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2005 J. Phys.: Condens. Matter 17 2625

(http://iopscience.iop.org/0953-8984/17/17/010)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **17** (2005) 2625–2632 doi:10.1088/0953-8984/17/17/010

Anomalies in the structure of solid Cd under pressure: an x-ray diffraction study

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Received 11 January 2005, in final form 6 March 2005
Published 15 April 2005
Online at stacks.iop.org/JPhysCM/17/2625

Abstract

The results of an x-ray diffraction energy-dispersive study on solid Cd under high-pressure conditions at room temperature are presented. The trends of the lattice parameters and of the axial ratio c/a as a function of pressure show that an anomalous slope change, previously discussed in connection with an electronic topological transition (ETT), is still observed using a different pressure transmitting medium for relative volume compression $V/V_0 \sim 0.86$. A detailed study of the peak positions shows that some Bragg reflections, in particular those related to the length of the c axis, are shifted with respect to the calculated positions for a typical hcp structure. This anomalous behaviour, observed for pressures above 4 GPa, is briefly discussed in terms of possible oriented lattice strains and non-hydrostatic effects.

1. Introduction

In the recent past, cadmium metal has been the subject of several theoretical [1–3] and experimental investigations [4–7], mainly because it is known to show anomalies of several physical properties as a function of pressure. Those anomalies are usually related to the occurrence of electronic topological transitions (ETTs) at high pressures. Analogous features have been widely studied in solid Zn, which also crystallizes in the hexagonal close packed (hcp) structure with an unusual large c/a axial ratio (1.856).

Evidence for an anomalous feature in solid Cd at $P = 3.5$ GPa has been observed in thermoelectric power measurements by Godwal *et al* [6] and by conductivity measurements by Bud'ko *et al* [8] at the same pressure. The behaviour of the axial ratio of Cd under pressure has been investigated by means of the x-ray diffraction technique [5, 7, 9], where some evidence

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for anomalous features were found only at higher pressures in the 10–13 GPa range. However, a recent high-pressure experiment performed with a helium pressure medium [10, 11] did not show any anomalous behaviour in the c/a trend for solid Zn, suggesting that anomalies could be related to non-hydrostatic conditions. No new data were presented for solid Cd.

On the other hand, the possible existence of the above-mentioned anomalies has stimulated theorists in performing total-energy, equation of state, and density of states calculations [1–3] on Cd at high pressure. Such calculations indicate that at least two anomalies, related to the occurrence of electronic topological transitions (ETTs), take place in Cd at high pressure for volume compressions V/V_0 of about 0.92–0.95 and 0.85 (corresponding to pressures of 3.5–5 and about 13 GPa respectively). These calculations provided a possible explanation for the observed anomalies in the transport properties [6, 8] and in the c/a axial ratio [5] of Cd under pressure. However, looking at the recent literature and results on solid Zn (see for example [10, 12–14]) it appears that the existence of the ETT and its possible correlation with the observed anomalies is still questionable.

The experiment presented in this work is aimed to shed some light on the current controversies about structural anomalies in solid Cd and Zn and their possible correlation with the ETT by collecting accurate EDXD (energy dispersive x-ray diffraction) spectra as a function of pressure in a wide range, 0–16 GPa, at room temperature. The experiment is designed to be directly compared with a previous study [5] performed increasing the number of experimental data points in the region of interest and using a different pressure medium.

2. Experimental details

The experiments were performed using a standard diamond anvil cell (DAC) as the pressure device. The sample, prepared starting from micrometric powders of high-purity cadmium, was manipulated in a glove box under Ar atmosphere, both for preventing oxidation and for security reasons due to the high toxicity of Cd.

The powder was placed at the centre of a 0.15 mm diameter hole in the metal gasket using silicon oil as pressure transmitting medium for measurements under quasi-hydrostatic conditions. Pressure was measured before and after each scan by using the standard ruby fluorescence technique.

