Symmetry change at the fcc–distorted-fcc phase transition of lanthanides under pressure

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The crystal structure of the distorted-fcc high-pressure phase of the rare-earth elements is discussed in connection with the Landau theory of phase transition. From x-ray-diffraction spectra the irreducible representation E_u^L is found to drive the (almost) continuous transition fcc→distorted fcc. Using just symmetry arguments four structures induced by E_u^L are compatible with the x-ray-diffraction pattern; but only one (space group $Cmmm$, $Z=8$) can have a continuous transition to fcc.

I. INTRODUCTION

The regular trivalent lanthanides (excluding Eu and Yb) crystallize at ambient conditions in the well-known sequence of close-packed structures fcc→dhcp→Sm-type→hcp. High-pressure studies have shown that each of the lanthanides follows this sequence in inverse order with increasing pressure. Systematic high-pressure x-ray-diffraction studies have revealed one more common structure for the regular lanthanides beyond the fcc phase. First indications of this additional phase have been found by resistivity measurements on lanthanum[1,2] almost twenty years ago. Already at this early stage it was noticed that the transition from the fcc phase appears to be continuous.[1] This has been confirmed later by x-ray-diffraction experiments.[3,4] At the transition from the fcc phase towards the new phase, superstructure reflections appear in the fcc diffraction pattern. Therefore this new phase has been designated "distorted fcc."[4] Up to now the distorted-fcc phase has been found in La, Pr, Nd, Pm, Sm, Gd, Tb, and Dy,[3–11] where the transition pressure to the distorted-fcc-phase increases with increasing atomic number. For the elements following Dy (Ho, Er, Tm, and Lu) the transition to distorted fcc is expected to appear at pressures above 45 GPa.[6,9,12] Besides the lanthanides this structure was also reported for Y (Refs. 4 and 13) and for the actinides Am and Cf.[12,14,15]

Although the distorted-fcc modification appears to be a true prototype for trivalent rare-earth metals under pressure there is no agreement on its structure, yet. Not even the assignment of the crystal system is clear. However, it is generally assumed that the structure of the distorted-fcc phase is the same for all the lanthanides and Y.

II. EXPERIMENTAL

The appearance of superlattice reflections at the transition fcc→distorted fcc indicates a displacive phase transition with an increase of the crystallographic base. Hence, diffraction lines from lattice planes with large d values have an important weight for the verification of the structure of the distorted-fcc phase. Some of the structures suggested for the distorted-fcc phase have medium strong reflections at d values greater 300 pm. In earlier experiments[3,4,16] Bragg reflections at sufficiently large d values were either outside the range of the measurements or at least hard to detect. Therefore special high-pressure energy-dispersive x-ray-diffraction (EDXD) experiments with unusually small diffraction angle ($2\theta=7.68°$) were performed on lanthanum with synchrotron radiation at HASYLAB/DESY. In these experiments Bragg reflection from lattice planes with d values up to about 740 pm could be detected. The general experimental setup with diamond-anvil cell and ruby manometer has been described previously.[17] Mineral oil was used as pressure transmitting medium which also prevents the sample from oxidation during sample preparation. The chemical analysis of the La material provided by K. A. Gschneidner, Jr., is given elsewhere.[9]

The x-ray-diffraction pattern of the distorted-fcc phase of lanthanum at 17 GPa is shown in Fig. 1. The diffraction lines of the distorted-fcc phase are indexed according to the parent fcc lattice; superlattice reflections are given with fractional indices. This indexing scheme does not depend on the lattice chosen for the distorted-fcc phase and is used throughout the text unless otherwise noted.

Usually there are some additional diffraction lines in the diffraction pattern of the distorted-fcc phase of La, Pr, and Nd.[3,4,16] The relative intensity of these additional lines shows large variation from preparation to preparation compared with the intensity of the superlattice reflections. As already pointed out[16] these lines must be attributed to the metallic monoxides of the elements which are obviously formed under pressure[18] from the (monoclinic) sesquioxide and crystallize in the cubic rocksalt-type structure. In the present sample there is no trace of this impurity (cf. Fig. 1).

