

PHYSICAL REVIEW B

CONDENSED MATTER

THIRD SERIES, VOLUME 36, NUMBER 18

15 DECEMBER 1987-II

Role of lattice matching in epitaxy: Novel Ce phase and new fcc-bcc epitaxial relationship

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(Received 31 July 1987)

We have grown a novel epitaxial phase of cerium on vanadium using molecular-beam epitaxy and characterized by high-energy electron and x-ray diffraction. The results show that the Ce phase is contracted by 8% in the basal plane and expanded 2% out of the plane when compared to the ambient-temperature and ambient-pressure fcc, γ -Ce. Furthermore, the relative orientation of the Ce(111) and the V(110) planes is different from the well-known epitaxial relationships found to date experimentally and theoretically. The present results imply that electronic structure beyond simple geometrical lattice-matching considerations is important for epitaxial growth.

Structural studies of epitaxial films¹ and superlattices² are subjects of current interest motivated by expectations of engineering novel materials at the atomic level^{3,4} and by theoretical predictions which imply the existence of metastable phases with unusual magnetic properties.^{5,6} Recently, lattice-matched systems have received considerable attention; for instance bcc Co was stabilized on GaAs substrates using molecular-beam epitaxy (MBE) techniques.⁷ Although the epitaxial growth of non-lattice-matched pairs has been studied for many years,⁸⁻¹³ it is not commonly recognized that high-quality epitaxial films can be grown even if lattice matching is absent.^{1,12,13} For more than 50 years, one of the most striking observations in non-lattice-matched fcc-bcc epitaxy has been the existence of only two allowed relative orientations^{8,9} between the fcc (111) and the bcc (110) planes, depending on the degree of lattice mismatch. This fact is substantiated by a number of theoretical calculations, which are based on the idea that geometrical factors alone are responsible for epitaxy.¹⁰⁻¹² In this paper we show that a new *non-lattice-matched* single-crystal Ce film has been grown, using MBE techniques, on V(110). The new trigonal epitaxial phase of Ce (Ce*) exhibits an 8% contraction in the (111) plane and a 2% expansion perpendicular to this plane when compared to the ambient-pressure and ambient-temperature γ -Ce phase. To the best of our knowledge this is the first time that a metastable phase of Ce has been grown. Surprisingly the epitaxial orienta-

tion between the Ce*(111) and V(110) planes is unlike any previously observed relationship between fcc and bcc materials.¹⁴ The results imply that simple geometrical factors are not sufficient and that further theoretical studies using combined quantum chemistry, thermodynamics, and band structure are desirable for the understanding of epitaxial growth.

In order to study the role of lattice matching and thermodynamic phase diagram on epitaxy we have undertaken an extensive study of the MBE growth of rare earths on vanadium. The growth of Ce on V is particularly interesting because in thermodynamic equilibrium the two are completely immiscible,¹⁵ they exhibit one of the largest lattice mismatches ($\sim 28\%$) (Ref. 16) ever studied, and because Ce exhibits a variety of phases as a function of pressure and temperature.¹⁷ Film growth was performed on temperature-controlled, single-crystal (11 $\bar{2}$ 0) α -Al₂O₃ substrates in a Riber metal MBE system with a base pressure of 4×10^{-11} Torr. The deposition rate control of the electron-beam gun evaporators was provided by quartz crystal monitors and electron-impact emission spectroscopy (EIES); the pressure during growth was less than 2×10^{-10} Torr. The structure of the growing film was monitored using *in situ* reflection high-energy electron diffraction (RHEED). Further x-ray studies were performed on a Rigaku DMAXII computer-controlled, two-circle diffractometer using Cu $K\alpha$ radiation and also using a precession camera technique with Mo $K\alpha$ radiation.

The initial growth of V on sapphire at 900°C is in a crystalline, epitaxial-island (Volmer-Weber, VW) growth mode, up to an average thickness of about 30 Å. This is evidenced by spotty RHEED diffraction patterns. Beyond this thickness, streaked RHEED patterns develop indicating an atomically smooth, two-dimensional V surface as shown in Figs. 1(c) and 1(d). From x-ray diffraction studies of films removed from the growth chamber it is established that the V grows with the $\langle 110 \rangle$ direction perpendicular to the substrate. The relative epitaxial arrangements are obtained from a detailed

