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SUPERLATTICE LEED PATTERNS OBSERVED FROM [111] AND [100] ORIENTED SINGLE CRYSTALS OF $TiPt_3$

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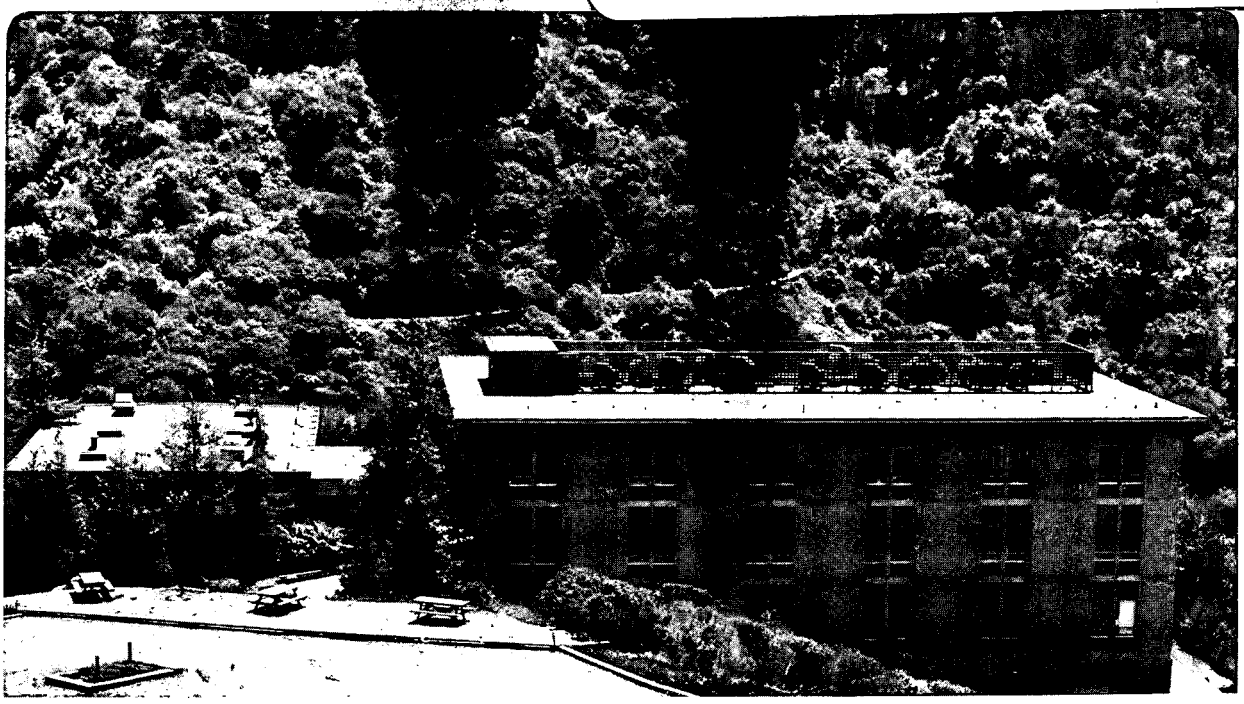

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# SUPERLATTICE LEED PATTERNS OBSERVED FROM [111] AND [100] ORIENTED SINGLE CRYSTALS OF $TiPt_3$

