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Electronic topological transitions in cadmium at pressure studied via theoretical and experimental x-ray absorption spectroscopy

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An electronic topological transition (ETT) in cadmium below 1 GPa is investigated in situ with experimental x-ray absorption spectroscopy and projecting calculated core-valence excitons onto the band structure. These projections are a useful application of the Bethe-Salpeter equation approach that considers many-body effects. The method described herein can be used for systems that are otherwise difficult to probe in situ; therefore, it provides a generalizable approach to identifying and understanding ETTs under high pressure. Although pressure-induced ETTs are often probed using indirect structural responses, our own x-ray diffraction and Raman studies suggest a second-order structural transition around 3 GPa but are largely insensitive to **or inconclusive for** the previously studied ETT in this region.

INTRODUCTION

The ground-state allotrope of elemental cadmium (Cd) remains in the hexagonal close-packed (hcp) structural motif under high-pressure compression up to 174 GPa [1]. Based on geometric and energetic considerations, the ideal c/a ratio for hcp is $\sqrt{8/3} \approx 1.633$; however, Cd has an unusually high ambient c/a ratio of about 1.86 [1]. Only zinc (Zn) and mercury (Hg) have comparably high c/a ratios [2]. Non-ideal c/a ratios often indicate some non-trivial electronic structure, and as such, materials with anomalous c/a ratios, like Cd, are excellent test cases for new probes of electronic structure. A discontinuity in the c/a ratio has historically been used as preliminary evidence of electronic structural changes and cause to further investigate such electronic properties via the topology of the Fermi surface [3–7].

The topology of the Fermi surface indicates the relative position in reciprocal space of the electrons at the Fermi energy, and can be used to understand a variety of other properties of a material in the metallic state [8]. With increasing pressures and no structural phase transitions, the Fermi surface will change continuously [9]. The presence of a non-continuous deformation of the Fermi surface indicates a non-trivial change in the electronic structure, and is known as an electronic topological transition (ETT) or Lifshitz transition [10]. While such phase transitions can be sampled by theoretical methods, characterizing these methods experimentally, particularly under high-pressure conditions, remains challenging. A variety of the probes used to characterize phase

transitions at high pressure, including diffraction, vibrational spectroscopy, or using other characteristic thermodynamic properties, are either largely insensitive to or do not provide an atomic-level understanding of the underlying ETT process [11]. When available, angle-resolved photoemission spectroscopy (ARPES) is ideal for understanding electronic behavior [12]; unfortunately, ARPES remains inapplicable for high-pressure materials.

Several previous works have investigated the possible relationship between c/a anomalies and ETTs in Cd at varying pressures [6, 13–15]; however, c/a discontinuities can occur for reasons other than ETTs [16, 17]. Although the electronic structure of Cd has been studied at low pressure [18, 19], these works do not provide direct quantifiable evidence of an ETT in Cd. Vibrational Raman spectroscopy is often used to investigate ETTs [10, 20–22]; however, there are disagreements even with the same system as to whether a mode should harden, soften, or just change linewidth as the system experiences an ETT. Additionally, some systems may not display optical Raman modes due to their crystal structures [9]. The Fermi surface of Cd was directly measured via the de Haas-van Alphen effect under ambient conditions [23] and attempts were made for measurements up to 2 GPa [24]; however, the pressure calibration and hydrostaticity of the pressure transmitting media (PTM) used in the latter work obfuscate the certainty of an ETT. Resistance measurements [25], magnetoresistance measurements [26], and structural measurements using x-ray diffraction (XRD) [1, 7, 27] suffer from similar hydrostaticity concerns and only infer the presence of an ETT.

Here, we observe a connection between the electronic behavior as observed spectroscopically and the projection of the calculated core-valence exciton density onto the electronic band structure, suggesting and describing an ETT in Cd below 1 GPa. This work further validates the technique of using x-ray absorption spectroscopy (XAS) to explore ETTs at high pressure [28] and, when paired with the computational results, gives new insights into the mechanism of ETTs under pressure. Structural data as determined by XRD is shown and compared with the spectroscopic data to separate electronic and structural effects. No XAS discontinuities are observed after the ETT, indicating that in the range studied, there are no further ETTs.

METHODS

The absorption length of Cd K-edge was calculated in *Hephaestus* to be 23 μm . Cd (99.999%, Sigma-Aldrich) samples were cut from wire in order to match the calculated absorption length, as commercially available Cd powder samples with the appropriate mesh size could not be sourced at the time of this work. All samples were handled in an inert argon (Ar) environment prior to and during loading. Samples were at no point exposed to ambient air conditions, and a lack of reaction with air was verified with Raman for surface effects and XRD for bulk effects. No oxidation effects were seen by XAS, Raman, or XRD. Ruby fluorescence was used as the primary pressure marker [29], with gold (Au) also loaded for use as an XRD pressure marker [30]. Ruby and Au had average dimensions of $15 \times 15 \mu\text{m}$ (length $\times$ width), and were arranged to be out of the absorption path of Cd. Using an in-house-designed diamond anvil cell (DAC), samples were gas-loaded with helium (He) in a pre-machined beryllium (Be) gasket, pre-indented to a thickness of about 23 μm . Samples were monitored via x-ray imaging to check for bridging between the diamonds and found to not be bridging (Fig. S5 [31]).

XRD and XAS experiments were carried out at 16-BMD, Sector 16 of the Advanced Photon Source [32]. XRD measurements ($\lambda = 0.4132 \text{ \AA}$) used axial geometry, while XAS measurements were taken in radial geometry through the x-ray transparent Be gasket on the Cd K-edge (26.7112 keV). The incoming x-ray beam size was around 4 μm at full width at half maximum, and the full width at about 1% of maximum is around 20 μm (Fig. S1 [31]). Due to focusing methods [32], there are no practical effects of a higher harmonic on the current measurement (see Supplemental Material (SM) [31] for further discussion).

