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Axial ratio anomalies and electronic topological transitions in $Cd_{0.80}Hg_{0.20}$ at high pressures

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ABSTRACT

High-pressure angle-dispersive X-ray diffraction measurements show that $Cd_{0.80}Hg_{0.20}$ alloy remains in the hcp structure up to 50 GPa. We observe subtle anomalies in the pressure variation of the lattice parameters and their ratio, and in normalized stress versus strain. Electronic-structure calculations, as well as experimental and theoretical results for Cd, suggest that these anomalies are related to the occurrence of electronic topological transitions. Our results support Lifshitz's prediction that electronic phase transitions can cause anomalies in structural and elastic properties of materials.

1. Introduction

At ambient conditions, Cd and Zn adopt a hexagonal close-packed (hcp) structure with an unusually large *c/a* ratio of lattice parameters, up to 15% larger than the ideal value of 1.633, leading to highly anisotropic Fermi surfaces. Changes in lattice parameter due to thermal expansion, pressure or alloying can affect the topology of the Fermi surface, with a shift in the Fermi level (E_F) relative to electronic-band extrema (critical points), leading to subtle electronic phase transitions: electronic topological transitions (ETT) causing anomalies in a range of physical properties, as proposed by Lifshitz [1]. The potential richness of effects due to such electronic phase transitions has stimulated theoretical and experimental investigations of both Zn and Cd, which have often been studied in comparison with each other [2–23].

In the case of Zn, past X-ray diffraction studies at high pressure and ambient temperature yield contradictory results regarding possible anomalies in the *c/a* ratio at pressures of 7–9 GPa [2–6]. Initial experimental evidence for an anomaly was eventually disproved, with the observations being explained as caused by nonhydrostaticity of the pressure medium [7]. In parallel, several theoretical studies also predicted the existence of *c/a* anomalies due to ETT in the same pressure range [8–12]. More recently, Steinle-Neumann et al. [13] presented computational results demonstrating the absence of structural effects of ETT in Zn, and showed that the previously calculated *c/a* anomalies were consequences of insufficient *k*-space sampling of the Brillouin zone. However, these results have also been questioned [14–16], and studies by Qiu et al. [15,16] predict *c/a* anomalies and anomalies in elastic moduli over a relatively large pressure range. The most recent computational studies tend to agree that structural anomalies due to ETT in Zn could be difficult to resolve by X-ray diffraction at high pressure and ambient temperature [13–17]. However, Qiu and Marcus [15] discuss the possibility that the anomalies predicted in the pressure dependence of the cell parameters between 7 and 14 GPa are also present, but less pronounced, in Takemura et al.'s [7] high-pressure X-ray diffraction results using He as a pressure-transmitting medium.

In addition to X-ray diffraction measurements, high-pressure Mössbauer spectra of Zn at low temperature show evidence of a discontinuous pressure dependence of the Lamb–Mössbauer factor at 6.6 GPa, which has been interpreted as an effect of ETT [19]. Inelastic neutron scattering shows contradictory evidence for acoustic-phonon softening at the predicted ETT pressure [20,21]. Finally, a high-pressure Raman study of Zn in a He pressure

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medium shows no signs of anomalies in the pressure dependence of the Brillouin zone-center transverse optic phonon (which is related to the shear elastic constant c_{44}), although there is a change in the sign of the pressure dependence of the Raman linewidth at about 11 GPa which could be related to changes in phonon–phonon and electron–phonon interactions induced by an ETT [22]. Besides this work, Garg et al. [23] carried out resistance measurements on Zn to 25 GPa, finding a minimum around 10 GPa, similar to that observed by Lynch and Drickamer [2]. Garg et al. [23] proposed that an ETT, not resolved in Takemura's pressure–volume (P–V) data [7,18], becomes discernible via the equation of state in the universal [24] as well as Holzapfel [25] form. Theoretical calculations of resistance based on the results of first-principles electronic-structure calculations were able to explain the experimental data with an ETT. Kechin [26] found a correlation between the density of states obtained from electronic band-structure calculations and the pressure variation of resistance of Lynch and Drickamer [2], supporting the existence of an ETT around 10 GPa. We thus note that for Zn there is broad consensus among the theoretical groups about the existence of an ETT; however, the experimental results are still inconclusive, possibly because the effects are small and at the limit of detection of the various methods.

The available data for Cd are sparse, and they also present contradictions. X-ray diffraction measurements by Lynch and Drickamer [2] show c/a anomalies at about 10 GPa, but energy-dispersive X-ray diffraction does not show evidence of such anomalies [6]. High-pressure results from Takemura [4] show an anomaly of the c/a ratio using a methanol–ethanol–water mixture as a pressure-transmitting medium.

