the structure and this was one of the reasons for attempting solution of the crystal structures of these compounds. Since the crystal structures have shown the solid state to be a tetramer, we do not feel that an estimation of a theoretical moment for a trimer of unknown structure would be meaningful.

Thus, for these three compounds there seem to be at least two factors affecting the dipole moments with increasing temperature: (1) the decrease in the degree of restriction of rotation of the alkoxy groups; (2) a decrease in molecular complexity. A change in solvent effect is also possible.

Acknowledgment.—The authors wish to acknowledge the support of this work by National Science Foundation Grant NSF-G 20622.

CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA,
LOS ALAMOS SCIENTIFIC LABORATORY, LOS ALAMOS, NEW MEXICO

X-Ray Diffraction Evidence for Microphases in CeCd$_{\sim4.5}$ Solid Solutions[1]

BY RAYMOND B. ROOF, JR., AND GUY R. B. ELLIOTT

Received November 2, 1964

If the actual composition of a compound differs from that associated with the crystallographically ideal structure, then defects have been created in the lattice. In the CeCd$_{4.3-4.7}$ region such defects may be randomly distributed throughout the lattice as was previously shown by vapor pressure measurements. In addition, the defects may order into many true phases which break up the random solution into ordered structures separated by two-phase regions. The ordered structures are called microphases and their existence is confirmed by the present X-ray diffraction results. All the superlattices observed may be classified by four characteristic key patterns which appear over wide areas between the reciprocal lattice spots of the parent structure. The superlattices appear to be orthorhombic, hexagonal, or monoclinic and may be correlated with vapor pressure measurements. All parent lattice distances are the same in the a axis direction. A hexagonal superlattice unit cell with a axis distance ∼126 Å., c axis distance ∼15.46 Å. has been identified. The c axis parent lattice distance is ∼15.55 Å. at CeCd$_{4.35}$ but decreases by ∼0.6% as the composition shifts to CeCd$_{4.65}$. The decrease in the c axis follows approximately the decrease of 0.64% in the electron/atom ratio, but the usual Brillouin zone argument seems inadequate to explain the shift for two reasons: first, the unchanging a axis distance is unusual and second, the apparently different superlattice symmetries would create different Brillouin zone shapes.

Introduction

The room temperature crystallographic structure of CeCe$_{\sim4.5}$ previously heat treated at 640° is a hexagonal lattice in which cerium and cadmium atoms each occupy their specific lattice sites. Thermal vibrations in such a lattice will always cause partial dissociation of the lattice and will create a range of solid composition. Vapor pressure measurements at the higher temperature[2] have indicated several features of this solid solution behavior: First, they show that the principal dissociation forms random cadmium vacancies and cadmium atoms randomly misplaced in some particular type of less tightly bonded position. Second, if the crystal varies from CeCe$_{4.5}$ in composition, additional random cadmium vacancies are created or more cadmium atoms randomly enter the less tightly bonded positions. Third, there is some annihilation between the two types of sites, following mass action behavior.

The above conclusions were not surprising. However, certain additional vapor pressure measurements could only be explained by assuming that the defects could also arrange themselves to give a large number of more complicated, ordered structures (microphases) having small composition ranges with very narrow two-phase regions separating them. Because these findings were so unexpected, it seemed important to confirm them independently. The present X-ray diffraction work does confirm many and contradicts none of the earlier conclusions; it extends our understanding of the microphases, particularly with regard to their structures.

Experimental

The physical appearances and chemical purities of the cerium and cadmium alloy constituents and the additional purification procedures used have been described elsewhere.[3] Three alloys were prepared, by different techniques, in out-gassed tantalum containers encapsulated in quartz.

Alloy I.—A CeCd$_{4.35}$ gross composition alloy was prepared by allowing small pieces of cadmium, in contact with a larger piece of cerium, to melt and diffuse into the cerium. This alloy was then heat treated for 2 days at 650°. In this preparation the intention was to create an alloy which was nearly but not completely uniform in composition.

Alloy II.—A CeCd$_{4.6}$ gross composition alloy was prepared in the same manner as alloy I but was heat treated for 1 year at 650° in an attempt to assure its homogeneity.

Alloy III.—First, CeCd$_{\sim6}$ was prepared in an isopiestic balance.[2,3] Then CdCd$_{\sim4.5}$ was obtained from the CeCd$_{\sim6}$ by allowing some of the cadmium to evaporate to the lower temperature reservoir. This alloy was used in a series of vapor

---

[1] Sponsored by the U. S. Atomic Energy Commission. Presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 10, 1964.

[2] G. R. B. Elliott and J. F. Lemons, Advances in Chemistry Series, No. 39, R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1964, pp. 144-152, 153-169.

[3] G. R. B. Elliott and J. F. Lemons, *J. Phys. Chem.*, **64**, 137 (1960).