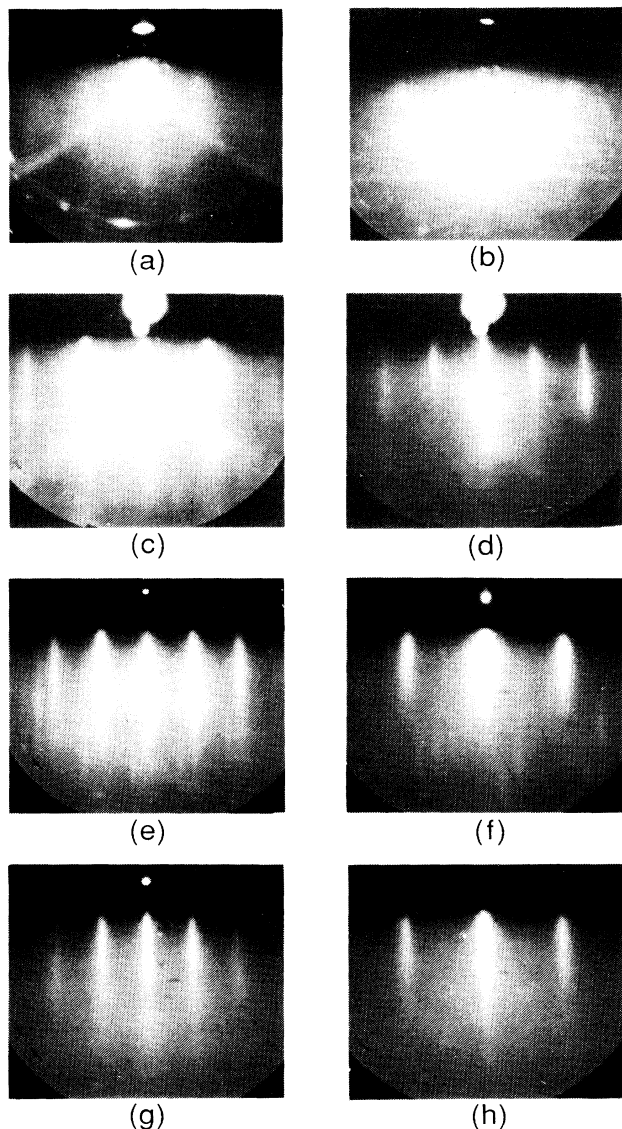


FIG. 1. RHEED patterns at 10 kV from Ce(111)/V(110) on sapphire; (a) and (b) show a sapphire substrate $\alpha\text{-Al}_2\text{O}_3(11\bar{2}0)$; (c) and (d) show a 1000-Å-thick V(110) film grown on $\alpha\text{-Al}_2\text{O}_3(11\bar{2}0)$; (e) and (f) show a 3-Å-thick and (g) and (h) show a 50-Å-thick Ce(111) film grown on the 1000-Å-thick V(110) film. Azimuths are (a) $\alpha\text{-Al}_2\text{O}_3[0001]$, (b) nearly $\alpha\text{-Al}_2\text{O}_3[\bar{1}104]$, (c) $\text{V}[\bar{1}\bar{1}\bar{1}]$, (d) $\text{V}[\bar{1}\bar{1}0]$, (e) and (g) $\text{Ce}[\bar{1}\bar{1}2]$, and (f) and (h) $\text{Ce}[\bar{1}\bar{1}0]$. The absolute angles are (a) and (c), 30°; (b) and (d), 65°; (e) and (g), 94°; and (f) and (h), 3°.

study of the diffraction streaks at different azimuthal angles around the normal to the film. A comparison of Figs. 1(a) and 1(b), and Figs. 1(c) and Fig. 1(d) in conjunction with the known structure and lattice spacing for V and $\alpha\text{-Al}_2\text{O}_3$ shows that the in-plane orientation is $\text{V}[\bar{1}\bar{1}\bar{1}]\parallel\alpha\text{-Al}_2\text{O}_3[0001]$ and $\text{V}[\bar{1}\bar{1}\bar{2}]\parallel\alpha\text{-Al}_2\text{O}_3[\bar{1}\bar{1}00]$. These are the same orientations as found earlier for the growth of Nb on Al_2O_3 .¹⁸ These results were confirmed by independent Buerger precession camera techniques and in-plane θ -2 θ diffraction after removal of the sample from the MBE system.

