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ORIENTATION AND TEMPERATURE DEPENDENCE OF THE Cd K-SHELL EXAFS OF SINGLE CRYSTAL Cd METAL: FIRST EXAFS OBSERVATION OF $R_2$

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Abstract - The K-shell X-ray absorption spectrum of a Cd single crystal has been measured at temperatures from 4 to 300K with the crystal in two orientations - one optimizing EXAFS from the first Cd distance ($R_1 = 2.97\AA$), the other optimizing EXAFS from the second Cd distance ($R_2 = 3.29\AA$). Clear evidence is obtained for $R_2$ although its visibility varies greatly with temperature on account of the large anisotropy in the thermal motion. The Debye-Waller factors for the thermal motion along $R_1$ and $R_2$ are derived and compared to theory.

I - INTRODUCTION

The local structure around each Cd atom in the distorted hexagonal close-packed structure of Cd metal consists of 6 nearest neighbours at 2.97\AA\ ($R_1$) in the basal plane (along the a or b directions) and 6 neighbours at 3.29\AA\ ($R_2$) at an angle of 30° to the c axis (see Fig. 2). The problem that this work addresses is the visibility of the second shell (3.29\AA) distance in Cd K-shell extended X-ray absorption fine structure (EXAFS). The K-shell photoabsorption spectrum of single crystal Cd was first reported by Weber /1/ who recorded spectra at both 300 and 83K with unpolarized X-rays incident along either the a direction, where the $R_1$ contribution will be zero, or the c direction, where the $R_1$ contribution will be maximum but contributions from both the $R_1$ and $R_2$ distances will occur. Weber /1/ observed that the EXAFS intensity was smaller with the X-rays incident along a than along c but there were no apparent changes in the periodicity or basic shape of the extended fine structure between the two orientations. No detailed analysis of the EXAFS was done. In 1983, Thulke and Rabe /2/ reported the Cd K EXAFS of polycrystalline Cd at 77K which showed a symmetric first peak in the Fourier transform (FT) with no signs of $R_2$ either as an asymmetry or a separate peak. Thulke and Rabe /2/ attributed the absence of detectable $R_2$ signal to a large thermal motion and thus large Debye-Waller factor (σ) for this signal.

In order to further investigate the intriguing question as to whether or not EXAFS can detect the $R_2$ distance of Cd we have studied the temperature dependence of the Cd K-shell EXAFS of single crystal Cd over temperatures from 4K to 300K with orientations chosen to optimize the $R_1$ and $R_2$ EXAFS signal. Orientation dependent EXAFS is well known to provide additional structural information as exemplified in the study by Brown et al /3/ of the orientation dependence of the EXAFS of single crystal Zn, which has a similar distorted hexagonal close-packed structure.
II - EXPERIMENTAL

The Cd single crystals were obtained from a shaped piece of Cd metal, 50μm thick. This was sandwiched between two glass slides with 50μm spacers, melted and Bridgeman cooled over a period of 12 hours. The orientation of several of the larger crystals was determined by transmission Laue. The crystal chosen for study was about 3 x 5mm² with its c axis at 10° to the surface normal. It was masked off with lead to a size of 1 x 2mm², clamped between two copper plates fastened to the bottom of a single stage cryostat, surrounded by a Be cup and immersed in liquid helium. Measurements at temperatures higher than 4K were carried out over several half-hour periods while the cryostat was warming up.

The Cd K-shell spectra (26.6 - 27.7 keV) were recorded on the C2 beam line at CHESS with the X-rays incident along either the c axis (美妆 vector in the basal plane along the R1 direction, denoted R1*), or with the X-rays incident 60° off the c axis (美妆 vector at 30° to the basal plane, denoted R2*) (see Fig. 2). With 100% polarized X-rays and a monocrystalline sample, K-shell EXAFS can be described by /4/:

\[ X(k) = \sum_i 3\cos^2 \theta_i X_i(k) = \sum_i 3\cos^2 \theta_i A_i(k) (N_i/k r_i^2) \exp(-2k^2 r_i^2) \sin(2kr_i + \delta_i(k)) \]

where the direction to the ith neighbour with EXAFS component \( X_i(k) \) makes an angle \( \theta_i \) with the X-ray polarization vector, and \( A_i(k) \) is the backscattering amplitude [phase shift] as a function of wavenumber \( k \) from each of the neighbouring atoms of type i, which are located at a distance \( r_i \) and have a mean-square relative displacement of \( \sigma^2 \). The \( 3\cos^2 \theta \) factor averages to 1 for polycrystalline samples. For the R1* measurements this factor is equal to 1.5 for \( R_1 \) and 0.33 for \( R_2 \) (assuming 100% polarisation and a perfect single crystal). For the R2* measurements the \( 3\cos^2 \theta \) factor is 0.375 for \( R_1 \) and 1.72 for \( R_2 \). Thus in the first case the \( R_1 \) component will dominate while in the second case, the \( R_2 \) component should be stronger. The extended fine structure was extracted by subtracting a 4-section cubic spline background, normalizing to the edge jump and converting from energy to wavenumber. The origin of the k-scale \( (E_0) \), initially chosen as the mid-point of the edge jump, was optimized during analysis which used Fourier filtering followed by curve-fitting applied to k²-weighted data, according to standard procedures /5/.

