular dissociation and structural changes; defects in the form of cavities, dislocation loops, and planar faults have been observed. The simultaneous occurrence of surface diffusion and evaporation shows that atomic mobility is high. Even so, it may be necessary to postulate an ionization interaction with the electron beam in order to interpret all the observations.

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* At the time this work was done, the author was Visiting Professor in the University of California, during a leave of absence from the H. H. Wills Physics Laboratory, University of Bristol, England.

I. INTRODUCTION

This work was stimulated by the controversy concerning the crystal structure of lanthanum trifluoride. According to Swanson, Gilfrich and Cook,[1] LaF_3 is hexagonal and belongs to space group PG_3/mcm (D^3_{6h}). Zalkin, Templeton and Hopkins,[2] however, report extra (weak) x-ray reflections, believe that the structure is trigonal with space group $P\bar{3}c\ell$ (D^4_{3d}), and suggest that the failure of previous workers to recognize this lower symmetry may be due to microstructural phenomena such as twinning. The aim of the present experiments was to study the microstructure of LaF_3 with an electron microscope, in an attempt to confirm this suggestion.

We were unable to examine crystals in the as-grown condition owing to the catastrophic incidence of both chemical and structural decomposition during electron irradiation. The decomposition processes are reported in this paper and constitute unusual examples of irradiation damage. The possibility that similar microstructural changes may occur during irradiation by x-rays is discussed.

II. EXPERIMENTAL

A transparent single crystal of lanthanum trifluoride was obtained from Varian Associates, Palo Alto, California. The nominal purity was 99.999%. This crystal was found to cleave fairly readily to give foils sufficiently thin for transmission electron microscopy.

The foils were examined in a Siemens Elmiskop-I electron microscope using projector pole piece two and an accelerating voltage of either 80 kV or 100 kV.

III. OBSERVATIONS AND DISCUSSION

Lanthanum trifluoride is extremely unstable in the electron microscope. As a consequence, it was impossible to carry out contrast or dark field experiments on the same area. At 80 kV and 100 kV, the microstructure degenerates very rapidly during observation and three apparently different processes have been identified. Before describing these, it should be noted that they do not necessarily represent successive stages of decomposition and may be variations due to differences in experimental conditions relating to specimen dimensions and incident electron flux.

A. Internal Cavities and Dislocations

The series of micrographs shown in Fig. 1 were taken in rapid succession during a total time of approximately one minute. It shows the development of a microstructure consisting of cavities and dislocation loops. The first photograph in the series was taken after the very active initial stage during which it was impossible to record the image. The cavities (A) present at that time do not change in size, position, or number during subsequent observation. There is, however, considerable growth of some dislocation loops (B) and migration of dislocations to form walls, (C,D). It is also evident from the development of holes (E) that there is a significant loss of material by evaporation during this sequence.' Selected area diffraction, Fig. 2, reveals the appearance of extra reflections, some of which are tentatively assigned to a surface film of LaOF.

The existence of cavities suggests the presence of undissolved gas, presumably fluorine. Since gas produced by oxidation reactions would be released at the specimen surface, it is necessary to consider processes which would generate fluorine within the crystal. Two possible processes are thermal decomposition and ionization. Since the heat formation of lanthanum trifluoride is very large[3] (probably > 300 kcal mole^{-1}), dissociation is unlikely to be produced as a result of the high energy bombardment. Ionization may be a more satisfactory explanation and has been previously proposed by Forty[4] to account for the decomposition of lead iodide during electron irradiation.

The dislocation loops (B) do not contain stacking faults. This means that they are not prismatic dislocations resulting from the condensation of point defects belonging to one species of atom; lanthanum and fluorine atoms must be involved in stoichiometric proportions. The double arc dislocation contrast suggests that they are perfect prismatic loops, with Burgers vector normal to the "line of no contrast" and tentatively identified as $\frac{1}{3}[11\bar{2}0]$.

In Fig. 1(f), the dislocation walls (C,D) are of two different orientations, neither of which is parallel to the (0001) plane. Assuming that each is an equilibrium array of parallel edge dislocations, the corresponding Burgers vector may be either perpendicular to or at 45° to the array. Trace analysis shows that a common Burgers vector of a $[11\bar{2}0]$ fits this assumption. Despite the large lattice parameters ($a = 7.184$Å, $c = 7.351$Å [2]), there is no resolvable extension of dislocations. The double dislocation contrast in the upper wall D is probably due to double diffraction, since many strong reflections are simultaneously excited for this specimen (Fig. 2).