The main feature of the transition fcc→distorted fcc is the appearance of superlattice reflections. Besides, a weak splitting of some diffraction lines indicates a small distortion of the superlattice from the cubic metric. There is no $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ superlattice reflection in the diffraction pattern of distorted-fcc La (cf. Fig. 1). For comparison, the intensity of the escape peaks (see inset of Fig. 1), which are produced by the detector, is about 1% of the parent peak intensities. Therefore, the intensity of the $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ superlattice reflection must be less than 0.1%. It should be noted, that for EDXD experiments no texture effects can falsify the intensity ratio of the $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ superlat-

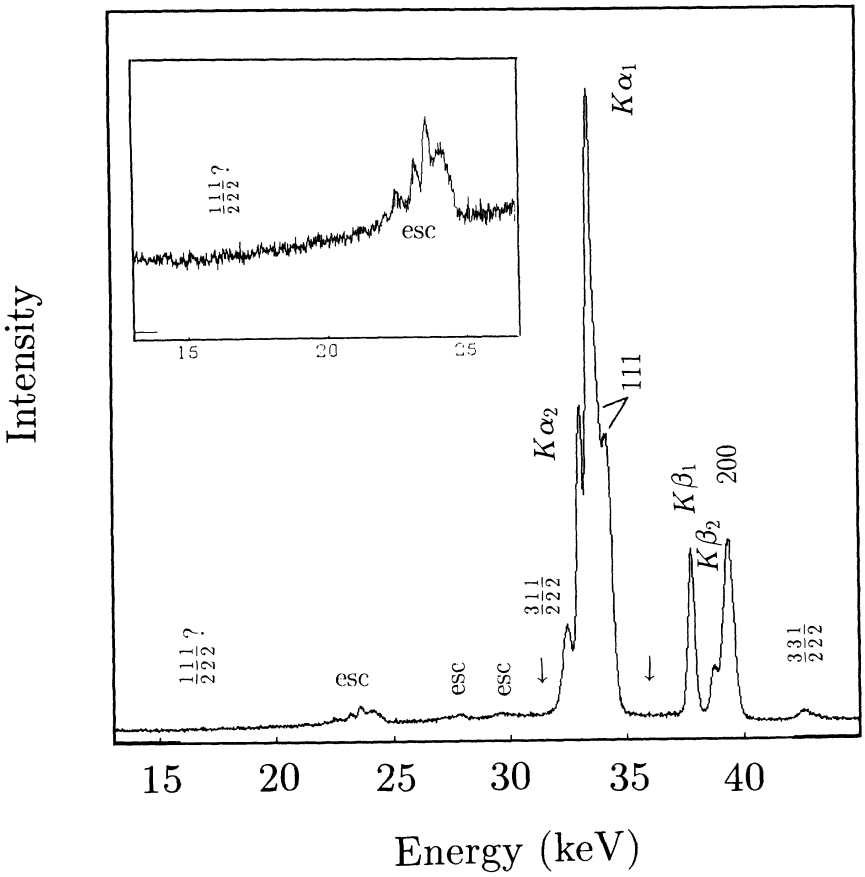

FIG. 1. Energy-dispersive x-ray-diffraction spectrum for the distorted-fcc phase of La at 17 GPa. Indexing according to the parent fcc phase. Superlattice reflections are given with fractional indices. Expected positions of diffraction lines from LaO are marked with arrows. The escape lines, which are produced by the detector are marked with "esc". Inset shows a section of the spectrum with intensity magnification ×10. No intensity is seen at the position of the $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ superlattice reflection.

tice reflection with respect to its fundamental 111 reflection because both come from the very same grains of the sample.

III. DISCUSSION

It is generally argued that the transition fcc→distorted fcc is a continuous phase transition. In the discussion that follows this presupposition will be used in order to derive possible structures for the distorted-fcc phase. The arguments given in the literature for the transition fcc→distorted fcc being an continuous transition are therefore recapitulated here:

(i) The fcc→distorted-fcc phase transitions do not show any hysteresis neither with pressure[4,19] nor with temperature variation, even at very low temperatures.[1] All other structural phase transitions of the lanthanide elements are accompanied by a perceptible hysteresis.[9]

(ii) There is no detectable discontinuity in resistivity[1] and volume[4] at the transition.

