Structure of the New Binary Antimonide Ti_2Sb From the RA-PDF Technique

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Introduction

A new metallic binary antimonide, Ti2Sb, was uncovered. Its most interesting structural feature is an unprecedented distortion of a metal atom layer that is a perfect square planar net in its aristotype La2Sb. The corresponding Ti net of Ti2Sb comprises squares and rhombs in a 1:1 ratio, as experimentally proven by X-ray structure studies and the pair distribution function technique based on both X-ray and neutron data, independent of the synthesis method applied. Electronic structure calculations indicate that the major driving force for the formation of the rhombs is enhanced Ti-Ti bonding along their diagonals [1].

An IP detector coupled with high-energy synchrotron radiation has been recently successfully used for atomic pair distribution function (PDF) analysis [2], with high probed momentum transfer Q_{max}, from several crystalline materials [3]. Medium-high real-space resolution PDF data analysis from crystalline materials has been performed using image-plate data and shows promising results. Comparable or even better statistics than from conventional X-ray measurements can be achieved with significantly shorter counting times. This new combination of a real-space probe and fast counting time, named RA-PDF, opens up a broad field for future applications to a wide variety of materials of both scientifc and technological interest [4].

Measurements were carried out using the RA-PDF method on a powdered Ti_2Sb sample to study structural properties of this new binary antimonide, in complement to the neutron PDF and single crystal X-ray structural studies that were also carried out on this material.

Methods and Materials

High energy X-ray diffraction experiment was performed at the 6-ID-D MU-CAT beam line at the Advanced Photon Source (APS) at Argonne National Laboratory. A powdered Ti2Sb sample of disk shape (thickness of 1.0 mm, diameter of 1.0 cm) was loaded into a hollow flat metal plate, and then sealed between thin Kapton films. Data acquisition at 300 K employed the recently developed rapid acquisition PDF (RA-PDF) technique [3] with an X-ray energy of 98.0 keV. A single exposure of the image plate detector was limited to two seconds to avoid detector saturation, and was repeated 20 times to achieve better counting statistics in the high-Q region.

Measurements were carried out in flat-plate transmission geometry. A Mar345 image-plate camera, a round disk with a usable diameter of 345 mm, was mounted orthogonal to the beam centered on the IP. Silicon standard sample was used to calibrate the sample-to-detector distance and the tilt of the IP relative to the beam path, using the software Fit2D [5, 6]. The sample to detector distance was 178.4 mm. All raw 2D data were integrated and converted to intensity versus 2θ format using the Fit2D program package [5, 6], where 2θ is the angle between the incident and scattered X-rays. Standard corrections for multiple scattering, polarization, absorption, Compton scattering and Laue diffuse scattering were applied to the integrated data to obtain the reduced total structure function F(Q). Direct Fourier transformation gives the pair distribution function G(r). Data correction and processing utilized the PDFgetX program package [7]. The structure models were refined using the profile-fitting least-squares regression program PDFFIT [8].

Results

Structural properties of new binary antimonide were addressed using the atomic PDF method, well suited for structural determination of structurally challenged materials [1]. The PDF gives the number of atoms in a spherical shell of unit thickness at a distance r from a reference atom. This gives peaks at characteristic distances separating pairs of atoms. Fourier transform from reciprocal to real space was carried out up to a very high value of Q, Q_{max}=30Å^{-1}. Beyond that value of Q the signal

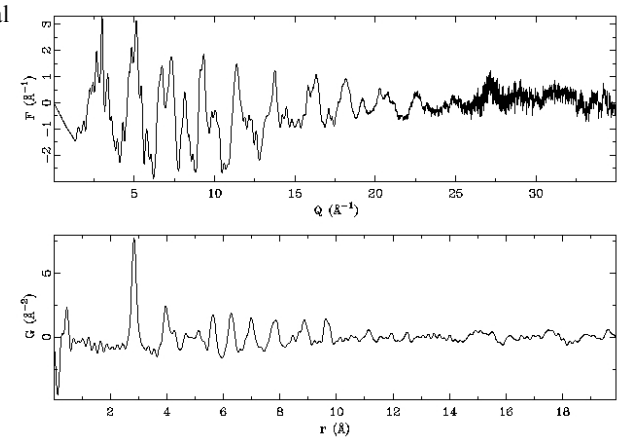

Fig.1. Experimental reduced total structure function F(Q)=Q(S(Q)-1) of the Ti_2Sb sample, (top), and corresponding G(r) (bottom). Data were collected at room temperature using the RA-PDF experimental setup. F(Q) was Fourier-transformed using Q_{max}=30Å^{-1}.