Cd energy-dispersive x-ray diffraction (EDXD) patterns as a function of pressure at room temperature were collected using the dispersive set-up that was available at LURE (DW11A wiggler beamline) and synchrotron radiation emitted by the DCI storage ring operating at 1.85 GeV (typical currents of 300 mA). EDXD patterns were recorded at the angle of 7.05°, measured using a reference sample at ambient conditions. The lattice parameters of solid Cd at atmospheric pressure were found to coincide within the errors with those reported in the literature. We collected several successive EDXD scans in selected energy range up to the maximum pressure reached ($\simeq$16.0 GPa) at room temperature. Some EDXD spectra collected under high-pressure conditions are shown in figure 1. Data are shown on a logarithmic scale for better identification of the weaker peaks. Typical background counts were around 1000 and the integration time for each scan was about 2000 s.

3. Results

Typical EDXD spectra collected under high-pressure conditions are shown in figure 1, where about ten Cd Bragg peaks are identified in a restricted energy range (the full range is extended up to 60 keV). Strong and isolated Bragg peaks associated with both a and c lattice parameters

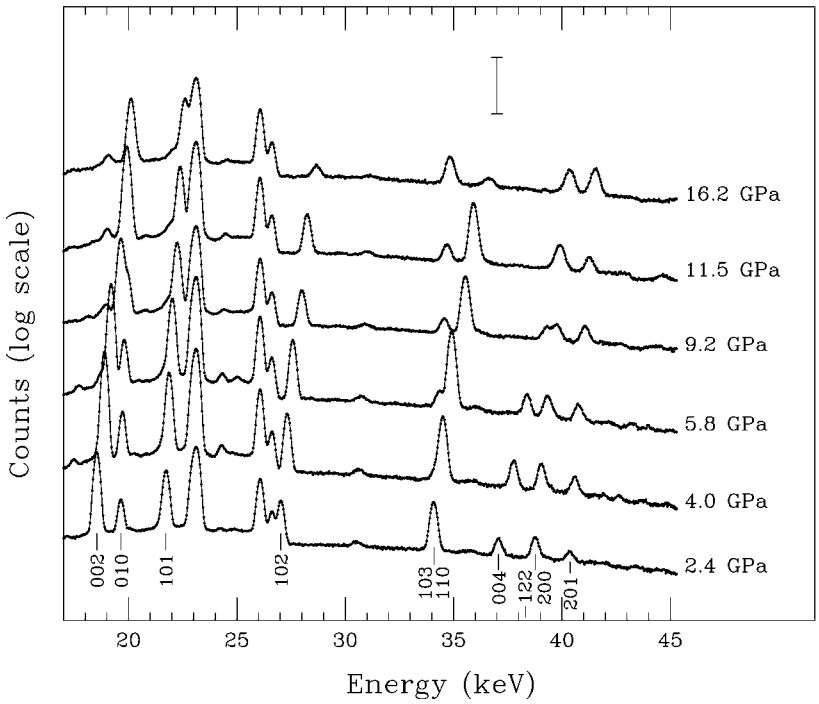

Figure 1. From the bottom to the top: diffraction patterns for increasing pressures up to about 16 GPa. The intensity is reported on a logarithmic scale for better visualization of weaker peaks (decades shown in the figure); background counts are around 1000. Peaks are indexed according to identified Cd hcp interplanar distances. Fluorescence Cd peaks are observed around 23 and 26 keV.

defining the hexagonal Cd cell are clearly identified in the spectra at various pressures, as shown in figure 1 (see indexing of the interplanar distances). Other peaks of known origin are present in the spectra (see figure 1), for example those at 23.17, 26.09 and 26.6 keV (Cd fluorescence). All of the peaks have been taken into account in the successive structural refinement for measuring a and c. Best-fit values of the lattice parameters a and c have been determined by a non-linear fitting procedure using the minuit subroutine from CERN libraries (`peakfit` program as a part of the `gnxas` package, see for example [15, 16]). The refinement is performed including in the fitting procedure both background and spurious peaks together with the selected Cd reflections (Gaussian peaks), obtaining reproducible background shapes and a more precise determination of the lattice parameters.