B. Bright Patches

Figure 3 shows an area of bright patches which has been photographed at intervals of five seconds. The appearance of these patches is virtually unaltered by tilting the foil and must, therefore, be attributed mainly to lack of absorption. Although the patches vary in size from 25Å up to 750Å diameter, their degree of brightness appears to be identical. This presumably means that they all represent regions where the foil is locally thin by an amount which is the same to within half an extinction distance.

A characteristic feature of the bright patches is that each has a "tail" joined to it. In all cases, the width of the tail equals the diameter of the patch. In Fig. 3, all the tails are identically oriented and have equal lengths. During observation, the common tail orientation changes. Sometimes this causes a tail to intersect a neighbouring patch, and the two patches so linked transform into a single patch. An example of this process can be seen in Fig. 3; patches A and B in 3(b) become patch C in 3(c). Re-orientation of the tails is no doubt due to changes in temperature or potential gradient caused by the adjustments made to the electron microscope before each photograph. Eventually, the patches and their tails start to disappear, 3(d).

Interpretation of the bright patches is open to question. They must indicate the presence of either holes or pits or internal cavities. The first possibility seems unlikely since it is difficult to envisage a process by means of which 25Å diameter holes could be bored through a foil of thickness typically 2,000Å. If the patches represent etch pits, then it is odd that their associated tails (or ledges) can be hooked as in Fig. 3(a). On the other hand, the tails could be regions of "debris" left behind migrating cavities, in which case hooked tails merely denote a change in the direction of migration. Whatever the nature of the patches, there can be no doubt that the re-orientations and migrations observed in Fig. 3 are evidence that large numbers of molecules can be quickly moved over many atomic distances in LaF_3 crystals.

C. Micro-Mosaic

Figure 4 shows the progress of a more severe damaging process which literally breaks the crystal into a micro-mosaic during a total time of about one minute. In addition to cavities and bright patches, damage in the form of planar defects is observed. Selected area diffraction of the resultant microstructure, Fig. 5, reveals that each LaF_3 spot is split into two or three or more spots as might be produced by twinning or ordering. Besides these, there are many extra spots which could not be indexed and which suggest the presence of a new low symmetry crystal structure.

It is interesting to note that the bright patches A and B in Fig. 4(a) are completely healed in Fig. 4(d). This means that the temperature is sufficiently high (say ~0.3 times the melting temperature ~500°C) for considerable surface diffusion to take place.

IV. CONCLUDING REMARKS

When irradiated with 40 kV x-rays, the flux passing through the specimen is $\sim 10^{15}$ phonons $cm^{-2} sec^{-1}$. Under such conditions, lanthanum trifluoride appears to be stable; no line broadening is developed even after many hours exposure.[5] In the present 80 kV and 100 kV transmission electron microscopy experiments, the flux is ~10^{17} electrons $cm^{-2}sec^{-1}$. It is difficult to believe that the rapid and very severe damage produced in this latter case is due to the slightly higher energy and flux of the electron irradiation. Either similar, although probably less drastic, sub-micron scale damage occurs during irradiation by x-rays, or some form of interaction (e.g., ionization) exists between the electron beam and the crystal.

The occurrence of evaporation and surface diffusion during these observations indicates that the specimen temperature is probably as high as 500°C. Ion exchange experiments[6] show that the fluorine lattice in LaF_3 is very mobile at this temperature. Consequently, any tendency to undergo chemical or structural change would be easily accommodated. For example, the electron microscope atmosphere is reducing and may induce non-stoichiometry. Also, phase transformations are fairly common in rare earth halides[5] and may exist under certain environmental conditions in LaF_3.