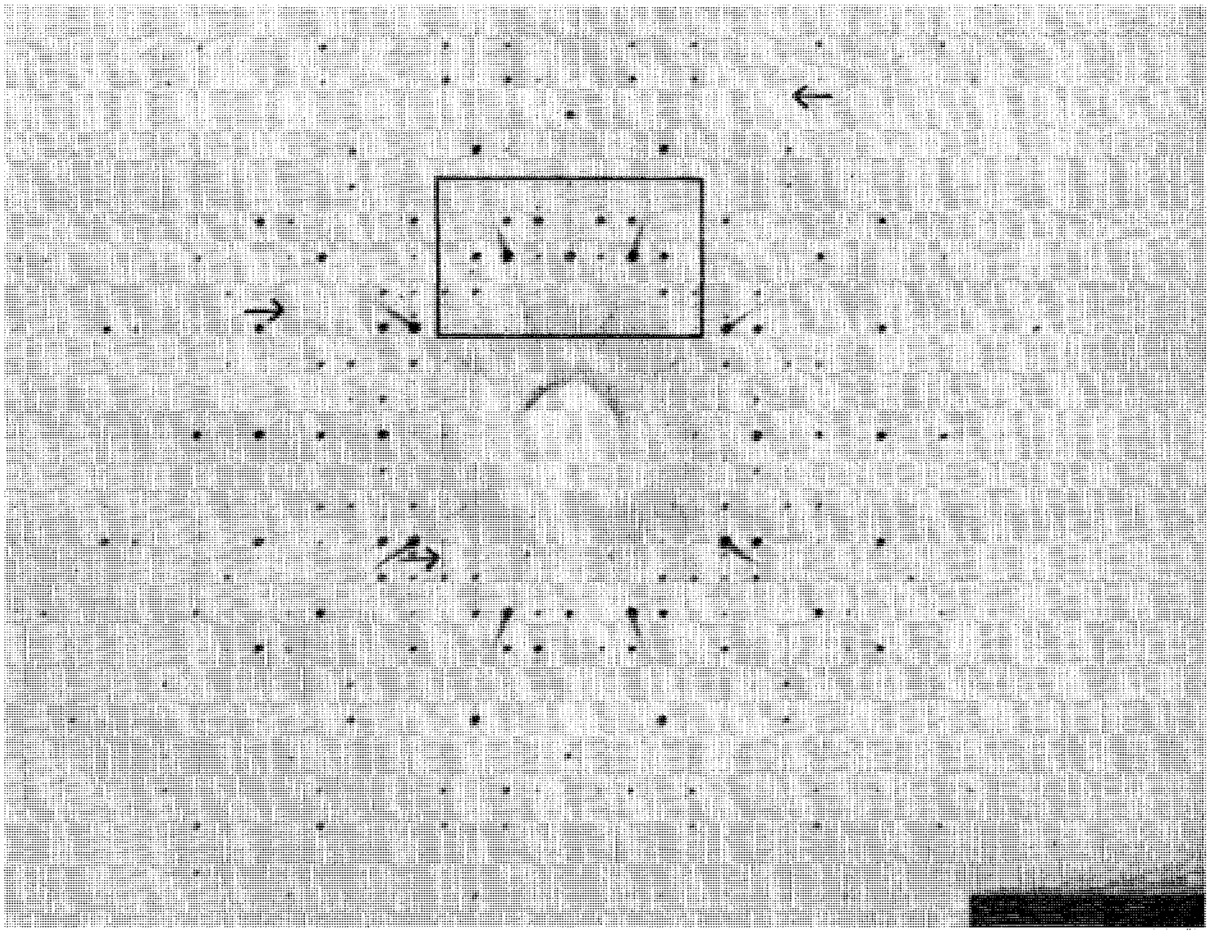

Figure 1.—Superlattice spots on an *h0l* view of the parent lattice for a crystal of $CeCd_{\sim 4.35}$; Mo Kα radiation.

pressure measurements in the $CeCd_{\sim 4.5}$ composition range. Before being cooled the alloy and reservoir were isolated by collapsing the connecting tube. The resultant $CeCd_{4.65}$ alloy is very porous but homogeneous.

All the alloys were cooled slowly so that there was no vaporization of cadmium to the container wall. With this procedure the desired compositions were maintained.

Portions of the alloy samples were crushed and fresh single-crystal fragments were selected for X-ray examination. After the fragments had been carefully oriented, Buerger precession photographs with Mo X-rays filtered through zirconium or Cu X-rays filtered through nickel were taken at 1–5-day exposures.

Results

The three alloy samples will be discussed separately.

Alloy I: A Nonhomogeneous Alloy of Over-all Composition $CeCd_{4.35}$.—Eleven single crystals were studied. All showed a hexagonal parent structure having unit cell dimensions of $a = \sim 15.75$ and $c = \sim 15.55$ Å. X-Ray photographs were taken of the *hk*0, *h0l*, and *hhl* lattice nets of the parent lattice and no superlattices were found in any view except *h0l*. Figure 1 shows one such *h0l* pattern obtained with Mo Kα radiation. The *h*00 direction is vertical and the 00*l* direction is horizontal in this photograph. Several areas showing superlattice spots are indicated by the arrows and may also be seen at their mirror positions top and bottom, left and right. The rectangular area encloses a region which is shown enlarged in Figure 2. The enlargement was achieved by two means, first, by the use of Cu Kα radiation and, second, by conventional photographic methods.

In Figure 2, the superlattice spots in reciprocal space appear at $^3/_8$ and $^5/_8$ of the distance between the parent lattice spots, thus increasing the dimension of a possible unit cell in this direction to $15.75 \times 8 = 126$ Å. We will speak of the ($^3/_8$, $^5/_8$) spacing as a key pattern of the lattice. This key pattern appears in many places in Figure 1.