Since the sample itself is pure elemental Cd, the lowest pressure sample (loaded inertly at ambient pressure in an Ar environment) is collected as the internally consistent reference for energy calibration and referred to as

the energy standard loadings within this work. Energy scans were made repeatedly to improve counting statistics. The scans were reproducible within 0.1–0.5 eV deviation depending on the number of repetitions applied for each measurement. While the source of deviation is, strictly speaking, unknown, it is suspected to be due to heat accumulation on the monochromator motor and a slight offset in the calibration parameter due to a thermal expansion of mechanical parts. The energy calibration scheme for 16-BMD, Sector 16 of the Advanced Photon Source can be found in the work of Park *et al.* [32].

Raw XAS data, primarily x-ray absorption near edge structure (XANES), were reduced using the *Athena* software. Extended x-ray absorption fine structure (EXAFS) data were fit using the *Artemis* software package, and further analysis details of EXAFS data can be found in the SM [31]. Ruby spectra were fit using *Fityk* for the central wavelength position which was used to calculate pressure [29]. XRD data were processed in *Dioplas* [33] and *GSASII* [34]. A La Bail refinement was carried out on each data point to extract lattice parameters. Au was fitted to the equation of state of Takemura and Dewaele [30] to compare to Ruby fluorescence measurements and was found to be in good agreement.

K-edge XAS calculations on Cd were performed with density functional theory (DFT) using the Bethe-Salpeter equation (BSE) as implemented in the *OCEAN* code [35–37] as a function of pressure with optimized structures every 0.5 GPa between 0 and 5 GPa. The Perdew-Burke-Ernzerhof (PBE) functional as implemented in the *Quantum Espresso* package was used with an energy cut-off of 2450 eV (180 Ry) for the DFT portion of the calculation [38–40]. The self-consistent field (SCF) calculation was done on a $10 \times 10 \times 10$ k-grid while the screening calculation was done on a $2 \times 2 \times 2$ k-grid. The pseudopotentials have a valency of $4s^2 4p^6 4d^{10} 5s^2$ [41]. The maximum energy for bands in the final state wave function was set to 150 eV above the edge. Lorentzian broadening was set to 7.32 eV to better match experimental data [42]. This formalism allows for using the experimentally determined crystallographic orientation of the sample obtained from XRD to be applied to XAS calculations. The same computational input parameters for the K-edge XAS calculations are used with the generalized minimal residual (GMRES) method [43] (rather than the Haydock recursion method) to solve the BSE and calculate the real-space excitonic wavefunction.

Ambient temperature Raman measurements as a function of pressure are also presented. Steel and rhenium (Re) gaskets are used with a lithium fluoride (LiF) PTM. $\text{Sm:SrB}_4\text{O}_7$ is used as a pressure marker for its temperature independence [44, 45]. A 532 nm excitation line is used with matching Optigrate filters. Further DAC specification followed the methods of Hinton *et al.* [46].

RESULTS AND DISCUSSION

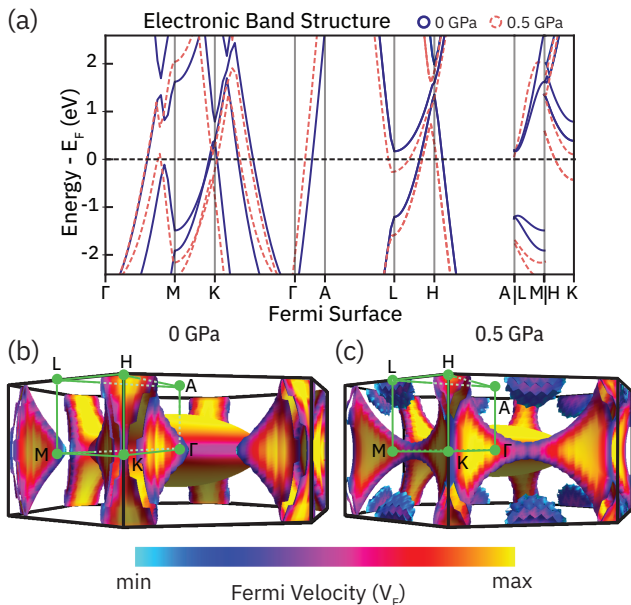


FIG. 1. Computational evidence for ETT between 0 and 1 GPa. (a): Electronic band structure of Cd for 0 GPa (solid blue) and 0.5 GPa (dashed orange). (b), (c): The Fermi surface of Cd in the first Brillouin zone, with high symmetry points marked in green (b): 0 GPa and (c): 0.5 GPa. Note the qualitative change in the Fermi surface between 0 and 0.5 GPa. Plotted with Fermisurfer software [47].

Previous calculations suggested an ETT in Cd at varying pressures depending on the details of the method [6, 13, 14, 48]. In our calculations probing for low pressure ETTs, distinct changes are observed in the band structure and in the topology of the Fermi surface between 0 and 0.5 GPa, particularly along the Γ -M, H-K, and H-L high symmetry paths in the first Brillouin zone. Between Γ and M, the peak of one band initially below the Fermi energy rises above it as the pressure is increased from 0 to 0.5 GPa (Fig. 1a). Across the same symmetry M-K path, a connection is formed in the 6-fold symmetric corner features of the Fermi surface (Figs. 1b and 1c). Along H-K, a surface that is connected at 0 GPa becomes disconnected at 0.5 GPa (Figs. 1b and 1c), and we observe a band crossing the Fermi energy along this same symmetry path (Fig. 1a). Along H-L, a new surface appears in the Fermi surface (Figs. 1b and 1c) and this corresponds to another band rising above the Fermi energy in Fig. 1a.