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FIGURE CAPTIONS

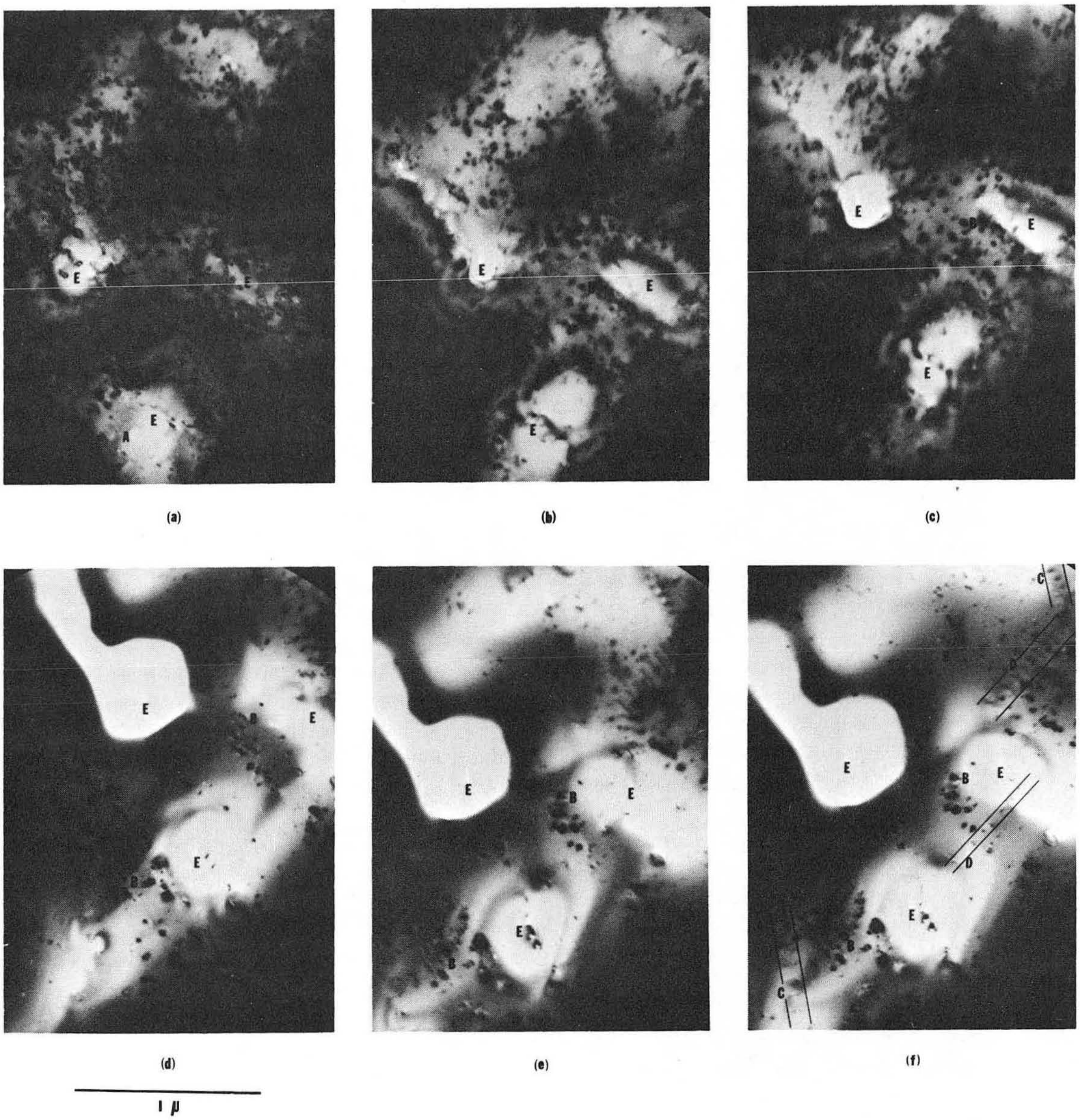
Fig. 1 Sequence showing the development of internal cavities (small white areas) and dislocation loops.

Fig. 2 Selected area diffraction pattern from Fig. 1(f). The foil normal is $\bar{1}2\bar{1}0$. Some of the diffraction spots have split into doublets or triplets - see Section III.C.

Fig. 3 Behaviour of bright patches during electron irradiation.

Fig. 4 Transformation to a micro-mosaic microstructure.

Fig. 5 Selected area diffraction pattern from Fig. 4(d).