The other two *h0l* views of the parent hexagonal lattice do not show a superlattice. This kind of difference among the three views indicates an apparently orthorhombic superlattice and the consequent destruction of the hexagonal symmetry of the crystal.

Figure 3 is a photograph taken of a different crystal in the same alloy. In this case the key pattern is ($^3/_8$, $^1/_2$). (In a few regions the ($^3/_8$, $^1/_2$) key pattern inverts and becomes ($^1/_2$, $^5/_8$).) In these crystals there are two other *h0l* views of the parent lattice which show the ($^3/_8$, $^1/_2$) key pattern. These views resemble each other but are different from the one shown, however, again indicating an apparently orthorhombic superlattice.

Figure 4 is a photograph of a third crystal from alloy I. In this case the key pattern is ($^1/_3$, $^2/_3$). However, another type of crystal structure having the same key pattern but a slightly different lattice pattern was also found. Both superlattice types apparently are ortho-

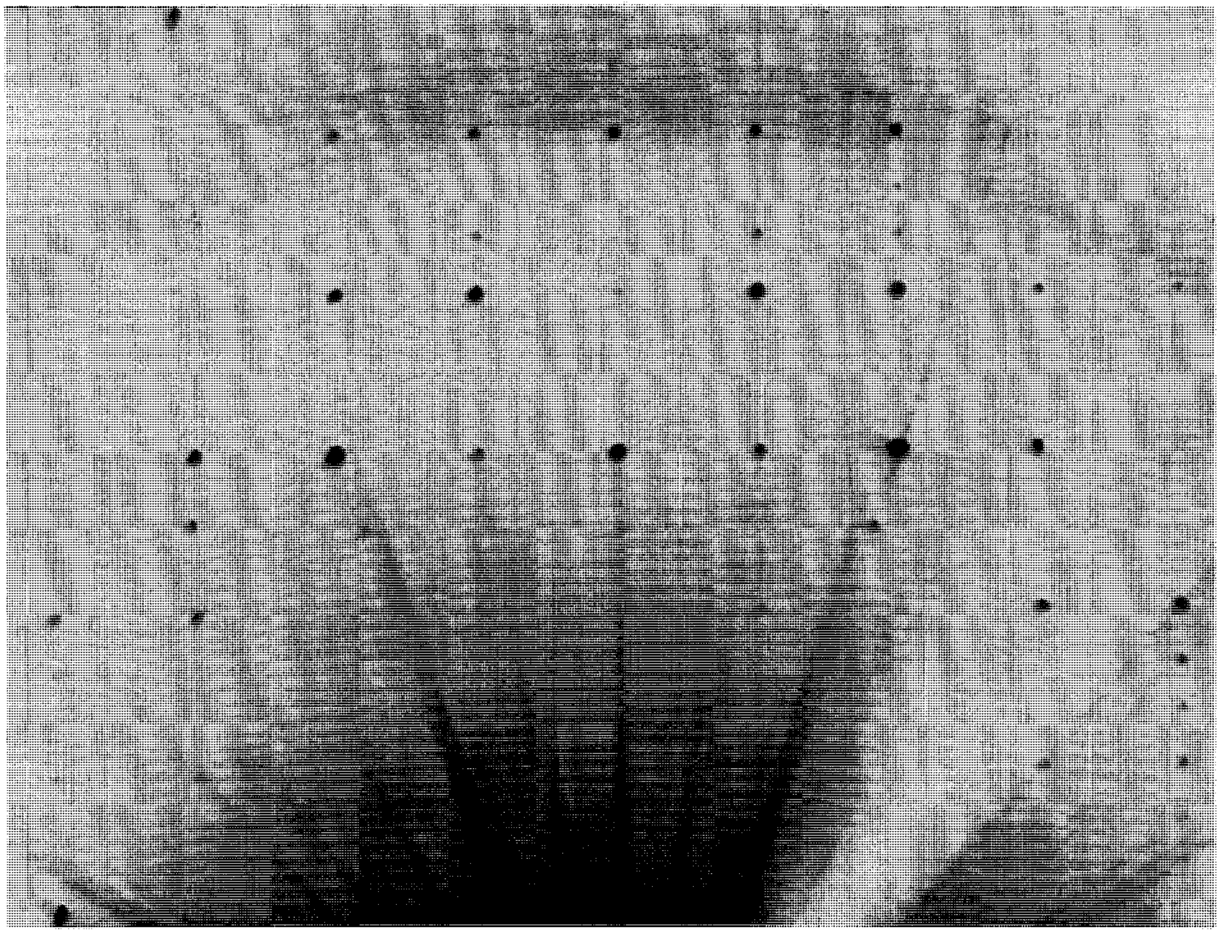

Figure 2.—Enlargement of the area enclosed by the rectangle in Figure 1; Cu Kα radiation. $CeCd_{\sim 4.35}$ ($^3/_8$, $^5/_8$) key pattern, on *h0l* view.

rhombic. The key pattern appears in the other two views of one type of crystal, but not of the other.