(iii) All the x-ray-diffraction lines of the high-symmetry fcc phase are preserved in the distorted-fcc phase. The distorted-fcc phase is characterized by the appearance of additional reflections indicating a superstructure. At higher pressure there is an additional splitting of the former fcc 111 line, indicating a slight distortion from the cubic metric.

(iv) The intensities of the superstructure reflections vary over a wide range with pressure. Within the experimental resolution the intensities go continuously to zero at the transition to the fcc phase.[4,16,19]

(v) Inelastic neutron-scattering experiments on lanthanum at ambient pressure reveal a soft-mode behavior of TA phonons close to the L point of the Brillouin zone.[20,21] This behavior has been related to the fcc→distorted-fcc transition under pressure.[22]

(vi) Theoretical calculations[23,24] for the lanthanide elements with fcc structure indicate Lifshitz-Dagens anomalies[25] under pressure caused by topological changes of the Fermi surface. Such anomalies are related to phonon softening and structural instabilities.

For continuous and weak first-order phase transitions the phenomenological Landau theory of phase transition is an appropriate and well established theoretical framework.[26–32] In particular the symmetry aspects of this theory are rigorous and result in strong conditions on possible symmetry changes at continuous phase transitions. For a transition from a high-symmetry (hs) to a low-symmetry (ls) phase the Landau expansion of the Gibbs free energy $G(P,T)$ can be expressed as a Taylor series of some order parameter $\mathbf{Q}$

$$G(P,T)=G^0(P,T)+\frac{\alpha}{2}\mathbf{Q}^2+\frac{\beta}{4}\mathbf{Q}^4+\frac{\gamma}{6}\mathbf{Q}^6+\cdots . \quad (1)$$

The order parameter $\mathbf{Q}$ is zero in the hs phase and different from zero in the ls phase. For a displacive phase transition with a single atomic displacement vector $\mathbf{u}=u\cdot\mathbf{u}^0$ the magnitude u of the displacement may serve as the order parameter $\mathbf{Q}$:

$$G(P,T)=G^0(P,T)+\frac{\alpha}{2}u^2+\frac{\beta}{4}u^4+\frac{\gamma}{6}u^6+\cdots . \quad (2)$$

The series expansion (1) must be invariant under the symmetry operations of the hs phase. In the present case it contains only even powers of **Q**, because the hs fcc phase has a center of inversion. $G^0(P,T)$ is the Gibbs free energy of the fcc phase which varies smoothly across the transition. α, β, and γ are the coefficients of the power expansion which gives the extra energy from the atomic displacement. For small atomic displacements (i.e., for continuous and weak first-order transitions) the leading terms of the power expansion determine the variation of the free energy and hence the structure of the ls phase. Coefficients of the power series which are not related to each other by symmetry are considered to vary different and independently with pressure and temperature. In the usual Landau ansatz only the leading term α varies (linearly) with temperature and pressure, whereas the higher-order coefficients are considered as constant. Therefore, the transition to the ls structure will be driven by a single irreducible representation (irrep) of the hs phase and all the possible transitions can be classified according to irreps which are characterized by a vector **k** in reciprocal space and an irrep of the point group of this vector. For phase transitions among commensurable structures the **k** vector must belong to a high-symmetry point at the surface of the Brillouin zone or to the center of the zone (Lifshitz condition).[27]

Many of the structures proposed for distorted fcc fail already with respect to the following two easy-to-check conditions which follow from Landau theory:

(i) Because the transition is controlled by a single irrep of the hs phase, the space group (SG) of the ls structure must be a subgroup of the SG of the hs structure. The hexagonal SG's are not subgroups of SG $Fm\bar{3}m$. Hence the triple hexagonal structures thcp(I) (SG $P6_3/mmc$) (Refs. 33 and 34) and thcp(II) (SG $P\bar{6}m2$) (Ref. 35) proposed for distorted fcc must be rejected.

(ii) According to the Lifshitz condition the number of atoms in the primitive cell can only increase by certain factors at the transition. These factors are determined by the SG of the hs phase and depend on the irrep involved in the transition. For fcc structures only the factors 1, 2, 4, 8, 16, and 32 are in accordance with the Lifshitz condition. The structural model for the distorted-fcc phase with SG $P3_221$ (Ref. 36) has six atoms (position 6*c*) in the primitive cell. This is forbidden by the Lifshitz condition.