Based on the recent results for Zn compressed in He, both Takemura [7] and Steinle-Neumann et al. [13] speculate that, in comparison with Zn, Cd may also show no resolvable structural effects due to a high-pressure ETT. However, other experimental and theoretical studies seem to support the idea that the behavior of the two metals could be different [10,16,27]. An energy-dispersive X-ray diffraction study of Cd (compressed in mineral oil) by Pratesi et al. [28] presents evidence of anomalies in the c/a ratio with pressure. In addition, a computational study by Qiu et al. [16] suggests that the structural effects of ETT transitions on Cd should be more visible than in Zn, and extended over a larger pressure range. It is evident that the available data on Cd do not furnish a clear picture of the high-pressure behavior of this hcp metal. Also, the latest experimental and computational results [16,27,28] pose new questions about the possibility of detecting the onset of electronic transitions in Cd by studying the pressure dependence of its elastic properties.

In order to increase the resolution at which we can detect a variation of c/a, we used synchrotron-based angle-dispersive X-ray diffraction (similar to Ref. [4]), achieving more than one order of magnitude higher resolution than energy-dispersive techniques (e.g. Ref. [29]) and making it possible to precisely determine lattice parameters at high pressure (e.g. Ref. [30]). In addition, in order to achieve higher sensitivity to compressibility anomalies, we studied $Cd_{0.80}Hg_{0.20}$, an alloy with the same structure as Cd but with a c/a ratio of 1.9 (1.1% larger than Cd) at ambient conditions. This effectively expands the range of compression across which we can monitor the effects of the electronic structural change. Lastly, we used the experimental lattice parameters as input to first-principles electronic-structure calculations to check for correlations between electronic transitions and anomalies in the lattice parameters.

Our X-ray diffraction measurements show the presence of anomalies in the pressure dependence of the lattice parameters of $Cd_{0.80}Hg_{0.20}$. The combination of these experimental observations with electronic-structure calculations supports the hypothesis that the observed anomalies are connected to electronic topological transition. Our experiments were performed using methanol–ethanol–water as a pressure-transmitting medium, which maintains hydrostatic conditions only up to 10–15 GPa. New high-pressure experiments under more hydrostatic conditions are required to better understand the complex relationships between electronic structure and elastic properties at the onset of isostructural phase transitions in metals: a subject attracting growing interest with respect to other systems, as well (e.g., Os [31–34]).

2. Experimental details

2.1. Sample

We used $Cd_{0.80}Hg_{0.20}$ alloy as an analog of Cd in order to increase the resolution of our observations. At ambient pressure the Cd–Hg system has a peritectic point at 188 °C at 30% Hg content [35]. Experiments [36,37] reveal that hcp is the most stable structure of $Cd_{1-x}Hg_x$ for $x<0.25$, with a c/a value higher than that for pure Cd, consistent with theoretical predictions [38], while at larger Hg contents the stable structures are tetragonal and resemble that of the β-polymorphic modifications of pure Hg [39]. However, high pressure stabilizes the hcp structure at least up to $x=0.35$ [37]. $Cd_{0.80}Hg_{0.20}$ has an initial c/a ratio 1.1% larger than pure Cd, and it has a larger compression range over which the ETT can lead to observable anomalies in the compressibility data. Measurements of positive-muon Knight shift (K_μ) [40] and of the total susceptibility χ_{tot} [41] give experimental evidence suggesting that ETTs involving symmetry point **K** are responsible for Van Hove singularities in the local density of state in Cd alloys as well as in pure Cd.

$Cd_{80}Hg_{20}$ was prepared by melting together appropriate amounts of Cd and Hg in an evacuated quartz tube. The sample was characterized by X-ray diffraction at ambient conditions, confirming that it has the hcp structure with $a=2.972\,(\pm0.001)$ Å and $c=5.671\ (\pm0.001)$ Å; hence $c/a=1.9081\ (\pm0.0007)$ and unit-cell volume $V=43.38\,(\pm0.03)$ Å^3. After synthesis, the sample material was ground to 5–10 μm average grain size, and loaded into an ~120 μm diameter sample chamber obtained by drilling a 250-μm-thick stainless steel foil that had been indented to a final thickness of ~45 μm.

2.2. Methods

The sample was compressed between two diamond anvils with 230-μm culets, using a mixture of methanol–ethanol–water (16:3:1 volume ratio) as a pressure-transmitting medium. A 10 μm-size fragment of Au foil and a few specks of ruby were loaded as pressure calibrants. High-pressure experiments were performed using a short piston-cylinder diamond-anvil cell (DAC) at beamline 12.2.2 of the Advanced Light Source at the Lawrence Berkeley National Laboratory [42]. Powder X-ray diffraction patterns were collected in angle-dispersive geometry using monochromatic radiation ($\lambda=0.48594\pm0.00004$ Å) and a MAR345 image-plate detector at a distance of 295.54 (±0.01) mm from the sample. The X-ray beam size was approximately 100 μm in the horizontal and vertical directions. Two experimental runs were performed, to 9 and 50 GPa. Pressure was determined by the ruby-fluorescence method, using the calibration of Mao et al. [43], and by X-ray diffraction of Au using the 300 K isotherm of Heinz and Jeanloz [44] and Shim et al. [45]. The sample-to-detector distance was calibrated by collecting the diffraction pattern of powdered LaB_6 measured at ambient conditions.