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Pt-Ti alloys are characterized by a highly exothermic heat of formation[1] that has been attributed by Brewer and co-workers[2] to arise from strong bonding interactions in the d-orbitals of each metal. In principal, such intermetallic bonding interactions would be expected to cause dramatic changes in the catalytic properties of both metals,[3] and in fact, such changes have been observed in the case of polycrystalline surface of the ordered alloy Ti $Pt_3$.[4] Another point of interest about these alloys is the order- disorder transition behavior, which has not been well-studied, but what data exists suggests these alloys have very high transition temperatures, e.g. 1350 K for Ti $Pt_3$,[5] and >1800 K for Ti $Pt_3$,[1] much higher than for the isomorphic alloys $AuCu_3$ and $SnPt_3$ frequently used as model ordered alloys in surface segregation studies.[6] The object of the present communication is to report the observations by LEED of ordered surface structures for Ti $Pt_3$ single crystals of orientation [111] and [100]. Superlattice patterns arising from the orderly substitution of Ti in the Pt lattice were observed at temperatures up to ca. 1200 K, the highest temperature we could achieve in our apparatus. The observation of these superlattice patterns of temperature independent symmetry is an indication that long-range order occurs in the surface as well as in the bulk and that the surface structure is a regular termination of the bulk structure.

Polycrystalline Ti $Pt_3$ was prepared by arc-melting the pure metals (Alpha Products Puratronic Grade Ti powder, 99.9%, and Englehard Pt "sponge", 99.99%) in an inert gas atmosphere and heat-treating at 1723 K in an homogenizing furnace. The formation of a single phase alloy in the cubic structure ($AuCu_3$ - $Li_2$ type) was confirmed by x-ray diffraction analysis. To obtain a single crystal, the polycrystalline material was zone-refined in

vacuum until recrystallization took place. The formation of a single crystal was confirmed by the Lane back-reflection x-ray diffraction pattern. Single crystal slices of orientation [111] and [100] were spark cut and mechanically polished following procedures used here for Pt crystals. The crystals were gold brazed to a Ta foil which served as a resistive heater. The experiments were performed in a conventional UHV chamber equipped with LEED optics, a single pass CMA with a glancing incidence electron gun, a quadrupole RGA, and argon ion gun. The procedure for producing clean $TiPt_3$ surfaces have been described before.[4] Briefly, it consisted of sequential annealing (923 K), oxygen doxing ($10^{-5}$ Pa, 500-600 K), and argon ion bombardment until annealing produced only AES signals for Ti and Pt.

The bulk structure for cubic $TiPt_3$ ($AuCu_3$ - $L1_2$ type) is shown in Figs. 1 and 2, along with the surface structures expected for simple termination of the bulk structure in planes normal to [111] and [100]. In the $TiPt_3$ structure, Ti atoms substitute for Pt at the corners of the fcc unit cell, producing an ABA sequence of planes normal to [100]. These {100} planes alternately have 50% Ti and 100% Pt composition, and thus there are two inequivalent regular terminations possible, which we shall designate as the (100) and the (200) terminations, respectively. The {111} planes are all equivalent compositionally. The bulk lattice parameter for $TiPt_3$ is 0.3906 nm, a less than 1% contract of the Pt lattice. Thus the fundamental diffraction beams should be located at nearly the same position on the LEED screen as for the pure Pt crystal. The LEED patterns for the clean annealed {111} and {100} surfaces of $TiPt_3$ are shown in Figs. 3 and 4. In terms of the notation developed previously

for overlayer structures, the LEED patterns for $TiPt_3$ {111} and $TiPt_3$ {100} surfaces would be designated p(2x2) and c(2x2), respectively. A c(2x2) LEED pattern was previously observed by Sundaram, et al.[7] for $AuCu_3$ {100}, which has an identical bulk crystal structure to cubic $TiPt_3$. Sundaram, et al. also observed that the half-order superlattice beams vanished at a crystal of 663 ± 4 K, which corresponds (to ± 4 degrees) to the critical temperature of the bulk crystal. In the case of $TiPt_3$ whose bulk transition temperature is much higher,[1] the half-order (superlattice) spots were observable to the highest temperature we could achieve with our crystal mounting method, 1200 K. Thus, the order- disorder transition temperature for both the surface and the bulk of $TiPt_3$ is extremely high.