There was a compilation of a great variety of structures with low symmetries as possible candidates for the distorted-fcc phase.[37] Most of them fulfill the two criteria given above, i.e., their space groups are subgroups of $Fm\bar{3}m$ and the number of atoms in the base is two or four. The authors tried to index all the observed diffraction lines of distorted-fcc Pr with these various structures. They favor two structures (SG $P2_1/m$, position 2*a* and SG $P2_1/c$, position 4*e*) which can index all the observed lines. However, the authors index also seven lines which fit to fcc PrO as belonging to the distorted-fcc structure.

In a recent paper[16] two rhombohedral structures were discussed for distorted fcc of Pr on the base of an x-ray-diffraction pattern obtained by an image plate technique. The published diffraction spectrum with an excellent resolution and signal-to-noise ratio reveals some additional, very weak diffraction peaks which have not been reported before for any distorted-fcc pattern. Rietveld refinements lead the authors to two possible structures for distorted fcc with SG $R\bar{3}m$ and SG $R32$, respectively, and eight atoms in the primitive cell. Both structures are in agreement with the two conditions from Landau theory given above. The authors prefer the structure with SG $R\bar{3}m$ because the observed intensities of the superlattice reflections are better reproduced. However, two strong fundamental reflections are excluded from the refinement because there seemed to be preferred orientations. Both of the two diffraction lines excluded (006 and 202 in the hexagonal indexing scheme) stem from the eight equivalent $\{111\}$ planes of the fcc phase and the intensity ratio should be 2:6 (in a first approximation) for a rhombohedral low-symmetry structure. Moreover, for any ls structure the intensity ratio of two lines derived from $\{111\}$ should be 2:6 or 4:4 (in a first approximation) if no preferred orientation is present. The observed intensity ratio of about 1:2 manifests a special preferred orientation which is a peculiarity at ferroelastic transitions. The spontaneous breaking of symmetry at the transition leads to an appropriate number of possible equivalent orientations for the ls structure. Under isotropic (hydrostatic) conditions all these possible orientations will appear with equal probability. However, nonhydrostatic stress may produce preferred orientations or switch the orientational state of the ferroelastic domains (ferroelastic switching).[38,39] The critical stress, at which the orientation of the domains changes, becomes very small close to the transition point. Therefore, small deviations from isotropic (hydrostatic) conditions within the high-pressure cell may produce serious deviations from a uniform orientational distribution of the domains, even if the distribution in the high-symmetry fcc phase has been uniform before the transition. This in turn effects the observed intensities for *all* the reflections of the low-symmetry phase. This kind of preferred orientation is a peculiarity of the ferroelastic phase and has carefully to be accounted for in Rietveld refinements.

In the next sections all the possible structures for the distorted-fcc phase consistent with a continuous or weak first-order transition to the fcc phase are deduced from Landau theory in connection with the experimental observations. To this end no quantitative diffraction intensities are used due to the problems mentioned above.

Because of the simple structure of fcc there is only a small number of irreps which can drive the fcc→distorted-fcc transition. For fcc lattices there are just three different kinds of points with high symmetry at the surface of the Brillouin zone which are compatible with the Lifshitz condition. These are the points with reciprocal-lattice vectors $\mathbf{k}^X=2\pi/a(0,1,0)$, $\mathbf{k}^L=2\pi/a(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, and $\mathbf{k}^W=2\pi/a(\frac{1}{2},1,0)$. As already noticed before[4] and indicated in Fig. 1 all the (strong) superlattice reflections of the distorted-fcc phase can be indexed with