XBB 678-4755

Fig. 1

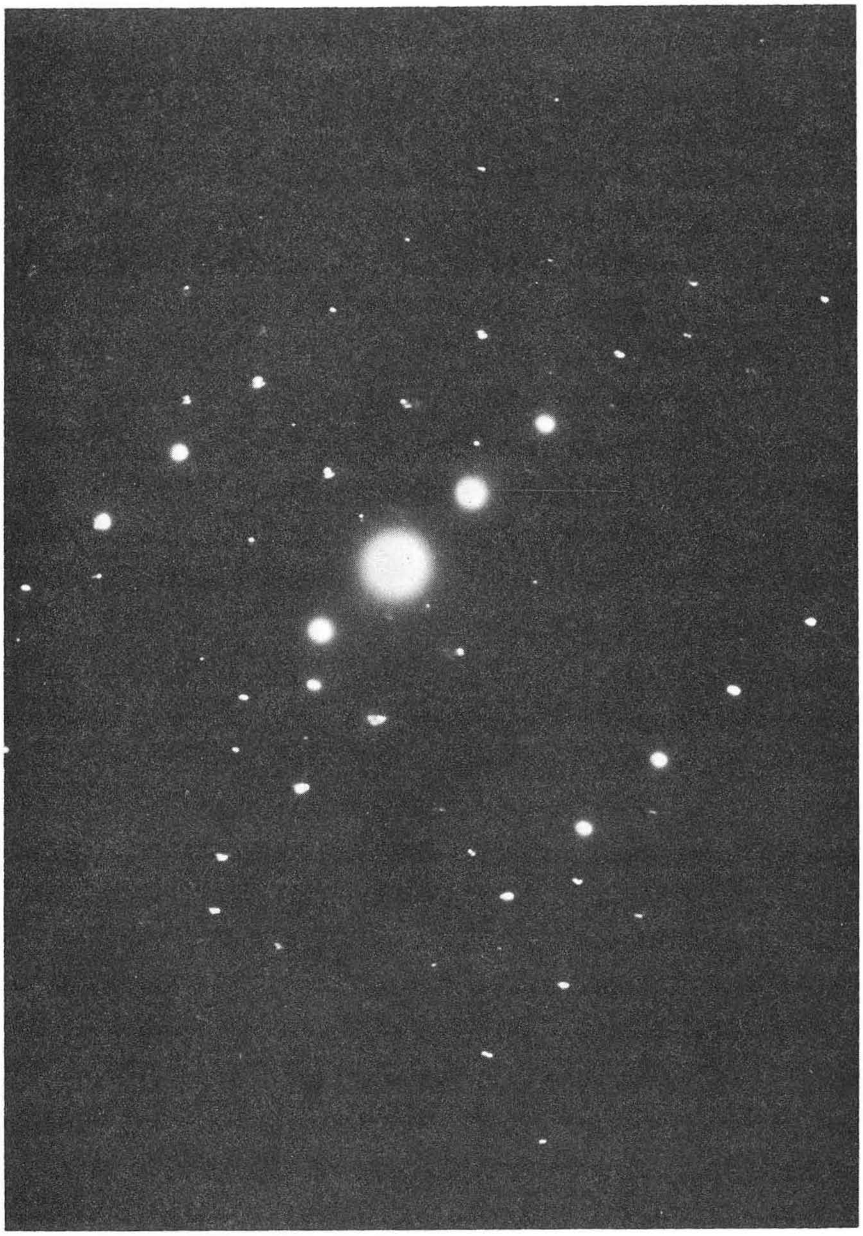


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Fig. 2