One other key pattern ($^1/_3$, $^1/_2$, $^2/_3$) was observed in the single crystals, but the photograph was not adequate for reproduction. This crystal was also apparently orthorhombic with faint superlattice spots in the other two similar views. A growth of whiskers on this crystal, while not completely destroying the superlattice, did prevent clear rephotographing (see below).

We examined eleven crystals from this nearly homogeneous alloy whose range of composition was estimated to be $CeCd_{4.32-4.38}$. Five were found to have individually different superlattices while six gave patterns that duplicated one or another of those of the five.

Alloy II: A Homogeneous, Dense Alloy of Composition near $CeCd_{4.5}$.—The one single crystal which was studied in detail had a ($^1/_3$, $^2/_3$) key pattern with apparently different lattice patterns in each of the three *h0l* views of the parent structure. Considering also the mirror planes in each view this indicates an apparently monoclinic superlattice. Clear photographs were not obtained of other crystals from this alloy, but the photographs obtained are consistent with our expectation that the alloy is homogeneous.

Alloy III: A Porous Homogeneous Alloy of Composition near $CeCd_{4.65}$.—Four single crystals were examined. The parent lattice unit cell dimensions are $a_p = \sim 15.75$ and $c_p = \sim 15.46$ Å. However, the comparison of these values with the $CeCd_{\sim 4.35}$ values can be made more accurately than the absolute values can be determined. There appears to be *no* change in the *a* axis distance while the *c* axis distance decreases by ~0.6%.

The key pattern of the lattice is ($^3/_8$, $^5/_8$). In this case, however, the three *h0l* views are identical, indicating a hexagonal superlattice. The unit cell of the superlattice is $a_s = 8a_p = \sim 126$ Å. and $c_s = c_p = \sim 15.46$ Å.

Subsequent Crystal Disproportionation at Room Temperature.—After several months at room temperature some of the $CeCd_{\sim 4.35}$ crystals had grown or were growing whiskers of metallic cadmium. The whiskers were identified both by powder[4] and single-crystal X-ray techniques. All rings visible in the single-crystal precession photographs taken after whisker formation had started could be attributed to cadmium or the mounting wax. No rings were seen at the strong Ce_2O_3 line positions, and no oxidation color was seen on the alloy specimens. The reaction that produced the whiskers seemed to be solely one of disproportionation.

Growth of the whiskers destroyed the superlattice apparently in direct proportion to the amount of

---

(4) We thank F. H. Ellinger for the powder work.