reciprocal-lattice vectors $\mathbf{K}$ according to $|\mathbf{K}| \cong |\mathbf{K}_{\rm fcc} \pm \mathbf{k}^L|$, where $\mathbf{K}_{\rm fcc}$ is any reciprocal-lattice vector of the fcc structure. Hence the transition fcc→distorted fcc is associated with an irrep with vector $\mathbf{k}^L$. There are four different but symmetry equivalent vectors $\mathbf{k}^L$ which form the star ${}^*\mathbf{k}^L$ (cf. Fig. 2). Because these four vectors are equivalent by symmetry the full star is to be considered in the free-energy expansion (1). Since the transition fcc → distorted fcc is of the displacive type, the irrep driving the transition must be contained in the mechanical representation[28] of the crystal. For the simple fcc structure there are only two such irreps with wave vector $\mathbf{k}^L$ which must be considered, namely, A_{2u}^L (τ_5, in the notation of Ref. 40) and E_u^L (τ_6). These irreps also represent the LA and TA phonon modes with wave vector $\mathbf{k}^L$ and the eigenvectors of these normal modes can be used as base vectors for the static displacement in the ls phase.

The displacement $\mathbf{u}_i$ of atom i from its hs position $\mathbf{r}_i^0$ in the ls phase induced by the irrep A_{2u}^L is given by

$$\mathbf{u}_i = \sum_j \mathbf{z}_j \exp(i\mathbf{k}_j^L \mathbf{r}_i^0) , \tag{3}$$

where the sum runs over all the four arms (vectors) of the star ${}^*\mathbf{k}^L$. Introducing the atomic displacement vector $\mathbf{u}_i$ [Eq. (3)] in the structure factor $F(\mathbf{q}_{hkl}) = \sum_i f_i \exp[i\mathbf{q}_{hkl}(\mathbf{r}_i^0 + \mathbf{u}_i)]$ [the sum is taken over all atoms of the (larger) primitive cell of the ls structure] reveals that superlattice reflections corresponding to reciprocal-lattice vectors with $\mathbf{K} = \mathbf{K}_{\rm fcc} \pm \mathbf{k}^L$ appear in the diffraction spectrum with intensities proportional to u^2 indicating the irrep involved in the transition. Because $\mathbf{z}_j$ is parallel to $\mathbf{k}_j$ the most pronounced effect for structures induced by these irrep would be the onset of a $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ superlattice reflection which is not observed in the present experiment. Hence this irrep must be discarded.

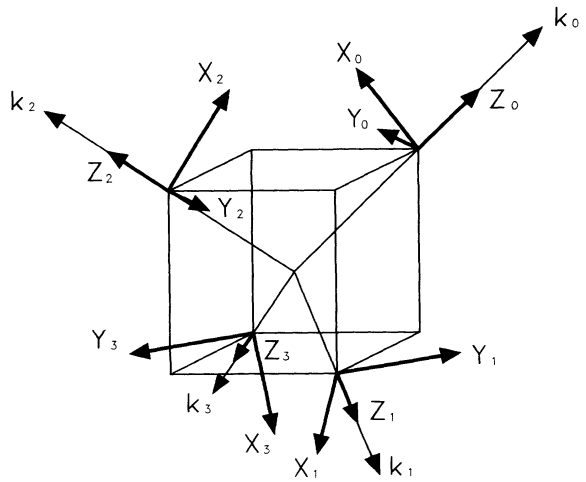

FIG. 2. The star ${}^*\mathbf{k}^L$ of the four different but symmetry equivalent reciprocal-lattice vectors $\mathbf{k}_j^L$ of the high-symmetry fcc phase and the corresponding base vectors $\mathbf{x}_j, \mathbf{y}_j, \mathbf{z}_j$ of the atomic displacements in the low-symmetry distorted-fcc phase. The static atomic displacement in the low-symmetry phase is given by Eqs. (3) and (4), respectively.

Therefore the transition must be driven by the irrep E_u^L. This agrees with the observed softening of the TA phonon mode close to the L point.[21,22] For the two-dimensional irrep E_u^L there are two (different) displacement amplitudes $\mathbf{x}_j$ and $\mathbf{y}_j$ for each $\mathbf{k}_j$ (cf. Fig. 2) and a general phase transition associated with this irrep is described by static atomic displacements according to

$$\mathbf{u}_i = \sum_j (\mathbf{x}_j + \mathbf{y}_j) \exp(i\mathbf{k}_j^L \mathbf{r}_i^0) . \tag{4}$$

TABLE I. All the possible structures which may result from a continuous or discontinuous transition from fcc induced by the irrep E_u^L (Ref. 41). Q= order parameter; n= number of independent components of Q; m= cell multiplication (of the primitive cell) at the transition from fcc; SG= space group; column 6 indicates whether a continuous transition to fcc is possible or not; multicomponent order parameter (OP) means $n > 1$; $\bar{\eta} = -\eta$; $\eta' = \sqrt{3}\eta$, etc.