In figure 2 we report typical results of the structural refinement under high-pressure conditions (2 and 5.4 GPa). EDXD experimental data are directly compared with the simulations (thick curves) obtained as a superposition of Gaussian peaks defining the individual reflections (thin curves) on a smooth background. Structural refinement was performed in an extended energy range including 11 Bragg reflections associated with both a and c structural parameters (ten shown in figure 1). The scattering angle was kept fixed at $\theta = 7.05°$ while spurious peaks (fluorescence, weak reflections from the gasket and escape peaks) were considered as additional contributions of Gaussian shape. Best-fit curves were found to reproduce the experimental data within the noise level up to moderate pressures (around 3.5 GPa). At higher pressures, we have found that the position of some Bragg reflections cannot

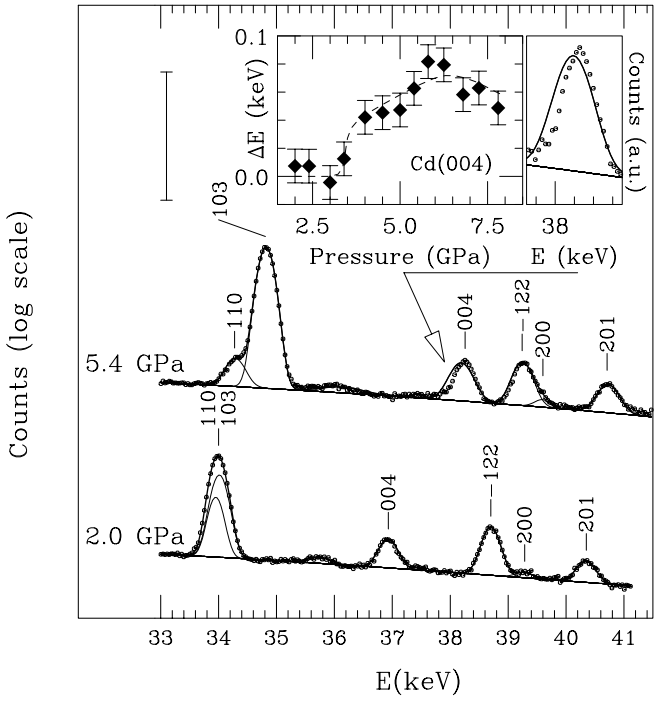

Figure 2. Diffraction patterns for solid Cd at 5.4 (upper curves) and 2 (lower curves) GPa (photon counts on a logarithmic scale, decades shown in the figure). Raw data (dots), background, individual peaks (thinner lines), and simulated patterns (thicker lines) are shown for both pressures. The Cd 004 peak position (see arrow) cannot be accurately reproduced at high pressure by any suitable choice of the a, c lattice parameters (see the magnification in the upper right inset). In the upper left inset, we report the deviation in the energy position of experimental and calculated Cd 004 Bragg reflections as a function of pressure.

be reproduced with sufficient accuracy with any suitable choice of the a, c cell parameters in the hcp structure. This is particularly evident in figure 2, upper curves, where the different positions of the Cd 004 peaks in the experimental and simulated patterns at about 5.8 GPa can be clearly seen (see arrow and magnification in the upper right inset). An accurate analysis of our structural refinements indicates that the position of reflections associated with interplanar distances depending upon c (in particular Cd 004) cannot be accurately reproduced above an external pressure of about 4 GPa. The deviation between the energy position of experimental and calculated Cd 004 Bragg reflections (resulting from best-fit refinements) is reported in the upper left inset of figure 2. The Cd 004 reflection is particularly suitable to study deviations of the calculated spectra because this peak is found at high energy and isolated in a wide range of pressures. The discrepancy in the energy position of the 004 peak is negligible up to about 3.5 GPa, slightly increases up to about 6 GPa and is maintained above this pressure. However, at higher pressures (above about 8 GPa) many important peaks merge (for example the 004 with the 122 and 200 ones) and it is more difficult to discuss the differences between experimental and calculated spectra. The deviation observed for the 004 peak increases from about 40 to 80 eV (see the upper right inset in figure 2) around 6 GPa, so corresponding deviations in the position of the 002 peak ($\Delta E \sim$ 20–40 eV) are much more difficult to detect due to the intrinsic uncertainty related to the line-width and to the fact that the 002 peak merges with the 010 one around 6 GPa.