The changes described lead to the formation of a new hole in the manifold, which represents a discontinuous change in the topology between 0 and 0.5 GPa. A new feature in the Fermi surface is also found with increasing pressure that occurs between the A and L points. These effects continue to increase in magnitude with increasing pressure and the manifold becomes increasingly

connected throughout the Brillouin zone parallel to M-K as the pressure is increased from 0.5 to 5 GPa. Despite these electronic changes at the Fermi energy, the total and partial densities of states show minimal changes as the ETT is crossed (Figs. S19 and S20 [31]). These computational observations suggest an ETT between 0 and 1 GPa, and no other ETT is predicted to occur up to 10 GPa.

To experimentally explore the predicted ETT, we first turn to XRD. Diffraction is widely used for observing phase transitions; however, it is largely insensitive to ETTs that do not correspond with significant first or second-order atomic structure changes. Here, the high-pressure diffraction is performed using a He PTM, the highest degree of hydrostaticity possible to compare to previous studies. Strong preferred orientation leading to poor powder averaging is observed across multiple samples (Figs. S6-8 [31]). Structural exploration revealed that previously observed anomalies in the c/a ratio with volume at about 12 GPa (or around $V/V_0=0.85$) [1, 7, 27] are not observed when a hydrostatic PTM, He, is used (Fig. 2a). No further structural discontinuities are observed in the c/a ratio experimental data. Although calculated volumes predict discontinuities in c/a between 0-1 and 2-3 GPa, no further structural discontinuities are observed in the c/a ratio experimental data.

A change in slope in the pressure derivative of the bulk modulus is observed in the F - f plot (Fig. 2b) corresponding to approximately 3 GPa. The change in slope suggests a second-order phase transition. No discontinuities to the Fermi surface or electronic band structure are observed in correlation with this second-order structural transition. While a change in slope cannot be ruled out between 0-1 GPa in the F - f plot, the lack of experimental data in this range and the fact that F - f plots cannot use points at 0 GPa prevent a definitive conclusion; therefore, we cannot assign the lowest data point alone as a slope change, since this being an outlier is a possibility. Our limited EXAFS data also shows no structural anomaly, supporting no structural phase transition below 1 GPa (Fig. S12 [31]).

The room temperature responses of the Raman active E_{2g} phonon mode of Cd frequency, linewidth, and intensity are shown in Figs. S26-35 and Table SIII [31] for pressures from 0-10 GPa. Data points were collected from compression, decompression, as well as for samples that were previously heated to above the melting temperature. The calculated zone-centered Raman frequencies, electron-phonon couplings, and phonon linewidths across the predicted 0.5 GPa ETT are given in Table SIV [31]. Further details and values of experimental frequency versus pressure and zone center phonon calculations are available in the SM [31]. Our experimental Raman data do not show clear discontinuities about the ETTs in the aggregate for frequency, linewidth, or intensity. Additionally, our calculated values do not indicate

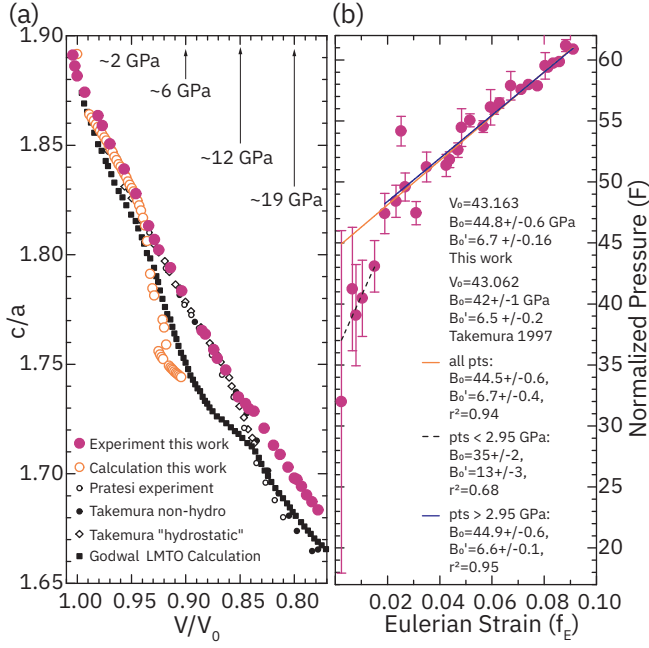


FIG. 2. Structural information for Cd obtained via XRD from 0 to 25 GPa. (a): c/a vs V/V_0 plot with experimental (closed pink circles) and computational data (open orange circles) from this work plotted over literature data of Pratesi *et al.* [27] (black open circles), Takemura [1] (black closed circles and black open diamonds), and Godwal *et al.* [13] (black closed squares). Errors for the experimental points are less than the diameter of the points shown. (b): Normalized pressure (F) vs Eulerian strain (f_E) plot from XRD where $F = P[3f_E(1 + 2f_E)^{5/2}]^{-1}$ and $f_E = (1/2)[(V_0/V)^{2/3} - 1]$. Linear fits of the data are shown for above and below 2.95 GPa, and for the full data set.

discontinuities in the frequency, linewidth, or electron-phonon-couplings. Taken together, this indicates that neither structural probe, diffraction nor vibrational Raman, were effective probes for identifying this ETT in Cd. Although it is still possible (and common) to investigate ETTs by both structural methods, our dataset for Cd makes a good case study for systems where these methods will not work based on the fundamental properties of the material. For example, it is possible for a material to have no Raman modes allowed, or experience an isostructural electronic change; in this case neither probe would be able to indicate a change.