The superlattice spots for $TiPt_3$ {100} were observed over a wide range of beam energies, from 40 eV to 200 eV, with relative intensities (at Bragg energies) that were not significantly different at the lowest beam energy than at the highest beam energy, so it seems likely that the surface termination is (100) rather than (200). The Ti/Pt Auger peak ratios also suggest this is the case. The peak ratios for {100} were 2.2 and for {111} were 1.8; since the (100) surface has a higher Ti concentration than {111} planes, and (200) has no Ti in the surface, it again seems likely that the surface termination for {100} is (100) rather than (200). A more definitive determination of the structure of the $TiPt_3$ {100} surface is in progress using LEED dynamical intensity analysis.

## ACKNOWLEDGMENT

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## FIGURE CAPTIONS

1. (TOP) fcc unit cell of $TiPt_3$ showing orderly substitution of Ti atoms (●) for Pt at corners; (BOTTOM) Ideal configuration of a (111) plane of $TiPt_3$.

2. (TOP) fcc unit cell of $TiPt_3$ showing ABA alternations of planes normal to [001]; (BOTTOM) Ideal configuration of alternating planes normal to [001].

3. (TOP) LEED pattern for {111} $TiPt_3$ at 105 eV; (BOTTOM) Schematic representation of the LEED pattern in terms of fundamental (o) and (●) superlattice beams.

4. (TOP) LEED pattern for {100} $TiPt_3$ at 105 eV; (BOTTOM) Schematic representation of the LEED pattern in terms of fundamental (o) and (●) superlattice beams.