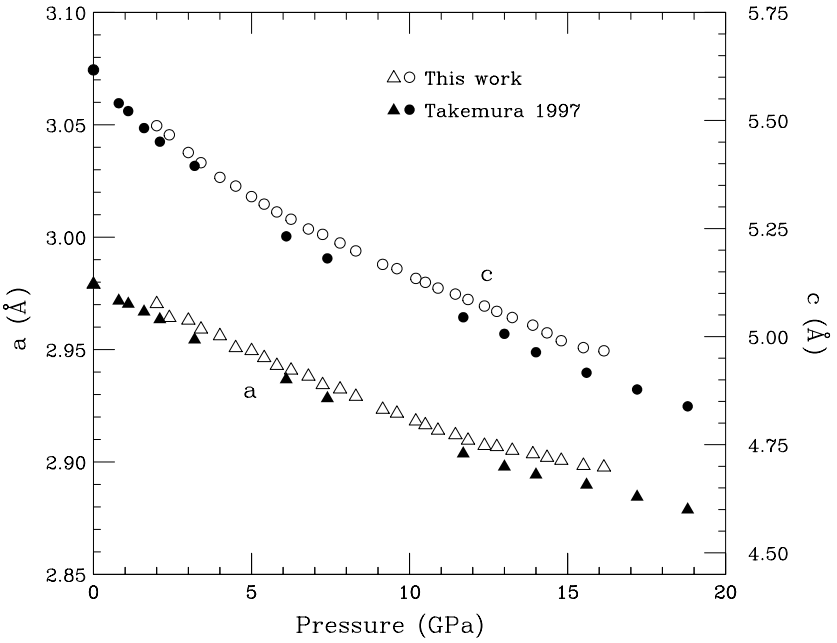

Figure 3. Trend of the Cd lattice parameters a and c as a function of pressure determined in this work (symbols) compared with previous results [5] (filled symbols).

The mentioned difficulties in reproducing the exact position of the Bragg reflections, and in particular those related to the c lattice parameter Cd 004, deserve careful consideration. As shown in the upper left inset of figure 2 the typical pressure (4 GPa) for which we observed detectable anomalies in the position of the 004 Bragg peak lies in the range where both previous experiments (resistivity and thermoelectric power) [6, 8] and calculations [1–3, 6] also reported anomalies interpreted as due to an ETT.

The large number of peaks considered in the data analysis allowed us to evaluate best-fit values for the two structural parameters a and c defining the hcp cell of crystalline Cd. The typical maximal error bars on a and c were estimated to be 0.003 and 0.005 Å respectively. It is important to remark that the discrepancy in the position of the 004 peak and the use of a subset of Bragg reflections for the structural refinement was not found to affect the numerical results on the lattice parameters a and c and that the spread of the a and c values was well within the mentioned error bars. In figure 3 we compare the trend of the Cd lattice parameters a and c as a function of pressure determined in this work with the most accurate results currently available in the literature in that pressure range (see [5]). Error bars are of the order of the symbol size in the figure. Present results are in good agreement with previous data [5] although Cd is found to be slightly less compressible in the high-pressure domain (the cell volume at 15 GPa is about 1% larger than reported in [5]). However, the agreement in both trend and numerical values of the data points is remarkable showing that the use of a different pressure medium (silicon oil instead of methanol–ethanol mixture [5]) does not affect critically the structural refinement in this range of pressures.