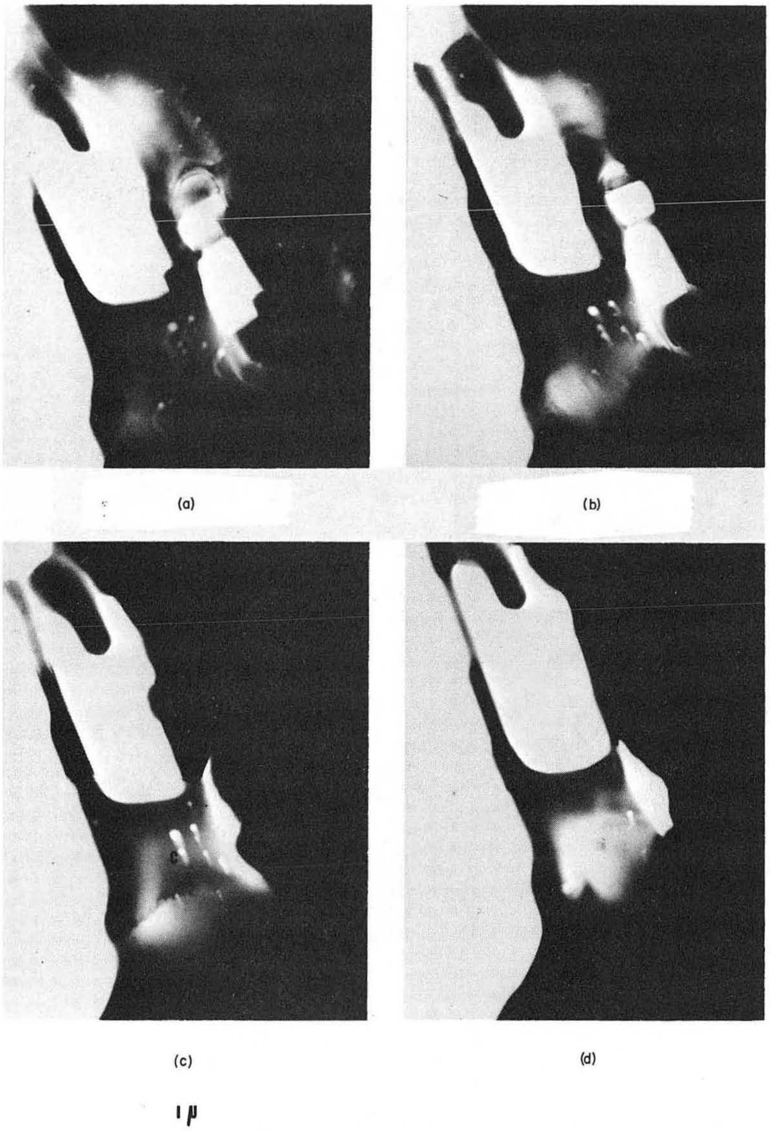

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Fig. 3

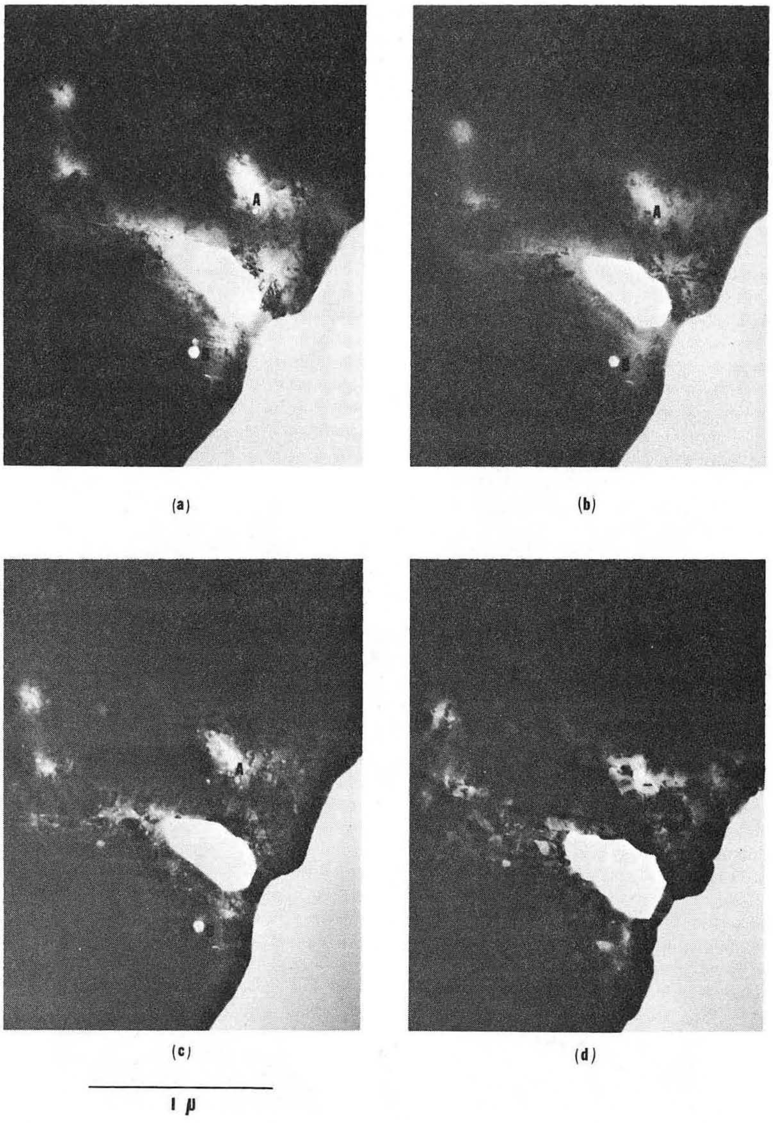