# $Pt_3Ti$-(111) Plane

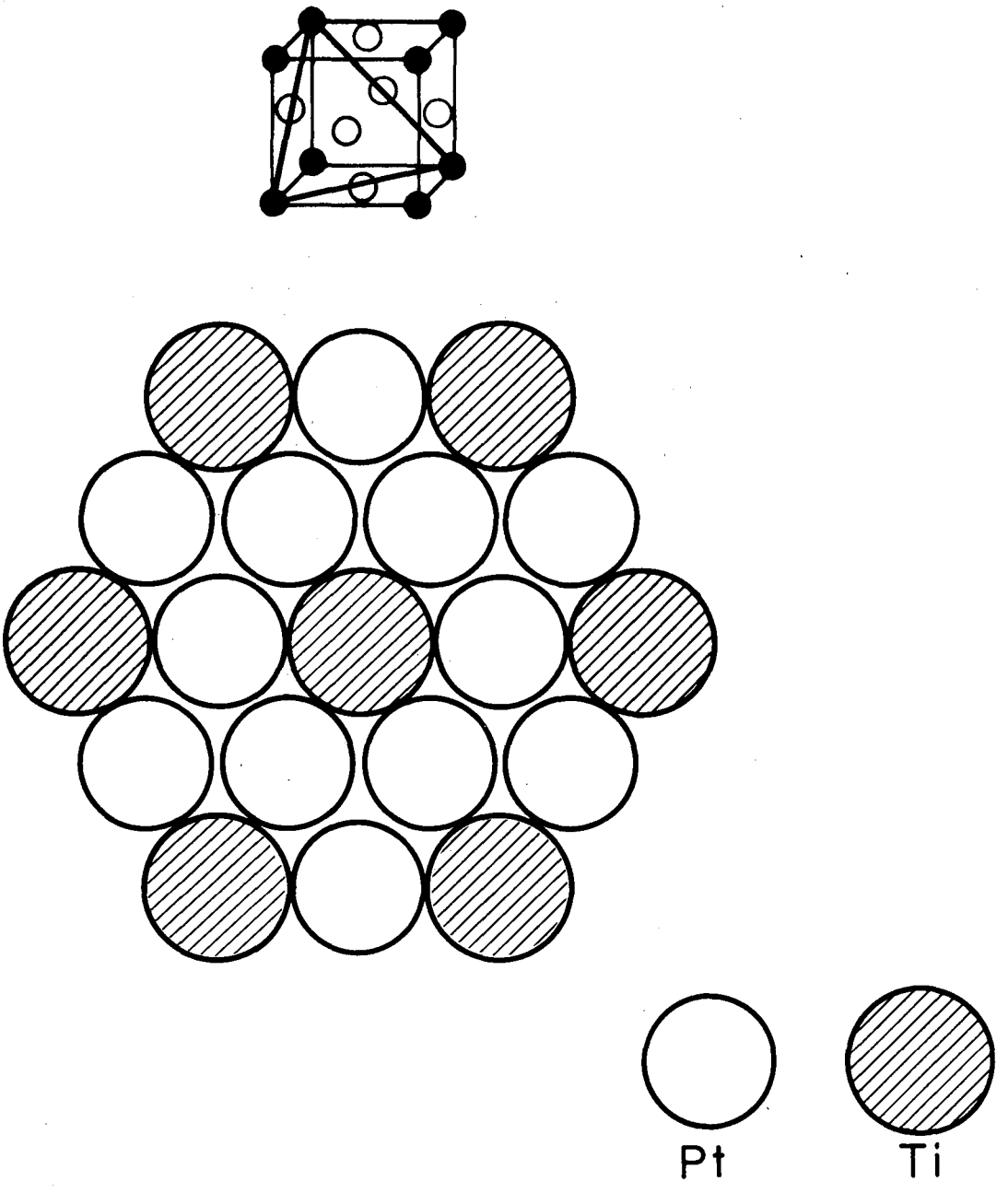


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Fig. 1