	$Q=(x_0,y_0,\ldots,x_3,y_3)$	n	m	SG	Continuous	Remarks
I	$(\eta,0,0,0,0,0,0,0)$	1	2	$C2/c$	+	Single arm of ${}^*\mathbf{k}^L$
II	$(0,\eta,0,0,0,0,0,0)$	1	2	$C2/m$	+	Single arm of ${}^*\mathbf{k}^L$
III	$(\eta,\rho,0,0,0,0,0,0)$	2	2	$P\bar{1}$	No	& multicomponent OP
IV	$(\eta',\eta,\eta',\eta,0,0,0,0)$	1	4	$Cmmm$	+	
V	$(\eta,\eta',0,0,\eta,\eta',0,0)$	1	4	$Cmma$	No	
VI	$(\eta,\rho,\eta,\rho,0,0,0,0)$	2	4	$C2/m$	No	Multicomponent OP
VII	$(\eta,\rho,\mu,\phi,0,0,0,0)$	4	4	$P\bar{1}$	No	Multicomponent OP
VIII	$(\bar{\eta}',\bar{\eta},\eta',\eta,0,2\eta,\eta',\bar{\eta})$	1	8	$I4/mmm$	+	Wrong line splitting
IX	$(\eta,\bar{\eta}',\eta,\bar{\eta}',2\bar{\eta},0,\eta,\eta')$	1	8	$I4/mcm$	+	Wrong line splitting
X	$(0,\eta,0,\eta,0,\eta,0,0)$	1	8	$R\bar{3}m$	No	
XI	$(\eta,0,\eta,0,\eta,0,0,0)$	1	8	$R\bar{3}c$	No	Wrong line splitting
XII	$(0,\eta,0,\rho,0,\rho,0,\mu)$	3	8	$C2/m$	No	Multicomponent OP
XIII	$(\eta,0,\rho,0,\rho,0,\mu,0)$	3	8	$C2/c$	No	Multicomponent OP
XIV	$(\eta',\eta,\rho',\rho,\mu',\mu,\mu',\mu)$	3	8	$C2/m$	No	Multicomponent OP
XV	$(\eta,\bar{\eta}',\rho,\bar{\rho}',\mu,\bar{\mu}',\mu,\bar{\mu}')$	3	8	$C2/c$	No	Multicomponent OP
XVI	$(\eta,\eta,\eta,\eta,\eta,\eta,\eta,\eta)$	1	8	$P\bar{1}$	No	

Again the sum runs over the four arms of the star $^*\mathbf{k}^L$. The magnitudes x_j, y_j of the amplitudes $\mathbf{x}_j = x_j \cdot \mathbf{x}_j^0$ and $\mathbf{y}_j$ are the components of an eight-dimensional order parameter $\mathbf{Q} = (x_0, y_0, \ldots, x_3, y_3)$. The possible stable states for the ls phase have to be found in the course of minimizing the free energy G with respect to this eight-dimensional order parameter $\mathbf{Q}$. Fortunately, the tedious work of finding all the possible ls SG's has already been done once forever with the help of group-theoretical methods.[41] There is a total of sixteen ls structures which may result from continuous or discontinous transition induced by the irrep E_u^L.[41] These structures are given in Table I along with the order parameter associated with the phase transition.

If more than one arm of the star $^*\mathbf{k}^L$ is involved in the transition (i.e., $\mathbf{x}_j + \mathbf{y}_j \neq 0$ for at least two j) additional (second order) superlattice reflections with $|\mathbf{K}| = |\mathbf{K}_{\text{fcc}} + \sum_j (\pm \mathbf{k}_j^L)|$ appear in the powder-diffraction spectrum with intensities proportional to Q^4. Such weak diffraction lines have been observed for Pr.[16] Hence, at least two arms of the star $^*\mathbf{k}^L$ are involved in the transition fcc→distorted fcc and the base of the ls distorted-fcc structure contains at least four atoms. This excludes structures I to III from Table I as possible candidates for distorted fcc.