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Fig. 4

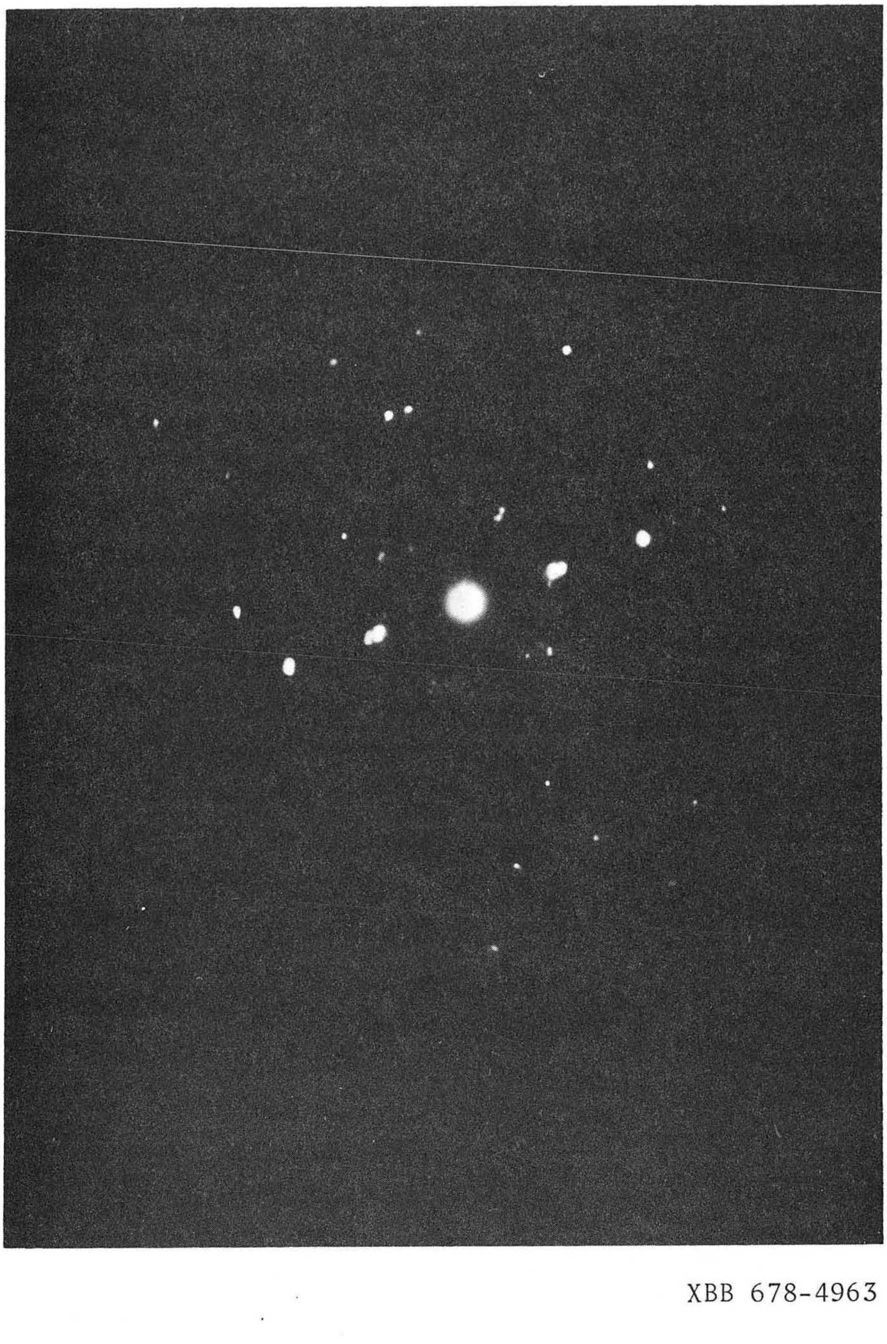

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Fig. 5