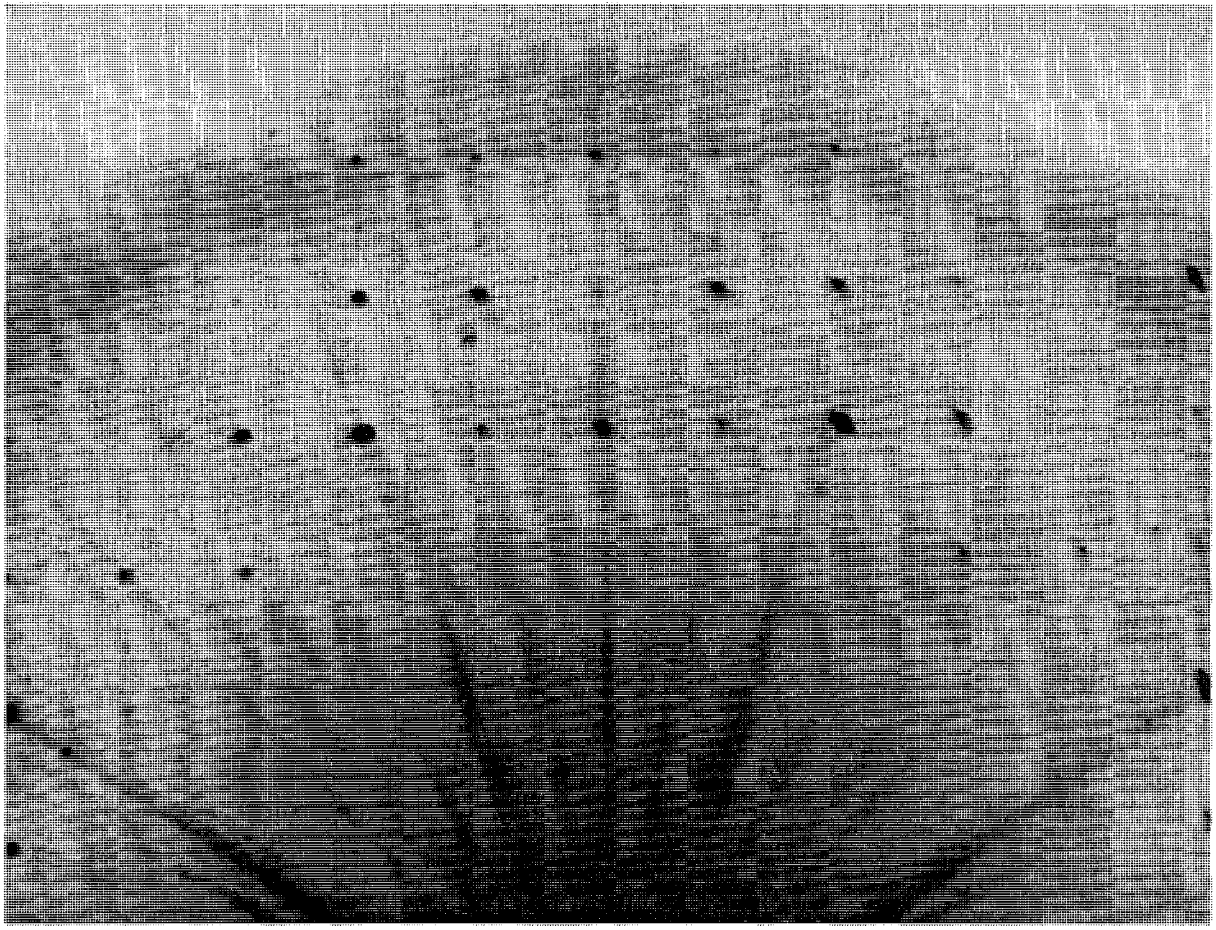

Figure 3.—A CeCd$_{\sim 4.35}$ crystal different from that of Figure 2, showing the ($^3/_8$, $^1/_2$) key pattern; Cu Kα radiation.

growth. Over a period of weeks the superlattice spots became fainter as growth continued, but in no case was there any change detected in the key lattice pattern during the superlattice destruction. None of the original photographs, as taken of freshly broken crystals, showed any sign of powder rings.

Discussion

As will be elaborated below, the conclusions from the X-ray results confirm in considerable detail the conclusions from the vapor pressure measurements.[2]

Most obvious at first is that many different crystals of homogeneous composition may occur in a nonhomogeneous alloy (alloy I). The very narrow microphase composition ranges in this alloy and the large number of structures are predicted accurately from the vapor pressure data.

The vapor pressure measurements also indicate that there are regions of rather different microphase behavior. One such region is around CeCd$_{4.65}$ (alloy III) where, for all the microphases, the same constant slope is obtained when mole fraction is plotted against cadmium vapor pressure. To have such a similarity in their toleration of deviations from ideal stoichiometry, the microphase structures must be very similar. Furthermore in the CeCd$_{\sim 4.65}$ region, if a single vapor pressure is considered, the two-phase composition gap separating the acceptable microphase compositions is always the same. Probably the simplest way to account for such behavior within a hexagonal parent would be to assume a large hexagonal superlattice which opens out in steps along the *c* axis. Completely consistent with the vapor pressure relationships, we have observed a large hexagonal superlattice in the alloy III specimens but not in any others.

The composition gaps mentioned in the first paragraph each have a width of 0.00002105 in mole fraction units. Thus the addition of one cadmium atom per 8035 atoms present in this region can completely change one structure to another. Since there are ten similar composition gaps, it seemed likely that there would be some unit cells containing at least 8000 atoms. The identified superlattice unit cell in alloy III has a volume of over 212×10^3 Å.^{3} and has space for 9600 close-packed atoms of size corresponding to the average metallic radius of four cadmium plus one cerium atoms. The patterns, of course, preclude simple hexagonal close packing.

The most extensive test of the vapor pressure conclusions has been made in the CeCd$_{\sim 4.35}$ region (alloy I). In this region the X-ray work demonstrates only apparently orthorhombic symmetry in all the crystals examined. This symmetry is intermediate between the observed extremes of hexagonal and apparently monoclinic symmetries. Crystal complexity and low symmetry may often be correlated, and in this case the