Although these structural probes did not provide conclusive evidence correlating to the ETT observed in calculations, XAS can also be used to investigate the presence of an ETT as it relates directly to the electronic behavior. XAS can be broken into two regions: the XANES region and EXAFS region. EXAFS uses high energy scattering states to probe local atomic structure (or short-range order) through scattering. The near edge is an indicator of electronic behavior—XAS at the K-edge excites the 1s core electron to states above the Fermi en-

ergy. By projection of the calculated core-valence excitonic wavefunction onto the electron band structure, we can infer the p-orbital character of the band. Since the XAS process involves forcing a core electron into an unoccupied state above the Fermi surface, examining the XANES regions provides information pertaining to the electronic behaviors of the predicted ETT.

Figure 3 gives the experimental and calculated XANES from 0 to 5 GPa, with experiment represented in dashed lines vertically offset above the calculations in solid lines. The spectra at 0 GPa, obtained from the energy standard DAC, are black and the higher pressures are in color as indicated by legend. The experimental XAS show a discontinuous change between 0 and 0.8 GPa indicated by the shift between 0 GPa and the higher pressure lines 0.8–4.5 GPa. Above 0.8 GPa, the changes are more gradual. The spectra shown in Fig. 3 are from one Cd sample (called Sample 2 in SM). We observe a similar shift in another sample (Sample 3 in SM). Sample 3 had been pressure-cycled and thus some hysteresis in the energy shift is observed. The behavior of Sample 3 suggests that the ETT observed in Sample 2 is reproducible. Further data and details are available in the SM [31].

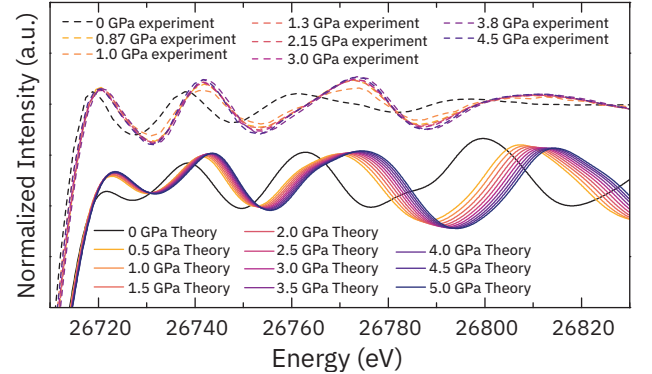


FIG. 3. Calculated and experimental XANES spectra collected for Cd between 0 and 5 GPa (dashed lines show experimental observations). The 0 GPa point is from the energy standard, and the subsequent points are from Sample 2. The large shift between the black lines at 0 GPa and the color lines at pressure is consistent with an electronic change occurring. Solid lines are calculated XANES spectra using OCEAN; the same energetic shift and scaling factor are applied to each calculated spectra. Points have 0.5 GPa resolution. The same large peaks at approximately 26,720, 26,740, and 26,775 eV, as well as the blue shift as a function of pressure are seen in both experiment and theory. See text and SM [31] for normalization and alignment details.

Theoretically calculated spectra are presented from 0.5–5.0 GPa in 0.5 GPa resolution. In addition to the energy offset applied to the calculated spectra, a scaling factor of about 16% is applied to the energy to account for the well-known DFT error of underestimating the band gap [49]. The same background correction used in experiment is applied to the calculated spectra to account

for the gradually dropping oscillator strength inherent to the calculation. Both of the above changes are for ease of visual comparison. See SM [31] for a comparison between experimental and calculated spectra that have not had scaling or background subtractions.

Our simulations show a large discontinuous change between 0 and 0.5 GPa, followed by a gradual change above 0.5 GPa. Theoretical calculations here consider both the orientation of the sample, and the polarization of incident light orientation. Since Cd is hexagonal, the contributions from the a and b planes will be equal to each other while the c plane is different. This can be accounted for in the crystal orientation tensor, and is most visible in the third XANES peak. The third peak will be asymmetric if the contribution from only one plane is considered, and the asymmetry shifts depending on which plane is considered. The asymmetry observed in the third peak is more obvious in experiment than in theory. Figure 3 shows that the third XANES peak of the experimental spectra is asymmetrical to the right, while the third XANES peak of the theoretically calculated spectra seems to show more of a doublet. This difference is likely due to the sample's intense preferred orientation, which is common for a sample sourced from wire. XRD patterns demonstrating different samples' preferred orientation are in the SM [31]. Both experiment and theory see the peak at $\sim 26,740$ eV move higher in energy with increasing pressure, even when considering preferred orientation, suggesting the electronic structure is well captured by the theory.

To explore the electronic nature of this change in the Cd XANES data further, the x-ray core-valence exciton distributions are projected onto the electronic band structure. To accomplish this, the core-valence exciton wavefunction at energy ω is defined using the two-particle Green's function and photon operator $\hat{T}$ acting on the ground state $|\Phi_0\rangle$:

$$|\Phi(\omega)\rangle = \frac{1}{\omega - H_{BSE} + i\eta} \hat{T} |\Phi_0\rangle. \quad (1)$$

Here, the two-particle Green's function is defined as $G_2(\omega) = (\omega - H_{BSE} + i\eta)^{-1}$ with the BSE Hamiltonian H_{BSE} and broadening parameter η , and the GMRES method is used to solve

$$(\omega - H_{BSE} + i\eta) |\Phi(\omega)\rangle = \hat{T} |\Phi_0\rangle \quad (2)$$

for $|\Phi(\omega)\rangle$. With $|\Phi(\omega)\rangle$, it is possible to know which bands contribute to a peak in the spectrum, as the exciton wavefunctions having a hole at core level α and electron in the band index n with momentum $\mathbf{k}$ are expressed as coefficients $C_{n\mathbf{k}\alpha}$ and Bloch states $|n\mathbf{k}\rangle = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$ [35]:

$$|\Phi(\omega)\rangle = \sum_{n\mathbf{k}\alpha} C_{n\mathbf{k}\alpha} e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}). \quad (3)$$

The core-valence exciton wavefunctions are then projected onto the bands in reciprocal space to understand what transitions the XANES spectrum represents or the imaginary part of the dielectric function $\epsilon_2(\omega)$, in terms of each band n and k-point [50]:

$$\begin{aligned} \epsilon_2(\omega) &= \langle \Phi(\omega) | \Phi(\omega) \rangle = \left\langle \Phi(\omega) \left| \left(\sum_{n\mathbf{k}} |n\mathbf{k}\rangle \langle n\mathbf{k}| \right) \right| \Phi(\omega) \right\rangle \\ &= \sum_{n\mathbf{k}} |\langle n\mathbf{k} | \Phi(\omega) \rangle|^2. \end{aligned} \quad (4)$$

This above projection is interpolated along high-symmetry lines since the k-points for the GMRES calculation are on a Monkhorst-Pack grid.