Because there was general agreement in the literature, that the transition fcc→distorted fcc is of second order, the ls structures compatible with such a transitions are considered at first. In a series of papers[42] all the possible ls SG's were given which may arise by *continuous* transitions from any hs SG. As a rigorous result from Landau theory, out of the 16 structures given in Table I only the five indicated in the table may arise by a continuous transition from fcc. Of course, these transitions may become discontinuous if higher-order terms or coupling to strain is taken into account. But for all the other structures the transition to fcc is necessarily of first order. Higher-order terms in the Landau free-energy expansion and coupling to strain modify the quantitative behavior but do not change the symmetry aspects of the transition.

As already noted before, structures I–III must be rejected because the observation of second-order superlattice reflections require at least two arms of the star taking part in the transition. In addition, the two tetragonal structures VIII and IX can be rejected immediately as candidates for distorted fcc. The persistence of the four-fold symmetry leaves the lattice spacings d in the directions [{111}] of the cubic lattice equivalent by symmetry in the low-symmetry phase. Hence the 111 line could not split in contradiction to the experimental observation. The only structures compatible with the experimental observations and a continuous transition to fcc is structure IV (SG *Cmmm*).

For completeness the remaining ls structures which may arise from fcc by a *first-order* Landau phase transition are considered also. For these structures there is a discontinuity at the phase transition and there should be some hysteresis in the phase transition. Perhaps these effects could be small and hence not detected or blurred by pressure inhomogeneities in the sample.

The structures III, VI, VII, and XII–XV have a multicomponent order parameter. These structures are subgroups of those with a single-component order parameter and are not considered further. Their order parameter is a linear combination of single-component order parameters and the same holds for the atomic displacements. At

TABLE II. The details of the structures, which remain as possible candidates for distorted fcc (structure XVI, SG $P\bar{1}$ not given).

	SG		Atomic positions		Lattice parameters
IV	*Cmmm*	4*j*	$0, y, \frac{1}{2}$	$y = \frac{1}{4} + \eta$	$a \approx 2a_{\text{fcc}}; b \approx \sqrt{2}a_{\text{fcc}}$
		4*g*	$x, 0, 0$	$x = \frac{1}{4} + \sqrt{2}\eta$	$c \approx a_{\text{fcc}}/\sqrt{2}$
V	*Cmma*	4*g*	$0, \frac{1}{4}, z$	$z = \frac{1}{2} + \eta$	$a \approx 2a_{\text{fcc}}; b \approx \sqrt{2}a_{\text{fcc}}$
		4*a*	$\frac{1}{4}, 0, 0$		$c \approx a_{\text{fcc}}/\sqrt{2}$
X	$R\bar{3}m$	18*h*	$x, \bar{x}, z$	$x = \frac{1}{2} + \eta; z = \frac{1}{4} - \eta$	$a \approx \sqrt{2}a_{\text{fcc}}$
		6*c*	$0, 0, z'$	$z' = \frac{1}{4} + 3\eta$	$c \approx 2\sqrt{3}a_{\text{fcc}}$

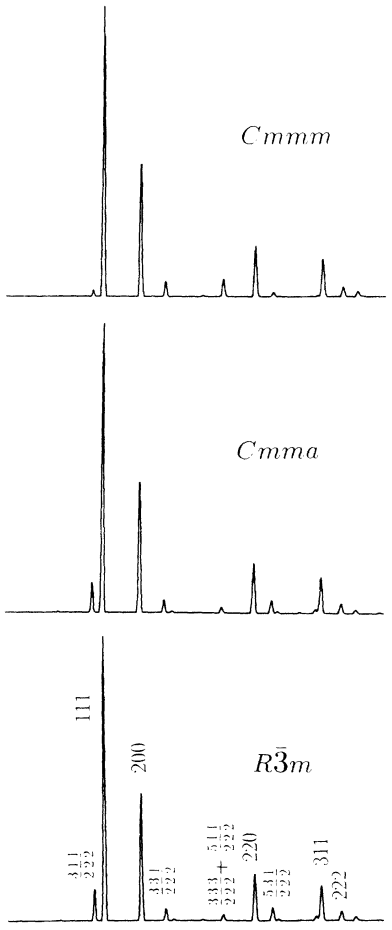

FIG. 3. Calculated diffraction spectra for structures IV (*Cmmm*), V (*Cmma*), and X ($R\bar{3}m$). The order parameters η are 0.02, 0.10, and 0.008, respectively. The spectra are calculated for the undistorted lattice (see text). Indexing according to the parent fcc lattice. Superlattice reflections are given with fractional indices.

