Colloq. 40, No. 6 (1979).
[2]The interpretation is in contrast to early theoretical work, e.g., W. Shockley, Phys. Rev. 91, 228 (1953); W. T. Read, Jr., Philos. Mag. 98, 116 (1954).
[3]J. P. Hirth and J. Lothe, *Theory of Dislocations* (McGraw-Hill, New York, 1968).
[4]A. Olsen and J. Spence, to be published; J. C. H. Spence, *Experimental High Resolution Electron Microscopy* (Oxford Univ. Press, Oxford, 1981).
[5]K. Wessel and H. Alexander, Philos. Mag. 35, 1523 (1977).
[6]D. J. Chadi, J. Vac. Sci. Technol. 16, 1290 (1979), and references therein.
[7]P. B. Hirsch, J. Phys. (Paris), Colloq. 40, C6-27 (1979).
[8]P. B. Hirsch, J. Microsc. (Oxford) 118, 3 (1980).
[9]J. E. Northrup, M. L. Cohen, J. R. Chelikowsky, J. Spence, and A. Olsen, Phys. Rev. 24, 4623 (1981).
[10]As in previous work (Ref. 9), I include two 30° partial dislocations separated by a stacking fault. The two partial dislocations have opposite Burgers vectors. This means that there is no strain field outside the supercell.
[11]S. Marklund, Phys. Status Solidi (b) 92, 83 (1979).
[12]S. Marklund, Phys. Status Solidi (b) 100, 77 (1980).
[13]M. J. Kirton, S. Brand, and M. Jaros, Philos. Mag. 42, 577 (1980).
[14]M. J. Kirton and M. Jaros, J. Phys. C 14, 2099 (1981).
[15]P. N. Keating, Phys. Rev. 145, 637 (1966), and 149, 674 (1966).
[16]S. G. Louie, Phys. Rev. B 22, 1933 (1980).
[17]I use two s-symmetry orbitals to reproduce accurately the lower conduction bands. Details of the computation are the same as in Ref. 9.
[18]L. C. Kimerling, J. R. Patel, J. L. Benton, and P. E. Freeland, in Proceedings of the International Conference on Defects in Semiconductors, Osio, Japan, 1980 (to be published).
[19]R. Jones, in *Microscopy of Semiconducting Materials–1981*, edited by A. G. Cullis and D. C. Joy, IOP Conference Proceedings No. 60 (Institute of Physics, London, 1981), p. 45.
[20]It has been suggested that the 90° partial dislocation need not involve a Peierls reconstruction [S. L. Altman, J. Phys. C 15, 907 (1982)].

Evidence for a Soft Phonon Mode and a New Structure in Rare-Earth Metals under Pressure

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High-pressure x-ray diffraction experiments up to 30–40 GPa on lanthanum, praseodymium, and yttrium metals demonstrate that there is one more crystal structure in the regular rare-earth crystal-structure sequence. This structure results from a second-order phase transition in fcc phase and could be described by a zone-boundary soft phonon mode with $\vec{q} = (2\pi/a_0)(\frac{1}{2},\frac{1}{2},\frac{1}{2})$.

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The alkali metals, alkaline-earth metals, and rare earths as well as early transition metals show electron transfer from s to d bands under pressure. This $s \rightarrow d$ transfer results from relative lowering of d-like conduction states in comparison to s and p states which rise rapidly under compression. This electronic transition, which occurs over a wide range in volume, results in many structural transitions as well as in bulk-modulus anomalies in the group-IA to IIB elements.[1-4] The rare-earth crystal-structure sequence hcp → Sm type → dhcp → fcc with decreasing atomic number and increasing pressure is one such example. In the course of $s \rightarrow d$ transfer in these materials, various band extrema pass through the Fermi energy, thereby changing the connectivity of the Fermi surface. It is recognized[5,6] that these topological changes of the Fermi surface can lead to anomalies in phonon frequencies and in some cases to phonon softening and structural phase transitions. Until recently, it was believed that the ultimate high-pressure phase of rare-earth metals is fcc. One earlier x-ray study[7] on Pr, however, reported an orthorhombic distortion of the fcc lattice. Also, electrical resistivity measurements at low temperature and high pressures[8,9] show resistance anomalies for Pr and La, in the fcc phase. The present x-ray diffraction measurements on La, Pr, and Y were intended to establish the microscopic

nature of this transition as well as its general occurrence in rare-earth metals.