This approach has been previously used to understand the physical origins of extreme ultraviolet photoexcited-state spectra [51, 52]. Here, the same approach is used for the first time to bridge the electronic changes in reciprocal space (Fig. 1) with the spectral changes in XANES (Fig. 3). As the technique allows for a detailed understanding of the cause of measured x-ray absorption spectra, it can be used to show the underlying causes of experimental changes, i.e. an ETT.

Figure 4 shows the core-valence exciton density projected onto the Cd band structure for the first and second XAS peaks around 26,720 and 26,740 eV, respectively, at three different pressures (0, 0.5, and 2.0 GPa). The size and color of the dots in the figure refer to the amplitude of the core-valence transition at that point in reciprocal space. For the first peak, only slight differences in the transition amplitudes are calculated between 0 and 0.5 GPa. The change in transition amplitudes is primarily along the Γ -A, Γ -M, and Γ -K paths with smaller changes in the A-L and L-M pathways. Transition amplitudes increase as the Γ point is approached in each case and new transitions become possible at energies closer to the Fermi level. Theoretically, this leads to an energy shift and shape change in the XAS spectra after the ETT.

For the second peak in Fig. 3 at $\sim 26,740$ eV, a more prominent and discontinuous spectral shift in the experimental and calculated XANES spectra is observed. In Fig. 4, excitons projected onto the band structure at 0.5 and 2.0 GPa show changes throughout reciprocal space when compared to 0 GPa. Specifically, transitions around 30 eV above the Fermi energy between the Γ and A points are more pronounced at 0 GPa than at higher pressures. The most intense transition is located near the K point at 0.5 and 2.0 GPa whereas it is located around the Γ point at 0 GPa. These changes should lead to a more blue-shifted peak with a longer tail, consistent with Fig. 3 and are strongly indicative of a phase transition.

Figure 4 in combination with the experiment therefore confirms that the changes in the band structure from the ETT, as calculated in Fig. 1, are probed by XANES