# $Pt_3Ti$ - (100) Plane

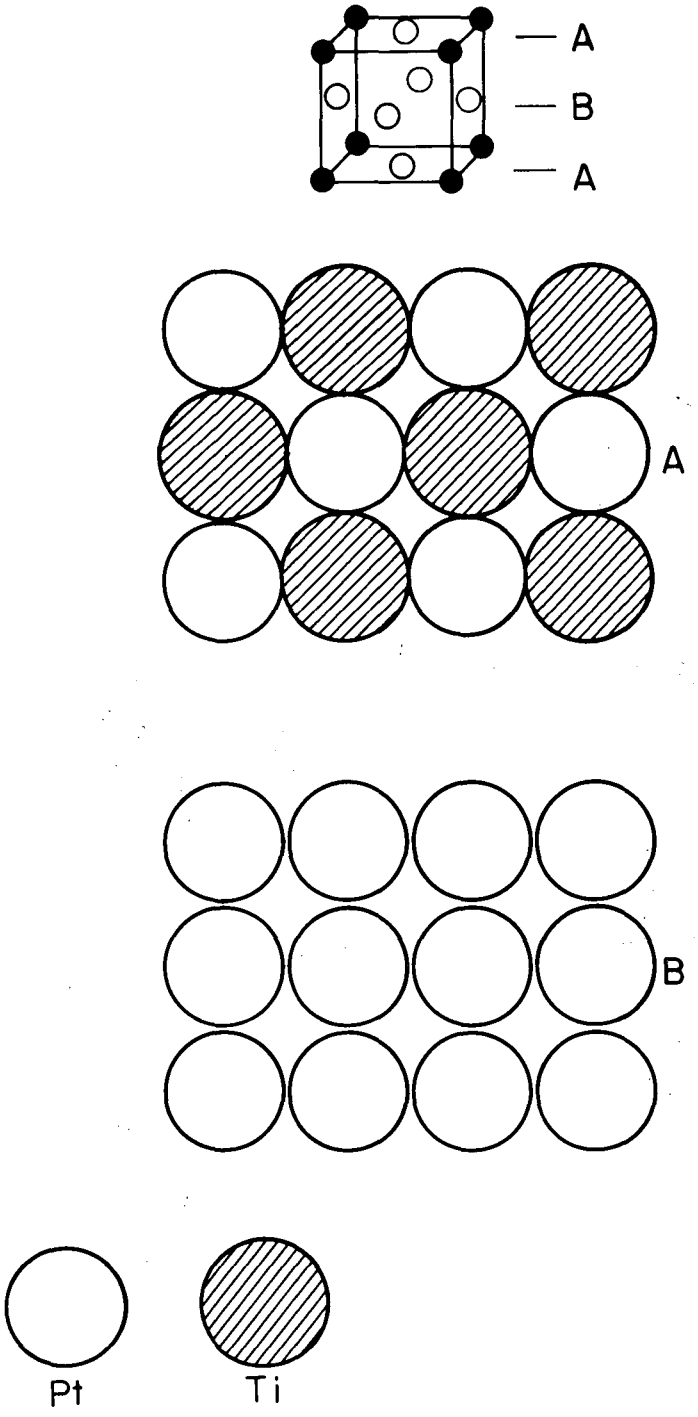


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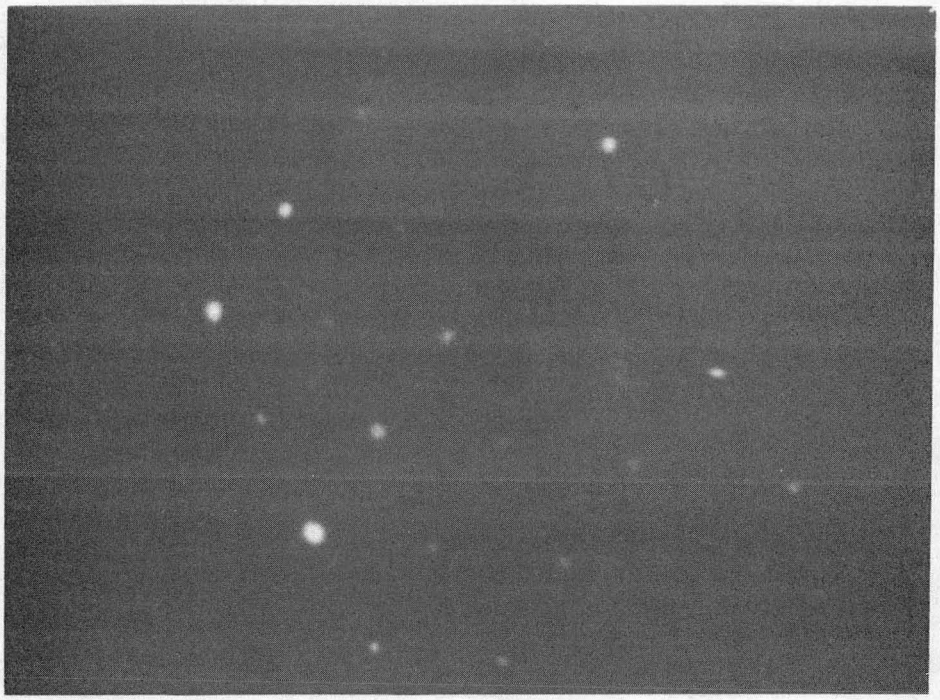
Fig. 2