The growth of Ce films was initiated on the smooth, single-crystal epitaxial V(110) films. From the very beginning, the Ce exhibits streaked RHEED patterns as shown for $d_{\text{Ce}} = 3$ Å [Figs. 1(e) and 1(f)] indicating that the Ce grows in a layer-by-layer (Frank-van der Merwe) mode. Up to a thickness of 50 Å the growth of Ce proceeds in a layer-by-layer mode as indicated by streaked RHEED patterns [Figs. 1(g) and 1(h)]. X-ray diffraction measurements normal to the film plane show that the new Ce phase (Ce^*) grows along the $\langle 111 \rangle$ direction, the lattice spacing being about 2% expanded (~ 3.029 Å) when compared to the ambient-pressure and ambient-temperature $\gamma\text{-Ce}$ (~ 2.980 Å). The in-plane structure of the Ce^* was obtained from a detailed analysis of the RHEED streaks in various azimuthal orientations. In addition, we found a large $\sim 8\%$, uniform compression ($a^{\text{Ce}^*} = 4.75$ Å) relative to the bulk value of $\gamma\text{-Ce}$ ($a^{\gamma\text{-Ce}} = 5.161$ Å). The in-plane structure of this new phase of epitaxial Ce is close to the high-pressure $\alpha\text{-Ce}$ phase ($a^{\alpha\text{-Ce}} = 4.824$ Å).¹⁷ This indicates

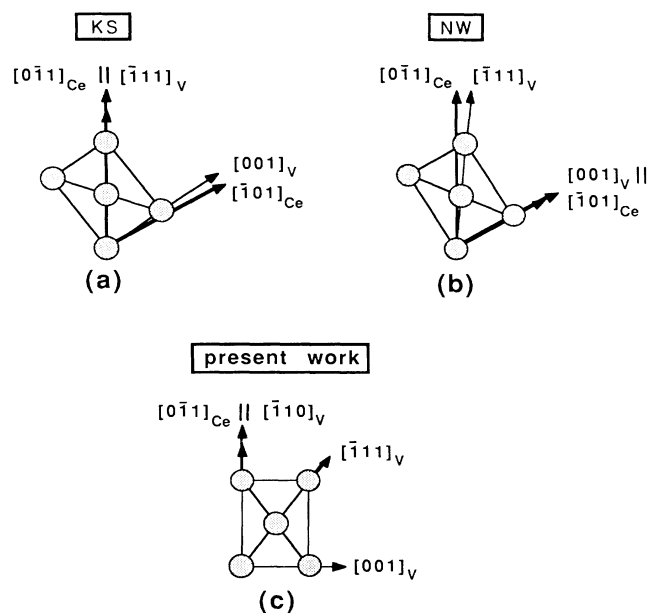


FIG. 2. Epitaxial arrangements of Ce(111) on V(110). (a) Kurdjumov-Sachs orientation $[\bar{1}\bar{1}\bar{1}]_V\parallel[0\bar{1}1]_{\text{Ce}}$, (b) Nishiyama-Wassermann orientation $[001]_V\parallel[\bar{1}01]_{\text{Ce}}$, and (c) the new orientation $[\bar{1}10]_V\parallel[0\bar{1}1]_{\text{Ce}}$ found in the present study.

that strain induced at the interface with V could be in part responsible for the new phase Ce*. Since the perpendicular spacing does not change as much as the in-plane spacing, the phase of Ce* is trigonal, unlike any previously reported stable or unstable phases of Ce. At this point we would like to stress that the new Ce* phase does not become lattice matched because of this contraction; i.e., the epitaxy is still between two unmatched structures.

The epitaxial relationship of the Ce*(111) and V(110) planes is also quite unlike any other observed for more than 50 years in many fcc (111) and bcc (110) systems.¹⁰ The relative in-plane orientations in *all* systems studied to date has been found to fall into two categories depending on the relative atomic sizes: the Kurdjumov-Sachs⁹ (KS) orientation, in which the bcc $[\bar{1}11]$ orientation is parallel to the fcc $[0\bar{1}1]$ [Fig. 2(a)], and the Nishiyama-Wassermann⁸ (NW) orientation, in which the bcc $[001]$ is parallel to the fcc $[\bar{1}01]$ orientation [Fig. 2(b)]. Notice that these two orientations differ only by 5.3° as shown in Fig. 2 and therefore high precision measurements are necessary to distinguish between them. The existence of these two orientations is also a consequence of a variety of geometrically based calculations, including Moiré patterns¹⁰ and phenomenological¹¹ and rigid-lattice models.¹² All these studies imply that the determining factor for epitaxial growth is the relative crystallographic lattice matching.

A careful analysis of the RHEED measurements [Figs. 1(c)–1(h)] results in a major surprise. The relative orientation of Ce*(111) on V(110) is neither NW nor KS. In the new orientation the Ce* $[0\bar{1}1]$ direction is parallel to the V $[\bar{1}10]$ direction as shown in Fig. 2(c). This orientation has never been observed before in any system.¹⁰ We should emphasize at this point that because Ce grows layer-by-layer (i.e., streaked RHEED pattern), at least two azimuthal orientations should be studied in order to determine uniquely the relative epitaxial relationships.