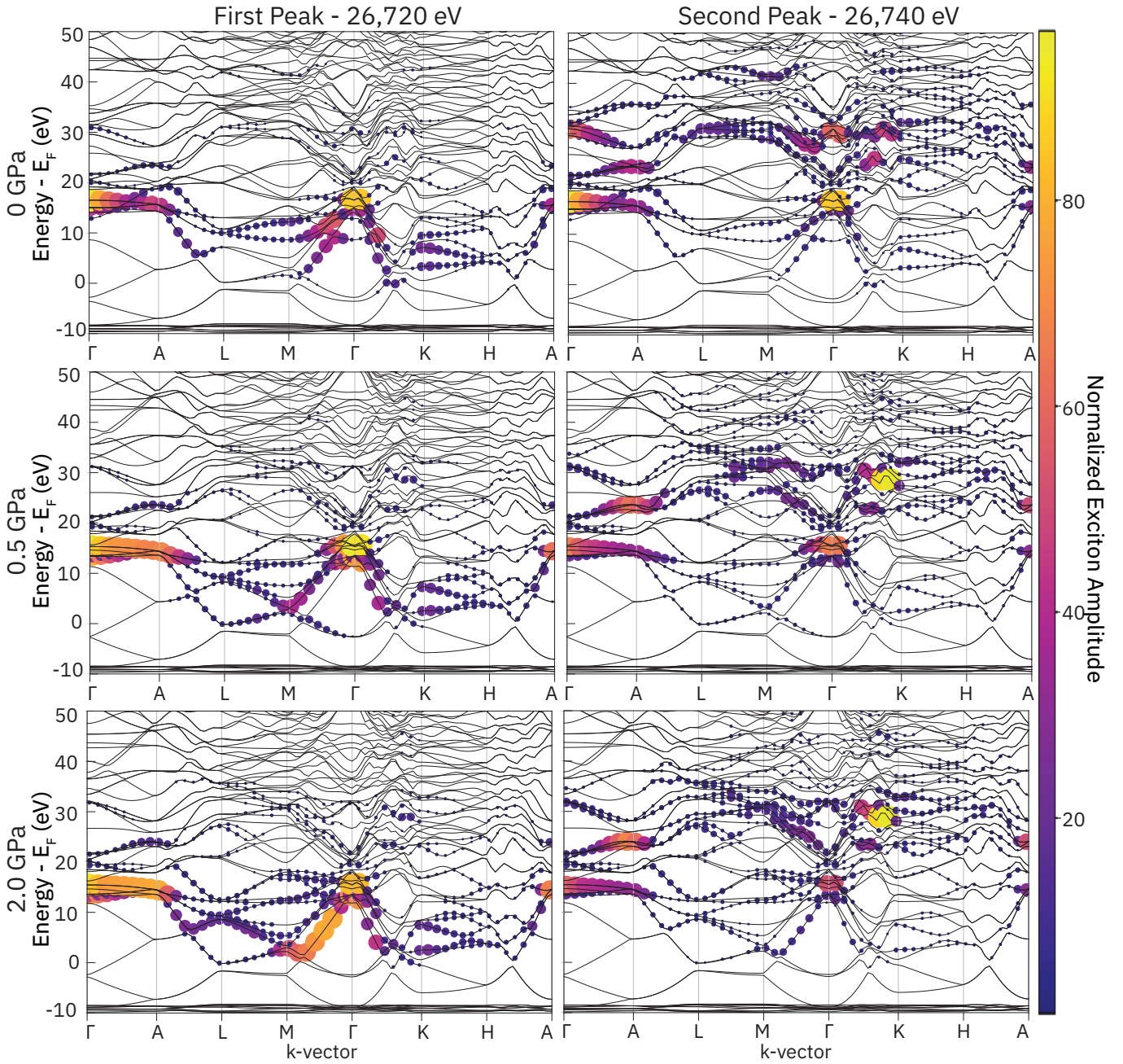


FIG. 4. Core-valence exciton projection on band structure for first and second peaks ($\sim 26,720$ and $26,740$ eV) at 0, 0.5, and 2 GPa. The sizes and colors of the circles indicate the strength of the projected amplitude, with indigo indicating a relatively small transition and yellow indicating a large projection. The first peak projections show changes in transition amplitudes between 0 and 0.5 GPa along the Γ -A, Γ -M, and Γ -K paths with smaller changes in the A-L and L-M pathways. The second peak projections show changes throughout reciprocal space in the same pressure range. Notably, the most intense transition is located around the Γ point at 0 GPa, and then becomes the K point at 0.5 and 2.0 GPa. These amplitude changes, along with the others described in the text, provide strong evidence for the ETT in Cd.

spectral changes. For Cd, the projected transition amplitudes also suggest a more p-orbital character after the ETT, given the dipole selection rules in XAS.

CONCLUSIONS

While diffraction remains a powerful tool for the study of most phase transitions, we show that for Cd, it is largely insensitive to ETTs. In order to explore this, experimental spectroscopic measurements of Cd XAS be-

tween 0 and 5 GPa were taken. The case study on Cd shown here, including experimental and computational XANES data combined with band structure projections, provides and establishes a protocol for future works. Other disputed systems [4, 5, 16, 17] can be revisited or new systems can be explored since this technique is available at pressures up to hundreds of GPa and for a wide variety of materials [53]. Based on all of our experimental and computational results, our data indicates the presence of an ETT in elemental Cd below 1 GPa. A second transition at a higher pressure is also observed, that is solely structural and second order in nature. We note that this technique is quite general and can be applied to a wide variety of experimental systems. Indeed, by taking advantage of the possibility of performing x-ray Raman spectroscopy in the cases where XAS will not work, almost all materials should be accessible [54]. This has wide implications in the field of static high pressure research.

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REFERENCES

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 - [1] K. Takemura, Structural study of Zn and Cd to ultra-high pressures, *Phys. Rev. B: Condens. Matter* **56**, 5170 (1997).
 - [2] K. Takemura, The Zinc Story under High Pressure, *Journal of Minerals and Materials Characterization and Engineering* **07**, 354 (2019).
 - [3] D. Novikov, A. Freeman, N. Christensen, and A. Svane, LDA simulations of pressure-induced anomalies in an electric-field gradients for Zn and Cd, *Phys. Rev. B: Condens. Matter* **56**, 7206 (1997).
 - [4] K. Takemura, Zn under Pressure: A Singularity in the hcp Structure at $c/a = \sqrt{3}$, *PPhys. Rev. Lett.* **74**, 252 (1995).
 - [5] K. Takemura, Absence of the c/a anomaly in Zn under high pressure with a helium-pressure medium, *Phys. Rev. B: Condens. Matter* **60**, 6171 (1999).
 - [6] B. K. Godwal, S. Meenakshi, R. S. Rao, and V. Vijayakumar, c/a anomalies, thermoelectric power and electronic topological transitions in Cd, *J. Phys. Chem. Solids* **59**, 747 (1998).
 - [7] B. K. Godwal, S. V. Raju, Z. Geballe, and R. Jeanloz, Electronic phase transitions in cadmium at high pressures, *J. Phys.: Conf. Series* **377**, 012033 (2012).
 - [8] S. B. Dugdale, Life on the edge: a beginner's guide to the Fermi surface, *Phys. Scr.* **91**, 053009 (2016).
 - [9] Y. Zhang, C. Yang, A. Alatas, A. H. Said, N. P. Salke, J. Hong, and J.-F. Lin, Pressure effect on Kohn anomaly and electronic topological transition in single-crystal tantalum, *Phys. Rev. B: Condens. Matter* **100**, 075145 (2019).
 - [10] I. M. Lifshitz, Anomalies of electron characteristics of a metal in the high pressure region, *Soviet Physics JETP* **11**, 1130 (1960).
 - [11] S. Beaulieu, S. Dong, N. Tancogne-Dejean, M. Dendzik, T. Pincelli, J. Maklar, R. P. Xian, M. A. Sentef, M. Wolf, A. Rubio, L. Rettig, and R. Ernstorfer, Ultrafast dynamical Lifshitz transition, *Sci. Adv.* **7**, eabd9275 (2021).
 - [12] Y. Zhang, C. Wang, L. Yu, G. Liu, A. Liang, J. Huang, S. Nie, X. Sun, Y. Zhang, B. Shen, J. Liu, H. Weng, L. Zhao, G. Chen, X. Jia, C. Hu, Y. Ding, W. Zhao, Q. Gao, C. Li, S. He, L. Zhao, F. Zhang, S. Zhang, F. Yang, Z. Wang, Q. Peng, X. Dai, Z. Fang, Z. Xu, C. Chen, and X. J. Zhou, Electronic evidence of temperature-induced Lifshitz transition and topological nature in ZrTe₅, *Nat. Commun.* **8**, 15512 (2017).
 - [13] B. Godwal, S. Meenakshi, and R. Rao, Anomalies and electronic topological transitions in Cd, *Phys. Rev. B: Condens. Matter* **56**, 14871 (1997).
 - [14] D. L. Novikov, M. I. Katsnelson, A. V. Trefilov, A. J. Freeman, N. E. Christensen, A. Svane, and C. O. Rodriguez, Anisotropy of thermal expansion and electronic topological transitions in Zn and Cd under pressure, *Phys. Rev. B: Condens. Matter* **59**, 4557 (1999).