The structural transitions in these metals under pressure up to 30–40 GPa were studied by energy-dispersive x-ray diffraction with a gasketed diamond anvil cell[10] with use of the ruby fluorescence method[11] for pressure measurements. The samples were prepared under oil to avoid possible oxidation and oil surrounded the sample also in the gasket of the high-pressure cell. It was evident from the ruby luminescence linewidth that the pressure conditions were not truly hydrostatic; however, no effects of nonhydrostatic stresses were observed in linewidths or line positions within the accuracy of the present technique.[10]

La and Pr like other light lanthanides crystallize in the dhcp structure, and Y-like heavy lanthanides crystallize in the hcp structure. The low-pressure phase transitions in La at 2.5 GPa and in Pr at 4 GPa to the fcc phase are well known.[12] Above 7 GPa, a gradual distortion of the fcc lattice was observed in La and Pr with continuous growth of superlattice reflections. The same distortion was observed in Y above 40 GPa after it had gone through the full rare-earth sequence.[3,13] The effect of different stress distributions was checked by cycling of the pressure, and only minor changes in the texture were observed without any noticeable change in the superlattice structure. The energy-dispersive x-ray diffraction patterns of the distorted fcc phase are shown in Fig. 1 for Y, La, and Pr. All the additional diffraction lines due to distortion can be indexed with $\vec{\Delta}k = \vec{G} = \vec{G}_{fcc} \pm \vec{q}$ where $\vec{q} = (2\pi/a_0) \times (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. This representation suggests the existence of a soft phonon mode $\vec{q}$ which ultimately results in the static distortion. This $\vec{q}$ corresponds to the zone-boundary point L in the Brillouin zone of the fcc lattice and is along the $\langle 111 \rangle$ cubic direction which is the c axis in the hexagonal representation of the fcc lattice. This zone-boundary softness results in a distortion which just doubles the c axis of the corresponding hexagonal cell. Figure 1 shows the indexing of this phase in terms of a hexagonal cell with $a = a_0/\sqrt{2}$ and $c = 2\sqrt{3}a_0$ with six atoms per unit cell, where a_0 is the lattice constant of the cubic phase. The Debye-Scherrer pattern for distorted fcc in Ref. 7 can also be indexed in terms of this smaller hexagonal cell.

The second-order nature of this transition can be inferred from Fig. 2 where the normalized intensity for the (105) superlattice reflection is

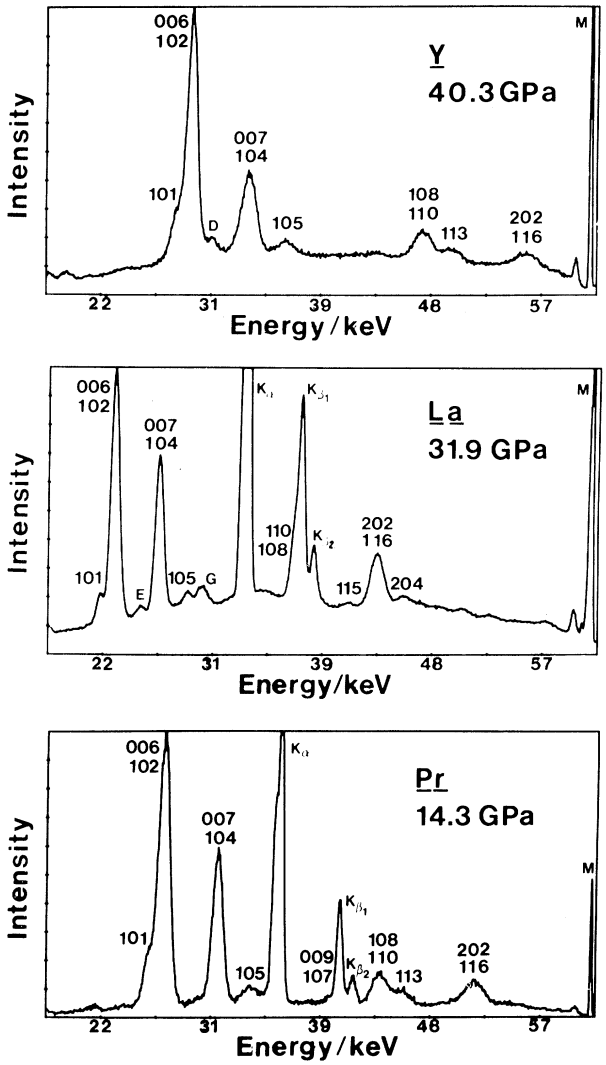

FIG. 1. Energy-dispersive x-ray diffraction patterns for Y, La, and Pr in the distorted fcc phase at various pressures. Y and Pr diffraction patterns are with $2\theta = 10°$ while La is with $2\theta = 12°$. These patterns were indexed to a hexagonal lattice with $c/a = (24)^{1/2}$. (hkl) reflections with even l values correspond to principal fcc reflections. M, marker; G, gasket; E, escape peak; D, remanent dhcp.