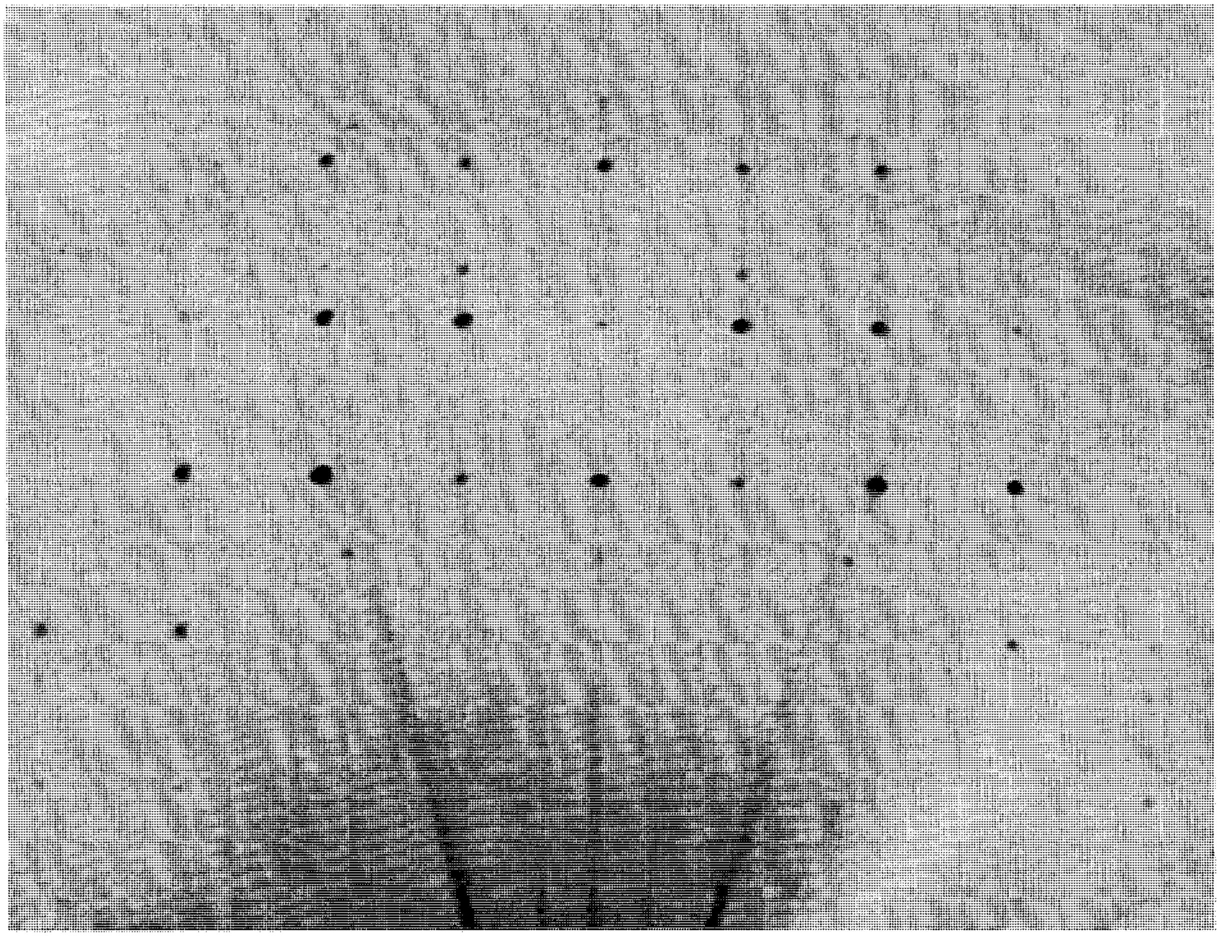

Figure 4.—Another CeCd$_{\sim 4.35}$ crystal, in this case showing the ($^1/_3$, $^2/_3$) key pattern; Cu Kα radiation.

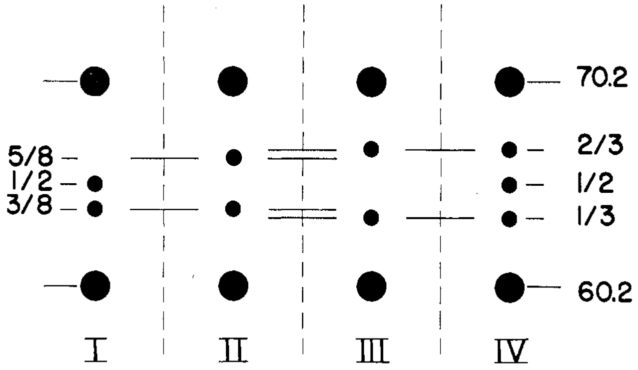

Figure 5.—Various key patterns observed with different crystals having compositions near CeCd$_{\sim 4.35}$ in the region between the 602 and 702 *hkl* positions of the hexagonal parent lattice.

complexity demonstrated by the vapor pressure studies is also intermediate as to the interrelationships between the microphases.

The key patterns from all the crystals examined from alloy I are presented in Figure 5.[5] Key patterns I and II divide the reciprocal lattice into eighths. The crystals of type I show the spots in all *h*0*l* views of the parent structure and require an 8-fold increase in each of two directions with an orthorhombic unit cell of a size comparable to that shown by the hexagonal alloy III cell. For type II the crystal shows the superlattice spots in only one parent *h*0*l* view and the superlattice unit cell could be smaller. For type III the multiplication is 3-fold in one or both directions of the parent *a* axis depending on which of the two types of crystal with this pattern is considered. The type IV crystal requires a 6-fold increase of the parent lattice in one *a* axis direction of the parent. The lowest common denominator to describe all the key pattern spots is 24, *i.e.*, the superlattice spots appear at $^8/$-, $^9/$-, $^{12}/$-, $^{15}/$-, and $^{16}/_{24}$ of the distance between the parent lattice spots. It seems inviting to us to correlate the microphases within such a single structural unit (1.9 × 10^6 Å.^{3}, with space for 86,000 atoms) because it unifies all the microphases into a single group and is consistent with the similarity of the ordering forces demonstrated in the vapor pressure studies.

The alloy I X-ray results demonstrating four key patterns indicate that there are at least four types of defect ordering in the family, but the 8-fold periodicity found in the vapor pressure work suggests eight lattice types which would open out along the parent *c* axis to give the periodicity in composition gaps and acceptable compositions. This four–eight anomaly disappears when we realize that at least one ($^1/_3$, $^2/_3$) and presumably all four key patterns appear in two different orthorhombic structures, thereby leading to the 8-fold periodicity.

[5] Alloy II also has the ($^1/_3$, $^2/_3$) key pattern and alloy III shows ($^3/_8$, $^5/_8$).

The ease of conversion of one structure to another once nucleation has occurred in the isopiestic balance indicates that no large movement of material has to take place during the conversion. This effect again suggests that the structures are rather similar.