- [15] S. L. Qiu, F. Apostol, and P. M. Marcus, Structural anomalies in hcp metals under pressure: Zn and Cd, *J. Phys. Cond. Matter* **16**, 6405 (2004).
- [16] L. Dubrovinsky, N. Dubrovinskaia, E. Bykova, M. Bykov, V. Prakapenka, C. Prescher, K. Glazyrin, H.-P. Liermann, M. Hanfland, M. Ekholm, Q. Feng, L. V. Pourovskii, M. I. Katsnelson, J. M. Wills, and I. A. Abrikosov, The most incompressible metal osmium at static pressures above 750 gigapascals, *Nature* **525**, 226 (2015).
- [17] G. A. Woolman and G. J. Ackland, Detectability of core-level crossing and electronic topological transformations: The case of osmium, *Phys. Rev. B: Condens. Matter* **106**, L081102 (2022).
- [18] P. Blaha, K. Schwarz, and P. H. Dederichs, Electronic structure of hcp metals, *Phys. Rev. B: Condens. Matter* **38**, 9368 (1988).
- [19] S. Daniuk, T. Jarlborg, G. Kontrym-Sznajd, J. Majsonerowski, and H. Stachowiak, Electronic structure of Mg, Zn and Cd, *J. Phys.: Condens. Matter* **1**, 8397 (1989).
- [20] G. K. Pradhan, A. Bera, P. Kumar, D. Muthu, and A. Sood, Raman signatures of pressure induced electronic topological and structural transitions in Bi₂Te₃, *Solid State Commun.* **152**, 284 (2012).
- [21] A. Bera, K. Pal, D. V. S. Muthu, U. V. Waghmare, and A. K. Sood, Pressure-induced phase transition in Bi₂Se₃ at 3 GPa: electronic topological transition or not?, *J. Phys.: Condens. Matter* **28**, 105401 (2016).
- [22] A. Zhang, X. Ma, C. Liu, R. Lou, Y. Wang, Q. Yu, Y. Wang, T.-l. Xia, S. Wang, L. Zhang, X. Wang, C. Chen, and Q. Zhang, Topological phase transition between distinct Weyl semimetal states in MoTe₂, *Phys. Rev. B: Condens. Matter* **100**, 201107 (2019).
- [23] D. C. Tsui and R. W. Stark, de Haas-van Alphen Effect, Magnetic Breakdown, and the Fermi Surface of Cadmium, *Phys. Rev. Lett.* **16**, 19 (1966).
- [24] S. L. Bud'ko, A. N. Voronovskii, A. G. Gapotchenko, and E. S. Itskevich, The Fermi surface of cadmium at an electron-topological phase transition under pressure, *JETP* **59**, 454 (1984).
- [25] R. Lynch and H. G. Drickamer, The effect of pressure on the resistance and lattice parameters of cadmium and zinc, *J. Phys. Chem. Solids* **26**, 63 (1965).
- [26] E. S. Itskevich and A. N. Voronovskii, Change of Topology of the fermi surface of cadmium under pressure, *Sov. Phys. JETP Lett.* **4**, 154 (1966).
- [27] G. Pratesi, A. D. Cicco, M. Minicucci, and J. P. Itié, Anomalies in the structure of solid Cd under pressure: An x-ray diffraction study, *J. Phys. Cond. Matter* **17**, 2625 (2005).
- [28] H. Yamaoka, H. O. Jeschke, X. Yang, T. He, H. Goto, N. Hiraoaka, H. Ishii, J. Mizuki, and Y. Kubozono, Electronic structures of bi₂se₃ and ag_xbi₂se₃ under pressure studied by high-resolution x-ray absorption spectroscopy and density functional theory calculations., *Phys. Rev. B: Condens. Matter* **102**, 155118 (2020).
- [29] G. Shen, Y. Wang, A. Dewaele, C. Wu, E. Dayne, J. Eggert, S. Klotz, K. F. Dziubek, P. Loubeyre, O. V. Fat, P. D. Asimow, T. Mashimo, M. M. Renata, G. Shen, Y. Wang, A. Dewaele, C. Wu, E. Fratanduono, J. Eggert, S. Klotz, K. F. Dziubek, P. Loubeyre, V. Oleg, P. D. Asimow, T. Mashimo, and R. M. M. Wentzcovitch, Toward an international practical pressure scale : A proposal for an IPPS ruby gauge (IPPS-Ruby2020), *High Pressure Res.* **40**, 299 (2020).
- [30] K. Takemura and A. Dewaele, Isothermal equation of state for gold with a He-pressure medium, *Phys. Rev. B: Condens. Matter* **78**, 1 (2008).
- [31] See Supplemental Material at [URL will be inserted by publisher] for XRD beam profile details, a table of lattice parameters and volumes, sample photos, x-ray absorption cross-sectional maps of samples, raw XRD and refinement example, additional representation and discussion of structural data collected via XRD and XAS, partial density of states, additional representations of Fermi surface and exciton projection band plots, and experimental and computational Raman data.
- [32] C. Park, D. Popov, D. Ikuta, C. Lin, C. Kenney-Benson, E. Rod, A. Bommanavar, and G. Shen, New developments in micro-X-ray diffraction and X-ray absorption spectroscopy for high-pressure research at 16-BM-D at the Advanced Photon Source, *Rev. Sci. Instrum.* **86**, 072205 (2015).
- [33] C. Prescher and V. B. Prakapenka, *DIOPTAS* : a program for reduction of two-dimensional X-ray diffraction data and data exploration, *High Pressure Res.* **35**, 223 (2015).
- [34] B. H. Toby and R. B. Von Dreele, *GSAS-II*: the genesis of a modern open-source all purpose crystallography software package, *J. Appl. Crystallogr.* **46**, 544 (2013).
- [35] J. Vinson, Advances in the ocean-3 spectroscopy package, *Phys. Chem. Chem. Phys.* **24**, 12787 (2022).
- [36] J. Vinson, J. J. Rehr, J. J. Kas, and E. L. Shirley, Bethe-Salpeter equation calculations of core excitation spectra, *Phys. Rev. B: Condens. Matter* **83**, 115106 (2011).
- [37] D. R. Hamann, Optimized norm-conserving Vanderbilt pseudopotentials, *Phys. Rev. B: Condens. Matter* **88**, 085117 (2013).
- [38] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [39] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. d. Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials, *J. Phys.: Condens. Matter* **21**, 395502 (2009).
- [40] P. Giannozzi, O. Andreussi, T. Brumme, O. Bunau, M. Buongiorno Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, N. Colonna, I. Carnimeo, A. Dal Corso, S. de Gironcoli, P. Delugas, R. A. DiStasio, A. Ferretti, A. Floris, G. Fratesi, G. Fugallo, R. Gebauer, U. Gerstmann, F. Giustino, T. Gorni, J. Jia, M. Kawamura, H.-Y. Ko, A. Kokalj, E. Küçükbenli, M. Lazzeri, M. Marrsili, N. Marzari, F. Mauri, N. L. Nguyen, H.-V. Nguyen, A. Otero-de-la Roza, L. Paulatto, S. Poncé, D. Rocca, R. Sabatini, B. Santra, M. Schlipf, A. P. Seitsonen, A. Smogunov, I. Timrov, T. Thonhauser, P. Umari, N. Vast, X. Wu, and S. Baroni, Advanced capabilities for materials modelling with Quantum ESPRESSO, *J. Phys.: Condens. Matter* **29**, 465901 (2017).