plotted as a function of pressure for Pr. From this plot one can estimate the critical pressure (P_c) for the transition to be as low as 6.2 GPa in Pr at room temperature. This continuous structural transition corresponds to a continuous periodic distortion of the layers ABC, $A'B'C'$ with respect to each other with increasing pressure. The critical pressure for La at room temperature is approximately the same as for Pr. It should be added that this transition remains second order to very low temperature (~ 50 K)[9] as

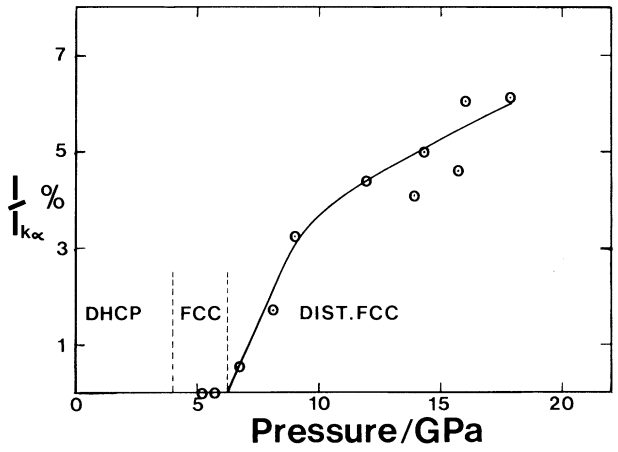

FIG. 2. The pressure dependence of the intensity (normalized to Pr $K\alpha$ fluorescent peak) of the (105) superlattice reflection of distorted fcc phase in Pr. The intensity drops down continously to zero at 6.2 GPa.

one would expect for a soft-mode transition and also occurs at lower pressures at lower temperatures. In an earlier x-ray study on La at room temperatures and pressures up to 10 GPa,[14] no lattice distortion was observed because this earlier technique did not allow for the observation of weak satellites in that limited pressure range.

The observation of this transition in light lanthanides (La, Pr) and in a typical heavy rare-earth metal (Y) indicates that this is an additional structure in the regular rare-earth metal sequence which can be observed, however, only at high pressures, after the appearance of the fcc phase.

In detailed band-structure calculations[15] on La under pressure, it was found that in the low-pressure range (0–5 GPa) there is a change in topology of the Fermi surface in the L-U-W-K plane. The bare electronic susceptibility $\chi_0(\vec{q})$ showed a strong maximum and a large change with pressure at the L point of the Brillouin zone. This, together with the large electron-phonon coupling, indicated by the large value of the superconducting transition temperature (T_c) and its rapid increase with pressure,[9] can be related to the phonon frequency renormalization at the L point. However, calculations of phonon dispersion curves under pressure for the rare-earth metals in the fcc phase are required to look for this phonon softening in more detail. Some softness in average phonon frequencies in the low-pressure region (0–5 GPa) has been considered earlier[9, 15-16] to explain the extra enhancement in T_c with pressure as well as anomalies in resistance-versus-temperature curves of La at various pressures.

It is interesting to note that no further transformation is observed in La up to pressures of 33 GPa. The $s \rightarrow d$ electronic transition is considered to be completed around 20 GPa in La as indicated by the shock anomaly,[17] and theoretical calculations show that, in this pressure range, the bottom of the s band moves above the Fermi energy with pressure.[18] It appears that the ultimate high-pressure phase of rare-earth metals with predominantly d character in their conduction band is distorted fcc (or in other words a hexagonal six-layer sequence). The complete rare-earth crystal-structure sequence is therefore hcp → Sm type → dhcp → fcc → distorted fcc. However, in the light lanthanides Ce, Pr, . . . , the localized $4f^n$ configuration can be affected by pressure to participate in bonding, and additional low-symmetry crystal structures are observed.[7] In Pr metal above 20 GPa, the α-uranium structure was observed[19] which remains stable up to 40 GPa. The appearance of this structure is related to delocalization of f electrons (or f bonding) at high pressures[20] in close analogy with Ce (Ref. 21) and Am (Ref 22).

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[1]I. V. Svechkarev and A. S. Paniflov, Phys. Status Solidi 63, 11 (1974).

[2]J. C. Duthie and D. G. Pettifor, Phys. Rev. Lett. 38, 564 (1977).

[3]Y. K. Vohra, H. Olijnyk, W. A. Grosshans, and W. B. Holzapfel, Phys. Rev. Lett. 41, 1065 (1981).

[4]L. V. Al'tshuler, A. A. Bakanova, and I. P. Dudoladov, Zh. Eksp. Teor. Fiz. 53, 1967 (1967) [Sov. Phys. JETP 26, 1115 (1968)].

[5]L. Dagens, J. Phys. F 8, 2093 (1978).