the present level of experimental accuracy there is no support for such structures and the introduction of a multicomponent order parameter is therefore not substantiated. For structure XI (SG $R\bar{3}c$) only a single diffraction line (211, with hexagonal indexing) would arise from the $\frac{3}{2}\frac{3}{2}\frac{1}{2}$ superlattice reflection. The other lines (107 and 205, with hexagonal indexing) which may arise also from $\frac{3}{2}\frac{3}{2}\frac{1}{2}$) are not allowed for SG $R\bar{3}c$. Since the published diffraction pattern[16] clearly shows a splitting of the $\frac{3}{2}\frac{3}{2}\frac{1}{2}$ superlattice reflection, structure XI must be rejected.

Using only symmetry arguments along with Landau's theory of phase transition, just the four structure IV, V, X, and XVI remain as possible candidates for distorted fcc (cf. Table II).

Calculated diffraction spectra for these structures are given in Fig. 3. Because the model does not give the distortion of the superlattice the spectra are calculated for the undistorted lattice. Therefore no line splittings are present in these spectra. The calculated spectra for structure V and X resemble the observed diffraction pattern for distorted fcc (cf. Fig. 1 and Refs. 16 and 19); for example the superlattice reflections $\frac{3}{2}\frac{1}{2}\frac{1}{2}$ and $\frac{5}{2}\frac{3}{2}\frac{1}{2}$ are stronger than the reflections $\frac{3}{2}\frac{3}{2}\frac{1}{2}$ and $\frac{3}{2}\frac{3}{2}\frac{3}{2}+\frac{5}{2}\frac{1}{2}\frac{1}{2}$, whereas for structure IV the opposite is true. Therefore, it is unlikely that distorted fcc has structure IV, even when effects of preferred orientation are taken into account. Structure X ($R\bar{3}m$) proposed by Ref. 16 is a good candidate for distorted fcc because the integrity of the 200 diffraction line is consistent with the persistence of a threefold-rotational axis. However, the transition from structure X to fcc is of first order. The only possible structure which is obtained by a continuous transition from fcc is structure IV.

IV. CONCLUSION

Most of the structures proposed for distorted fcc are not compatible with Landau theory for displacive phase transitions. The structural models thcp(I) (SG $P6_3/mmc$) (Refs. 33 and 34) and thcp(II) (SG $P\bar{6}m2$) (Ref. 35) do not fulfill the group-subgroup relation and the model with SG $P3_221$ (Ref. 36) violates the Lifshitz condition. Some monoclinic structures (SG $P2_1/m$ and $P2_1/c$) (Ref. 37) are not compatible with a transition induced by the irrep E_u^L. The x-ray-diffraction spectra clearly indicate that the transition fcc→distorted fcc is induced by the irrep E_u^L of the fcc phase. This is in agreement with the observed phonon softening in fcc La.[21]

Because special texture effects at ferroelastic phase transitions usually falsify the diffraction intensities in high-pressure experiments, no quantitative intensity data (i.e., no structure refinement) have been used in the present discussion to pick out possible structures for distorted fcc. Just four structures are found to be compatible with the experimental observations. Out of them, only structure IV (SG *Cmmm*) can appear in a continuous transition from fcc. All the other structures (V, X, and XVI with SG's *Cmma*, $R\bar{3}m$, and $P\bar{1}$, respectively) involve first-order transitions to fcc in contradiction to the usual assumption of a continuous transition. Structure X ($R\bar{3}m$) appears to be a good candidate for distorted fcc. Structural refinement which takes into account preferred orientation will help to discriminate with ultimate certainty between the present proposal of structure IV against the three other structures which would have a first-order transition to fcc.

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