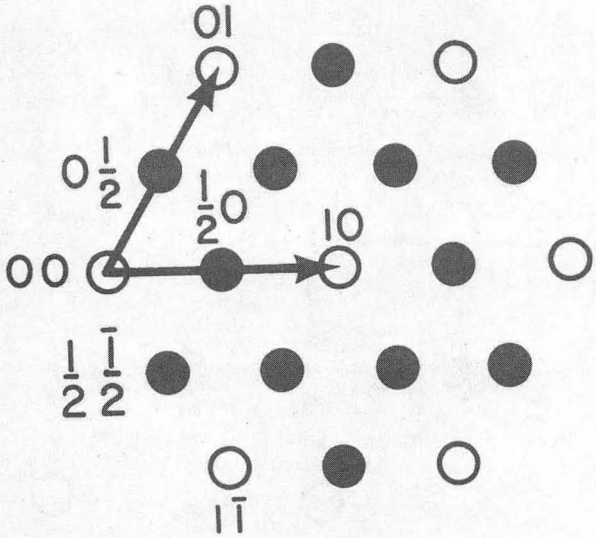



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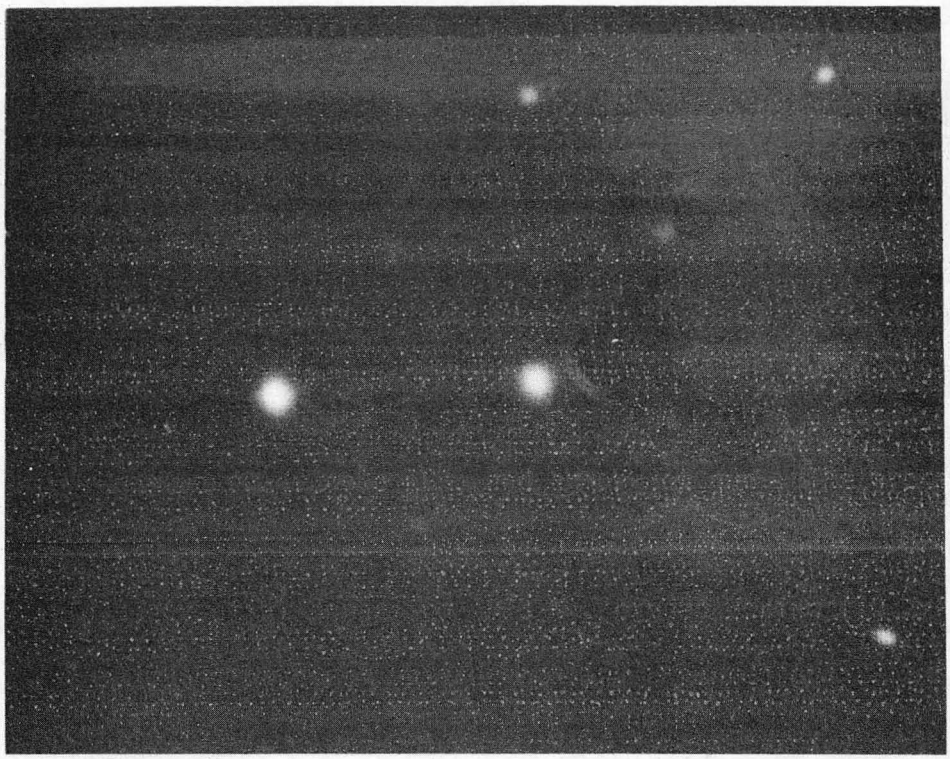
Fig. 3



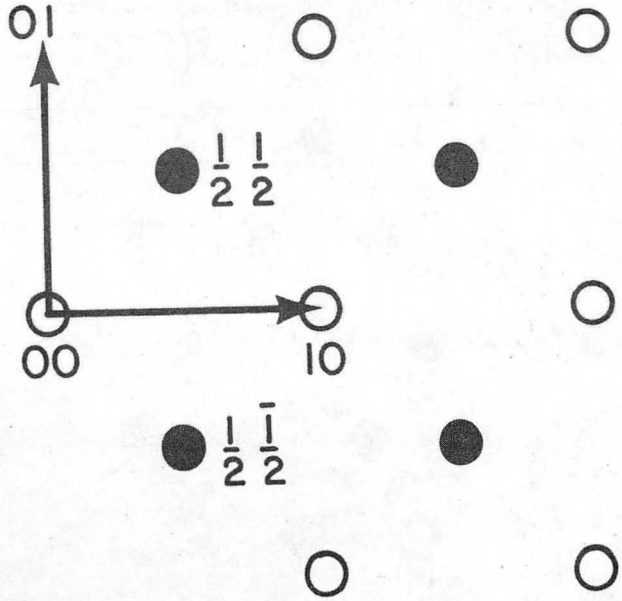



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Fig. 4

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