The observation of non-lattice-matched epitaxy and the existence of the new epitaxial relationship implies that additional mechanisms beyond geometric factors are operational in some cases. The large in-plane compression of Ce* shows that there is a strong interaction between the Ce and V. If only size effects would be important the only two allowed orientations should be NW

and KS. Although a large in-plane compression is present the perpendicular spacing changes little, showing that simple Poisson ratios are not responsible and the effect is not purely due to the fact that α - and γ -Ce phases are energetically close. What is quite surprising is that Ce* can be stabilized for films as thick as 50 Å.⁷ Naively, one might expect that any electronic effect would be a strongly decreasing function of the thickness in a metallic system, possibly within a screening length which is of the order of a few Å's in any metal. A recent theoretical idea¹⁹ has been advanced which claims that due to the boundary conditions the screening length in a thin film can be substantially different from that in the bulk.

The electronic properties of the new Ce* phase must be unlike any other known phase. Further theoretical and experimental work is needed to understand the origin of the compression and of the new fcc (111)/bcc (110) epitaxial orientation and to ascertain the other physical properties of Ce*. A variety of investigations come immediately to mind including structural phase transitions as a function of temperature and pressure, and electronic structure investigations using photoelectron spectroscopy and magnetic and transport phenomena.

In summary, we have grown epitaxially without lattice matching a new phase of Ce which shows an in-plane structure close to the high-pressure α -Ce and a perpendicular spacing slightly expanded ($\sim 2\%$) relative to the ambient-pressure γ -Ce. Furthermore, the relative Ce*(111)/V(110) epitaxial orientation is quite different from the well-known and studied KS and NW orientations. We hope that this work will motivate further work on *non-lattice-matched, immiscible* epitaxial systems and further theoretical work on the electronic and magnetic properties of epitaxial rare earths, in particular Ce in new phases.

We thank C. Aita, T. W. Barbee, Jr., L. Cooper, R. C. Dynes, A. J. Freeman, K. Hathaway, G. A. Prinz, and J. H. van der Merwe for useful conversations and criticism. This work was supported by the U.S. Office of Naval Research under Contract No. N00014-83-F-0031 and the U.S. Department of Energy (Basic Energy Sciences Program, Sciences Division) under Contract No. W-31-109-ENG-38.

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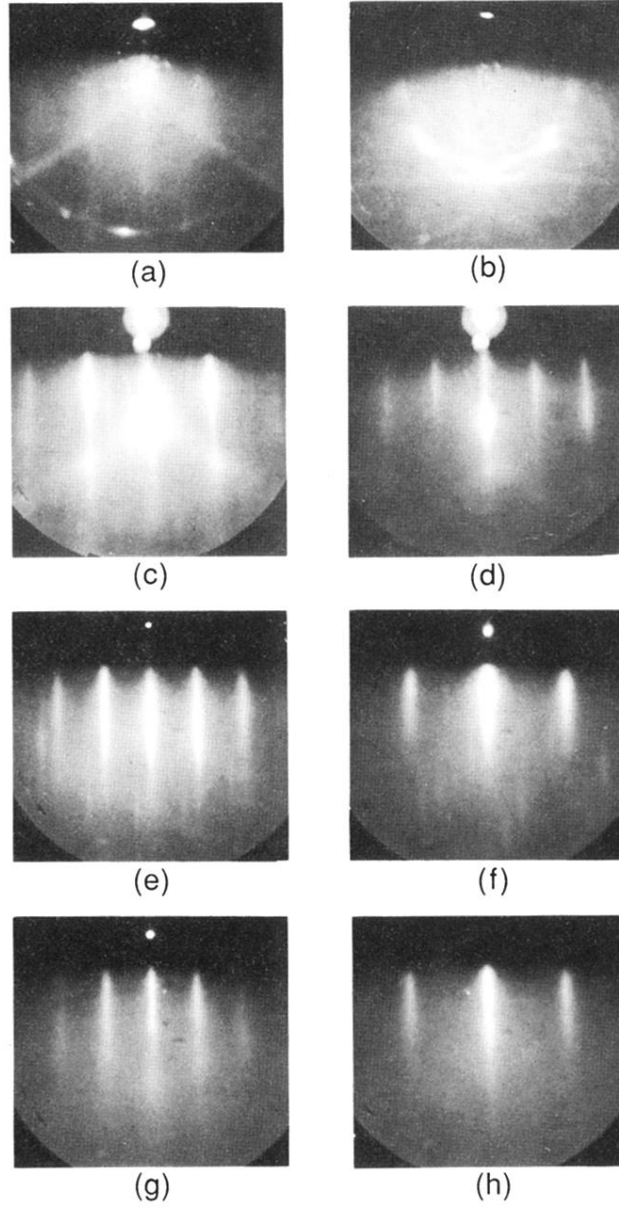


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