For the region around $CeCd_{4.5}$ (alloy III region) when vapor pressure is plotted against mole fraction, there is no precise regularity apparent either in the acceptable microphase compositions at any vapor pressure or in the changes of composition with pressure within the various microphases. This lack of precise regularity in behavior could be explained if the group were assumed to have monoclinic lattices. The type which is found is indeed apparently monoclinic. However, the microphases do have some rough relationship to each other as they appear with a rough semblance of regularity as composition is changed, a behavior which correlates with the unchanging a axis distance of the parent lattice.

It is frequently observed in hexagonal lattices that the atoms exhibit an axial ratio, c/a, different from that of close-packed hard spheres. In this process the atomic volumes are usually not changed, but the a axis becomes shorter while the c axis becomes longer, or *vice versa*. Furthermore, if the number of electrons per atom of alloy is shifted (by changing the ratio of divalent to monovalent metals, for example), the ratio of the c axis distance to the a axis distance in materials also shifts to follow proportionately the electron-per-atom changes.[6,7] The experimental fact of the correlation is undeniable; the theoretical explanation is not rigorous.

Briefly, theory says that if a Brillouin zone falls just above the Fermi surface of a metal, the uppermost occupied energy levels will be depressed. This depression of the levels lowers the system energy and stabilizes the crystal. Therefore, the real-space lattice actually alters its shape to find a more stable Fermi level–Brillouin zone relationship.

In our system we do find that the composition-established electron-per-atom ratio shifts 0.64% while the axial ratio c/a shifts $\sim 0.6\%$. However, our system is unusual in two ways. First, the a axis does not change at all as far as can be detected in the present photographs; all the change occurs in the c axis. Second, the differences in the apparent symmetry of the superlattices lead to different Brillouin zone shapes so that the Fermi level–Brillouin zone argument seems inapplicable in this case.

In one of the earlier papers[2] the source of energy for forming the microphases was discussed qualitatively. We suspect that low-lying electron levels are disturbed, levels well below the limit of thermal disturbance. The present work has given us no reason to alter greatly the previous suggestions, but has given us more facts to work with.

The X-ray diffraction results suggest that the ordered defect structures have a somewhat different character than was hypothesized earlier. The ordered defect arrays were described as behaving like the walls of a box in the electron-in-a-box problem. Such walls were presumed to perturb strongly certain electron energy levels. It was suggested that the boxes expanded in half-wave length units corresponding to the disturbed levels. It now seems more appropriate to us to think of dividing the sample into a number of single boxes, 378 Å. wide (24 times the parent unit cell length), whose depth can be shifted by altering the parent c axis unit cell and whose volume can be divided into compartments by several different types of vertical walls.

Contrary to our suggestion expressed earlier, it seems clear that there are sources of long-distance communication between atoms other than simply by the conduction electrons. For example, the many oxide "pseudo-phases" of Eyring and Hyde[8] appear in structures which would not be expected to have significant electron conductivity.

The disproportionation shown at room temperature by the $CeCd_{\sim 4.85}$ microphases shifts the composition in the direction of $CeCd_4$, and the amount of material in the whiskers is estimated to be consistent with a $CeCd_4$ limit.

This shift of composition is also consistent with the conclusions drawn from the vapor pressure work.[2] The random defect solution was apparently based on a mass action relationship within a $CeCd_{4.5}$ lattice, between cadmium vacancies and cadmium atoms in less tightly bonded positions, either interstitial or, perhaps more likely, normally unoccupied positions in the lattice. However, the microphases showed no change in behavior at $CeCd_{4.5}$, so it was concluded that they were based on some parent structure lying outside the stable composition range for the microphases at 640°. $CeCd_4$ was suggested as the microphase parent structure.

The disproportionation is consistent with the following: Probably the composition range for the microphase group and the composition range for $CeCd_{\sim 3}$ both become less broad as the solid solutions cool. The narrowing $CeCd_{\sim 3}$ range reduces the competition with the microphase family for the available cadmium atoms and allows the $CeCd_4$ microphase parent to become stable. The lower amplitude of thermal vibrations of the $CeCd_4$ lattice at lower temperatures causes the lattice to be less tolerant of the interstitials, and these atoms are rejected to form whiskers.

Conclusions

It is evident that a large number of superlattices occur in the region $CeCd_{\sim 4.5}$ and that these superlattices can be detected with standard equipment and techniques. While the exact nature of the superlattices

---

(6) B. Henderson and G. V. Raynor, *Trans. Faraday Soc.*, **58**, 1 (1962), and other references.

(7) T. B. Massalski and H. W. King, *Progr. Mater. Sci.*, **10**, 1 (1961), and other references.

(8) B. G. Hyde and L. Eyring, "On Phase Equilibria and Phase Reactions in TbO_x–O_2 and Related Systems," Session V, Fourth Rare Earth Research Conference, Phoenix, Ariz., April 1964.

and the crystal structures is not known, a strong correlation is suggested with the vapor pressure measurements previously made in this alloy system. In order to place the suggested correlation on a better theoretical basis and perhaps to determine the crystal structure of the parent hexagonal lattice the authors plan a continued X-ray diffraction examination of the microphases in this alloy system.

CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY,
UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINNESOTA 55455

Arsenic(IV) as an Intermediate in the Iron(III) and Copper(II) Catalyzed Arsenic(III)–Persulfate Reaction[1]

BY R. WOODS, I. M. KOLTHOFF, AND E. J. MEEHAN

Received December 29, 1964

It is postulated that the iron(III) and copper(II) catalyzed oxidation of arsenic(III) by persulfate proceeds by a chain mechanism initiated by the symmetrical decomposition of persulfate into two sulfate free radicals. The chain involves the intermediate formation of arsenic(IV). The kinetics of the iron(III) catalysis and the values of the rate constants are in agreement with the results of previous investigations. The rate of oxidation of HO_2 by copper is not affected by a change in pH between 2.7 and 1.3, while that of iron(III) changes nearly in proportion to concentration of $FeOH^{2+}$. An interpretation has been given of the fact that the catalytic effect of small concentrations of copper(II) in the presence of oxygen is much larger than that observed in the absence of oxygen, whereas hardly any difference is observed at high copper concentrations. The acid-catalyzed decomposition of persulfate results in a two-electron transfer oxidation of arsenic(III) to arsenic(V) without the formation of reactive intermediates.

The induced oxidation of arsenic(III) by the iron(II)–persulfate reaction and the photoreduction of iron(III)[2,3] and by the iron(II)–hydrogen peroxide reaction[4] have been interpreted on the basis of the intermediate formation of the 4+ valence state of arsenic by the reaction of sulfate and hydroxyl free radicals with arsenic(III). In the absence of oxygen the intermediate arsenic(IV) was postulated to reduce iron(III) and copper(II) and oxidize iron(II). Arsenic(IV) was found to be very sensitive to oxygen, reacting to give hydroperoxo radical.

Sulfate free radicals which are formed in the thermal decomposition of persulfate[5] can oxidize arsenic(III) to arsenic(IV). If either iron(III) or copper(II) is also present, arsenic(IV) reduces these ions, the iron(II) or copper(I) produced reacting with persulfate to give sulfate free radical.[6-9] It is anticipated from these results that in the presence of iron(III) or copper(II) a chain oxidation of arsenic(III) by persulfate will occur. The kinetics of these reactions were investigated to substantiate further the reactions postulated in the preceding publications.[2-4]

In acid solution the thermal decomposition of persulfate proceeds by two parallel paths[5]

$$S_2O_8^{2-} \longrightarrow 2SO_4^{\underset{\cdot}{-}} \qquad (1)$$

$$H^+ + S_2O_8^{2-} \longrightarrow SO_4 + HSO_4^- \qquad (2)$$

In order to interpret the kinetics of a chain reaction initiated by reaction 1, it is necessary to know the extent of possible oxidation by SO_4 formed in reaction 2 and also of direct reaction between arsenic(III) and persulfate comparable to the oxidation of arsenic(III) by hydrogen peroxide.[3,4] Therefore, the kinetics of the arsenic(III)-persulfate reaction were also investigated in the absence of added metal ions.

Experimental

All materials used were identical with those described previously.[2] For the reactions in the absence of added metal ions, solutions of perchloric acid, arsenic trioxide, and sufficient sodium perchlorate to make the ionic strength 0.1 were pipetted into the reaction flasks and placed in a water bath at 25°. If the reaction was to be studied in the absence of oxygen, the solution was deaerated with nitrogen. Deaerated or air-saturated potassium persulfate solution was added and, after desired times, aliquot samples were removed and analyzed for persulfate. For the copper(II) catalyzed reactions, cupric perchlorate was added to the original mixture and the procedure followed as before. In the presence of iron(III) the reaction flasks were covered with black adhesive tape to eliminate photoreactions.[2,3] In order to oxidize any trace of iron(II) in the iron(III), solutions of sodium perchlorate, perchloric acid, ferric perchlorate, and potassium persulfate were pipetted into the reaction flasks and allowed to stand overnight at room temperature. Where relevant the solution was then deaerated and deaerated or air-saturated arsenic trioxide solution added, the reaction mixture being sampled and analyzed as before.

Persulfate was determined polarographically, the sodium perchlorate and perchloric acid present acting as supporting electrolyte. (Polyacrylamide in a concentration of 0.01% was used as a maximum suppressor.) In the presence of iron(III), sodium fluoride in a concentration of 0.1 *M* was added to the

(1) This investigation was carried out under a grant from the National Science Foundation.

(2) R. Woods, I. M. Kolthoff, and E. J. Meehan, *J. Am. Chem. Soc.*, **85**, 2385 (1963).

(3) R. Woods, I. M. Kolthoff, and E. J. Meehan, *ibid.*, **85**, 3334 (1963).

(4) R. Woods, I. M. Kolthoff, and E. J. Meehan, *ibid.*, **86**, 1698 (1964).

(5) I. M. Kolthoff and I. K. Miller, *ibid.*, **73**, 3055 (1951).

(6) J. H. Mertz and W. A. Waters, *Discussions Faraday Soc.*, **2**, 179 (1947).

(7) J. W. L. Fordham and H. L. Williams, *J. Am. Chem. Soc.*, **73**, 1634 (1951).

(8) J. W. L. Fordham and H. L. Williams, *ibid.*, **73**, 4855 (1951).

(9) I. M. Kolthoff, I. K. Miller, and H. P. Raaen, *ibid.*, **73**, 1733 (1951).