- [41] M. van Setten, M. Giantomassi, E. Bousquet, M. Verstraete, D. Hamann, X. Gonze, and G.-M. Rignanese, The PseudoDojo: Training and grading a 85 element optimized norm-conserving pseudopotential table, *Comp. Phys. Commun.* **226**, 39 (2018).
- [42] J. Campbell and T. Papp, Widths of the atomic k-n7 levels, *Atomic and Nuclear Data Tables* **77**, 1 (2001).
- [43] Y. Saad and M. H. Schultz, GMRES: A Generalized Minimal Residual Algorithm for Solving Nonsymmetric Linear Systems, *SIAM Journal on Scientific and Statistical Computing* **7**, 856 (1986).
- [44] S. V. Rashchenko, A. Y. Likhacheva, and T. B. Bekker, Preparation of a macrocrystalline pressure calibrant SrB₄O₇:Sm²⁺ suitable for the H P -H T powder diffraction, *High Pressure Res.* **33**, 720 (2013).
- [45] S. V. Rashchenko, A. Kurnosov, L. Dubrovinsky, and K. D. Litasov, Revised calibration of the Sm:SrB₄O₇ pressure sensor using the Sm-doped yttrium-aluminum garnet primary pressure scale, *J. Appl. Phys.* **117**, 145902 (2015).
- [46] J. K. Hinton, C. Childs, D. Smith, P. B. Ellison, K. V. Lawler, and A. Salamat, Response of the mode Gruneisen parameters with anisotropic compression: A pressure and temperature dependent Raman study of β -Sn, *Phys. Rev. B: Condens. Matter* **102**, 184112 (2020).
- [47] M. Kawamura, FermiSurfer: Fermi-surface viewer providing multiple representation schemes, *Comp. Phys. Commun.* **239**, 197 (2019).
- [48] V. Srinivasan, B. K. Godwal, J. C. Grossman, and R. Jeanloz, Electronic topological transitions in Cd at high pressures, *Arxiv* (2015), [arXiv:1511.01989](https://arxiv.org/abs/1511.01989).
- [49] J. P. Perdew, Density functional theory and the band gap problem, *Int. J. Quantum Chem.* **28**, 497 (1985).
- [50] L. X. Benedict and E. L. Shirley, *Ab initio* calculation of $\epsilon_2(\omega)$ including the electron-hole interaction: Application to GaN and CaF₂, *Phys. Rev. B: Condens. Matter* **59**, 5441 (1999).
- [51] I. M. Klein, H. Liu, D. Nimlos, A. Krotz, and S. K. Cushing, *Ab Initio* Prediction of Excited-State and Polaron Effects in Transient XUV Measurements of α -Fe₂O₃, *J. Am. Chem. Soc.* **144**, 12834 (2022).
- [52] I. M. Klein, A. Krotz, W. Lee, J. M. Michelsen, and S. K. Cushing, *Ab Initio* Calculations of XUV Ground and Excited States for First-Row Transition Metal Oxides, *J. Phys. Chem. C* **127**, 1077 (2023).
- [53] J. Purans, A. P. Menushenkov, S. P. Besedin, A. A. Ivanov, V. S. Minkov, I. Pudza, A. Kuzmin, K. V. Klementiev, S. Pascarelli, O. Mathon, A. D. Rosa, T. Irifune, and M. I. Erements, Local electronic structure rearrangements and strong anharmonicity in YH₃ under pressures up to 180 GPa, *Nat. Commun.* **12**, 1765 (2021).
- [54] Y. Mizuno and Y. Ohmura, Theory of X-Ray Raman Scattering, *J. Phys. Soc. Jpn.* **22**, 445 (1967).