III - RESULTS AND DISCUSSION

The k¹-weighted EXAFS extracted from the Cd K absorption spectra recorded at 4K in the R1* and R2* orientations and the transforms of this data are presented in Fig. 1, along with the results at room temperature. The prominent side-lobe observed in all

Fig. 1: k¹-weighted EXAFS and magnitudes of the Fourier transforms (FT) obtained from the Cd K-shell EXAFS of single crystal Cd recorded in the R1* and R2* orientations at 4 and 300K.
transforms at 2.2 Å* (Å* signifies phase shifted distance) is associated with the structured backscattering amplitude function of heavy atoms /6/. As expected, the R1* data is totally dominated by R3 signal which produces a symmetric first shell peak in the transform at 2.7 Å*. In the R2* geometry the R3 component still dominates, even though the R2 signal should be weighted 5 times that of the R1 signal if the orientation is correct and the X-rays 100% polarized. Although there is no clear evidence of R2 in the 300K spectrum, the R2 signal does produce a prominent shoulder on the main peak at 4K. In addition, there is a shift in the periodicity of the kχ(k) signal relative to the 4K R1* data which can be seen in the overplot and there is a distinct beat pattern between the R3 and R2 components as evidenced by the damped intensity and irregular pattern between 5 and 7 Å⁻¹ in the 4K spectrum.

The magnitude of the R1 signal in the R2* spectrum is about 60% of that in the R1* spectra recorded at similar temperatures. According to the predicted polarization dependence this ratio should be only 25%. The additional R1 signal can be explained by misalignment from the desired orientation during measurements, incomplete polarization of the X-rays or imperfect crystallinity of the Cd sample. All of these factors probably contribute to some extent. An approximate R2 component was obtained at various temperatures by subtracting 0.6 R1* from the R2* EXAFS. The transforms of these subtracted spectra (Fig. 2) indicate that the R2 signal in Cd metal decreases very rapidly with increasing temperature. Above 100K it is very difficult to detect R2. Interestingly at 4K the higher shells of surrounding cadmiums become more visible in this presentation.

In order to quantify the effect of anisotropic thermal motion on the EXAFS of Cd, multiparameter fits were made to the Fourier-filtered first-shell EXAFS data from measurements at a range of temperatures between 4 and 300K. The model amplitude and phase shift functions were obtained from an experimental R1 Cd backscattering signal derived from 1.07(R1* - 0.12 R2*). The distances derived for both R1 (2.963(6) Å average over all data) and R2 (3.220(12) Å average over all data) are smaller by 0.01Å (R1) and 0.06Å (R2) than the crystallographic values. The differences may be attributed to the limitations of an analysis based on a Gaussian pair distribution being applied to an anharmonic system /7/. The number of nearest neighbours, N1 is 6±1 at all temperatures. However the N2 values are consistently too low by more than a factor of 2. Since our analysis treats the R1 and R2 directions similarly and produces a reasonable N1 value, the 50% error in N2 suggests that the anharmonicities in the two directions are appreciably different. However, we do not believe this can be the complete story since an N2 value of only 3±1 was obtained from the R2* data.

![Fig. 2: FT magnitude spectra of the weighted difference (XR1* - 0.6XR2*) of the single crystal Cd EXAFS as a function of temperature. This signal approximates that from backscattering in the R2 direction only. The inset shows the distorted hexagonal close packed structure of Cd (R1 = 2.973Å, R2 = 3.291Å) and the directions of X-ray incidence for the two crystal orientations studied.](image-url)
at 4K, where anharmonicity effects on the EXAFS amplitudes should be minimal.

The mean-square relative displacements (\( \Delta \sigma^2 \)) derived from the curve fits for both \( R_1 \) and \( R_2 \) components (measured relative to the 4K value for the \( R_1 \) component) are plotted as a function of temperature in Fig. 3. These values are compared to the values of \( \Delta \sigma^2 \) calculated by the correlated Debye model /8/ with Debye temperatures of 200K and 140K for the \( R_1 \) and \( R_2 \) components respectively, which were chosen for best fit of the calculated curve to the data. They are somewhat higher than those of 164K and 160K obtained from thermal expansion data /10/. At least some of the discrepancy between the calculated and observed temperature dependence is probably due to the assumptions of no static disorder and strictly harmonic motion. A well-known effect of applying an EXAFS analysis based on a Gaussian distribution to systems with appreciable disorder or anharmonicity is to produce distances that decrease with increasing temperature rather than increasing as required by thermal expansion /7/. This effect is observed in the present analysis giving clear evidence that the Cd-Cd potential is anharmonic. Neglect of anharmonicity in EXAFS analysis underestimates \( \sigma \) as well as \( R /11/ \). Thus if the analysis was modified to account for non-Gaussian distance distributions one would expect higher \( \sigma \) values. This would produce an even better agreement with the correlated Debye model, suggesting that the Debye temperatures of Cd are lower than we have estimated and are similar to the values from X-ray diffraction /9/. Non-gaussian pair distribution can be taken into account in a more rigorous analysis by several approaches including cumulant analysis or by fits to assumed models of the pair distributions. Analysis of our data along these lines is presently in progress.

**Fig. 3:** Temperature dependence of \( \Delta \sigma^2 \) for \( R_1 \) and \( R_2 \) of Cd metal obtained from non-linear least square fits to the Fourier filtered first-shell data for single crystal Cd. The solid line represents the correlated Debye model of Beni and Platzman /8/ calculated for the known \( R_1 \) and \( R_2 \) distances with Debye temperatures of 200K and 140K respectively.

**REFERENCES**