[6]J. E. Schirber, in *High Pressure Science and Technology*, edited by K. D. Timmerhaus and M. S. Barber (Plenum, New York, 1979), Vol. 1, p. 130.

[7]H. K. Mao, R. M. Hazen, P. M. Bell, and J. Wittig, J. Appl. Phys. 52, 4572 (1981).

[8]M. Heinrichs and J. Wittig, J. Phys. (Paris), Colloq. 39, C6-1072 (1978).

[9]H. Balster and J. Wittig, J. Low Temp. Phys. 21,

377 (1978).
[10]W. B. Holzapfel and W. May, in *High Pressure Research in Geophysics*, edited by S. Akimoto and M. H. Manghnani (Center of Academic Publications, Japan, 1982).
[11]G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman, J. Appl. Phys. 46, 2774 (1975).
[12]G. J. Piermarini and S. Block, Science 144, 69 (1964).
[13]W. A. Grosshans, Y. K. Vohra, and W. B. Holzapfel, in Proceedings of Rare Earths and Actinides 82, Durham, United Kingdom (to be published).
[14]K. Syassen and W. B. Holzapfel, Solid State Commun. 16, 533 (1975).
[15]W. E. Pickett, A. J. Freeman, and D. D. Koelling, Phys. Rev. B 22, 2695 (1980).
[16]R. Glocker and L. Fritsche, Phys. Status Solidi (b) 88, 539 (1978).
[17]W. J. Carter, J. N. Fritz, S. P. Marsh, and R. G. McQueen, J. Phys. Chem. Solids 36, 741 (1975).
[18]A. K. McMahan, H. L. Skiver, and B. Johansson, in *Physics of Solids Under High Pressure*, edited by J. S. Schilling and R. N. Shelton (North-Holland, Amsterdam, 1981), p. 169.
[19]W. A. Grosshans, Y. K. Vohra, and W. B. Holzapfel, to be published.
[20]H. L. Skiver, in *Physics of Solids Under High Pressure*, edited by J. S. Schilling and R. N. Shelton (North-Holland, Amsterdam, 1981), p. 279.
[21]W. H. Zachariasen and F. H. Ellinger, Acta Crystallogr., Sect. A 33, 155 (1975).
[22]R. B. Roof, R. G. Haire, D. Schieferl, L. A. Schwalbe, E. A. Kmetko, and J. L. Smith, Science 207, 1353 (1980).

Critical Surface Phenomena at First-Order Bulk Transitions

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Semi-infinite systems which undergo a first-order bulk transition are considered. A new type of surface phase transition is predicted which has two unexpected features: (1) It exhibits some universal properties since a variety of surface exponents can be defined although there are no bulk exponents; (2) a layer of the disordered phase appears between the free surface and the ordered bulk. The interface between the disordered and the ordered phases becomes delocalized as in the wetting and in the pinning transition.

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Critical behavior at surfaces has been the subject of much recent interest.[1-12] Up to now, both theory and experiments have been devoted to semi-infinite systems which undergo a second-order bulk transition. In this case, the bulk order parameter is proportional to $|T-T_c|^{\beta}$ as the critical temperature $T=T_c$ is approached from below while the surface order parameter behaves as $|T-T_c|^{\beta_1}$ with $\beta_1 \neq \beta$. This surface critical exponent has been calculated by various methods for the Ising model,[2-5] for the n-vector model,[6-8] and for the two-dimensional q-state Potts-model with $q=3,4$.[9] The exponent β_1 has been measured for the antiferromagnet NiO by low-energy electron diffraction (LEED)[10] and for the ferromagnet Ni by spin-polarized LEED.[11] In this Letter, we consider semi-infinite systems which undergo a *first-order bulk transition*. As a consequence, the bulk order parameter jumps at the transition temperature $T=T^*$. However, it is shown below that *the surface order parameter may nevertheless behave continuously like* $|T-T^*|^{\beta_1}$. A variety of surface exponents can be defined which are expected to be universal. This is rather surprising since there are no corresponding bulk exponents. This new type of surface phase transition has an additional unexpected feature: as T^* is approached from below, *a layer of the disordered phase intervenes between the free surface and the ordered bulk.* Thus, an interface appears which separates the disordered surface layer from the ordered phase in the bulk. At $T=T^*$, this interface becomes delocalized as in the wetting[1,13,14] and in the pinning transition.[15-17] This implies a disordered surface layer of macroscopic thickness.

Consider a d-dimensional semi-infinite system with a $(d-1)$-dimensional free surface. The coordinate perpendicular to the surface is denoted by z. As a result of the broken translational invariance, the order parameter M depends on z: $M=M(z)$. The Landau expansion for the free en-