An important quantity that was previously used to highlight possible anomalies related to ETT transitions is the trend of the axial ratio c/a as a function of pressure. The c/a numerical values obtained in this work are reported in figure 4 as a function of the relative compression V/V_0, for better visualization of the results and for avoiding possible uncertainties in the

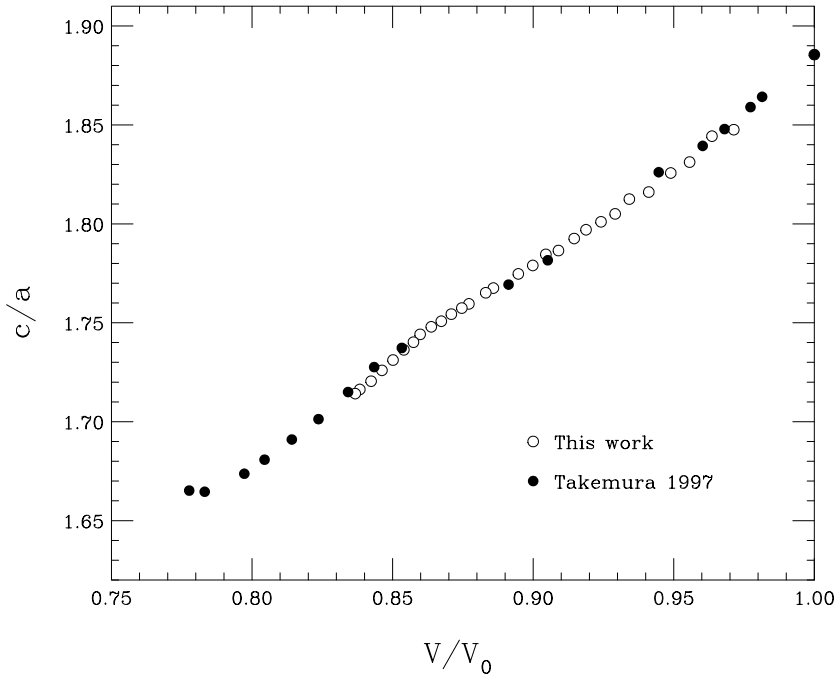

Figure 4. Trend of the axial ratio c/a as a function of the volume compression (V/V_0) obtained in this work (empty symbols). Data are compared with previous results [5] obtained using a different pressure medium (filled symbols).

pressure scale. Present data are compared with those published in [5] where the presence of an anomaly around $c/a \sim 1.73$ was pointed out. Looking at figure 4 it is clear that the behaviour of the axial ratio is practically identical to the one obtained in [5]. In particular, the anomaly in the slope of the c/a curve is found exactly in the same pressure range, corresponding to volume compressions $V/V_0 \sim 0.86$ ($P \sim 12.5$ GPa). An important aspect of this work is that the present result is obtained using a different pressure medium (silicon oil instead of methanol–ethanol mixture [5]). Therefore, a simple explanation of the anomaly as an artifact due to non-hydrostatic conditions in the pressure medium, as happens for Zn [10], is unlikely because in this case the occurrence and shape of the slope change would depend on the particular pressure medium under consideration.

4. Discussion

Present results show the occurrence of two clear 'anomalies', possibly related to each other, in the x-ray diffraction patterns as a function of pressure. The first one, observed here for the first time, is the deviation of the positions of the Bragg peaks from those of a simple hcp structure. The deviation affects principally the peaks related to the most compressible (c) crystallographic axis, with an evident effect on the 004 peak. It is not clear to the authors whether and to what extent this effect could be associated with an ETT, but certainly a possible origin for the observed anomalies is oriented lattice strains induced by the compression [17–19].

In fact, according to a recently developed theory for the analysis of lattice strains measured under non-hydrostatic pressure conditions (see for example [17] and references therein), the diffraction peaks can be significantly shifted as a function of the particular *hkl* plane and of

the angle ψ between the load direction and the diffracting plane normal. According to [17] the measured interplanar distances d_{m} (hkl) are related to those obtainable under truly hydrostatic conditions d_{hyd} (hkl) by

$$d_{\mathrm{m}}(hkl) = d_{\mathrm{hyd}}(hkl)[1 + (1 - 3\cos^2\psi)Q(hkl)] \tag{1}$$

where $Q(hkl)$ depends on the particular (hkl) plane (see [17] and references therein for the hexagonal system) and on the uniaxial stress component.

In our case, assuming that the load direction is parallel to the DAC axis, $\psi = 90 - \theta$ where θ is the angle at which the detector is positioned respect to the incoming beam (here $\theta = 7.05°$, $\psi \sim 83°$). Therefore, the dependence on hkl is not negligible and equation (1) transforms to

$$d_{\mathrm{m}} \sim d_{\mathrm{hyd}}[1 + 0.95Q(hkl)]. \tag{2}$$

The order of magnitude of $Q(hkl)$ is usually [17] around 10^{-3} and the effect on the position of the peaks should be of the same size. The relative energy shift observed for the 004 peak is in fact about 2×10^{-3}, compatible with the possible effect of lattice strains due to local non-hydrostatic conditions. Of course, a precise determination of $Q(hkl)$ is usually a very difficult task, implying measurements for different angles ψ, and this is beyond the scope of the present work. However, present data indicate that there are significant shifts of the Bragg peak positions (and of the related measured interplanar distances d_{m}) under nominal quasi-hydrostatic conditions, which are possibly explained by the presence of residual uniaxial stress in the Cd grains.

The larger compressibility of the c axis provides an explanation for the special sensitivity of the Cd 004 peak to residual stress, as the effect of an oriented force field is obviously larger. However, the presence of significant oriented lattice strains in quasi-hydrostatic conditions is partly unexpected and further experiments are needed to clarify this point. On the other hand, the total energy curve (see for example [2]), is flat (or even double well) as a function of the axial ratio c/a so several metastable conditions, possibly related to local (even temporary) gradients of pressures, can be easily reached upon pressurization at room temperature. Certainly, an important improvement to present knowledge in solid Cd in this region of pressures would be reaching stable hydrostatic conditions. Considering that fluid used as the pressure transmitting medium (silicon oil) should be quasi-hydrostatic in the range of interest (0–10 GPa) it is likely that residual oriented stress in the Cd grains could be removed by annealing the sample after each pressurization.

The second anomaly, observed at higher pressures ($V/V_0 \sim 0.86$, see figure 4), confirms previous observation by Takemura [5] using a different pressure transmitting medium. For pressures higher than about 8 GPa we were not able to detect deviations of the peaks from the expected hcp positions, possibly related to oriented lattice strains. In any case, no significant relationship between observed deviations and a, c numerical values was observed in our study. This anomaly seems then to be a genuine feature in the axial ratio behaviour under compression at room temperature using a quasi-hydrostatic fluid as a pressure medium. Nevertheless, we are not able to rule out possible effects of residual stress in the Cd grains affecting present and previous data. In fact, the softness of the c axis and the flatness of the total energy curve as a function of the axial ratio is likely to favour the occurrence of oriented stress and preservation of metastable conditions. Again, one can wonder whether an oriented stress component in the Cd grains could be removed by sample annealing, therefore recovering stable hydrostatic conditions at high pressure.

5. Conclusions

We have presented a detailed study of x-ray diffraction data of solid Cd collected at high pressures up to about 16 GPa using the energy-dispersive technique. A detailed study of the Bragg reflections shows that those related to the length of the c axis (in particular the 004 one) are significantly shifted with respect to the typical hcp structure, in a wide range of pressures, 4–8 GPa. This anomalous feature could be related to an ETT but can be more likely explained in terms of oriented lattice strains and local non-hydrostatic conditions. Lattice parameters of hcp Cd have been accurately measured, showing that an anomalous slope change in the trend of the axial ratio c/a, previously observed using a different pressure transmitting medium, is still observed for a relative volume compression $V/V_0 \sim 0.86$ ($P \sim 12.5$ GPa). Our results for c/a are found to reproduce very closely those obtained in different experimental conditions, showing that the anomaly actually exists and is observed under compression at room temperature using different fluids as the pressure transmitting medium.

Therefore, while it is expected that further experiments at room temperature would lead to results similar to those presented in this work, we think that some new efforts should be devoted to experiments where possible residual stress is avoided or removed by stabilizing the sample with a proper annealing at each pressure step. A new experiment of this kind should be able to give a definite answer of whether the observed anomalies are related to the equilibrium Cd structure and dynamics or to residual oriented stress.

Acknowledgments

We gratefully thank L Comez, M Cesaroni, and P Munsch for their help during the initial stages of the experiment.

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