Experimental reduced total structure function, F(Q)=Q(S(Q)-1), and corresponding atomic G(r)'s for the Ti_2Sb sample are shown in Fig. 1

Discussion

The PDFs, G(r), are shown in Fig. 2 as the dots, with (a) and (b) showing the X-ray data, and (c) and (d) the neutron data. The data were modeled quantitatively using a real-space profile

fitting program PDFFIT. This program can refine the crystallographic model to the data, in analogy with Rietveld refinements. However, local structural distortions can be introduced into the models *even when they are not long-range ordered* and no crystallographic superstructure reflections are observed as in the current case.

Two different models were attempted (see Ref. 1 for details). We first fitted the data with the undistorted model, and show the results in Fig. 2a (X-ray) and 2c (neutron). Clearly, the undistorted model proves to be insufficient, as evident from the difference curves below the data. Fluctuations significantly larger than the experimental uncertainties (the estimated errors at the 1σ level are shown as dotted lines associated with the difference curves) are observed over the whole fitting range. One of the strengths of the PDF technique is that it yields quantitatively reliable intermediate range information on nanometer length-scales. The persistence of the fluctuations in the difference curve of Fig. 2c are significant and a clear indication that the undistorted model fit to the data is lacking.

Next, the distorted model with split Ti_2 sites was tried, with the fitting results shown in Fig. 2b (X-ray) and 2d (neutron). Compared to the undistorted model, the agreements to both X-ray and neutron PDFs improved significantly over the entire range, with the addition of only one additional refinement parameter, and gave rather satisfactory fits given that the distorted model is an average of the unknown superstructure. The superstructure model in the Cmca space group was also tried and gave comparable fits. The structure data from the PDF refined models are in excellent agreement with those refined from the single-crystal X-ray study as shown in Table 2 of Ref. 1.

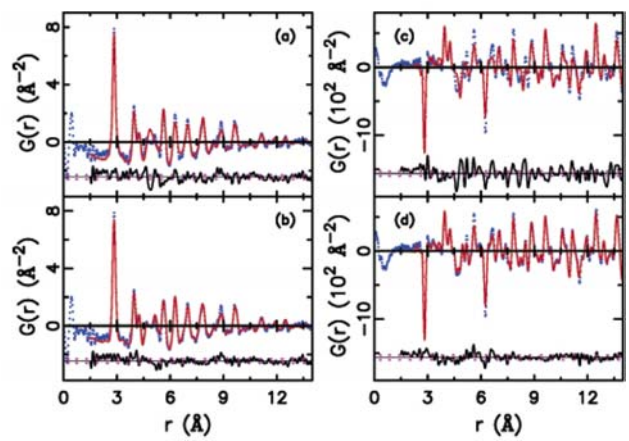

Fig.2. PDFs, G(r). (a), (b): X-ray data; (c), (d): neutron data (shown as the blue dots in both cases). Solid lines are the fits to the model data, with (a) and (c) from the undistorted model and (b) and (d) from the split site model. Difference curves are shown below the data. The dotted linesaround the difference curves indicate the standard uncertainties due torandom counting statistics on the data at the 1σ level.

The full profile PDF refinements confirm that the distorted model describes both the local and average structure to great accuracy and is far superior to the undistorted model. The superstructure model in the Cmca space group gives comparable agreement to the split site model, which shows that this model is also consistent with the data as well as making better physical sense. For detailed discussion and further important results obtained this study please consult recently published article [1].

References:

[1] S. Derakhshan, A. Assoud, K. M. Kleinke, E. Dashjav, X. Qiu, S.J.L. Billinge, and H. Kleinke, J. Am. Chem. Soc. 126, 8295-8302 (2004)

[2] T. Egami and S. J. L. Billinge, *Underneath the Bragg Peaks: Structural analysis of complex materials*, Pergamon Press Elsevier, Oxford, England, (2003).

[3] P. J. Chupas, X. Qiu, J. C. Hanson, P. L. Lee, C. P. Grey, S. J. L. Billinge, J.Appl. Cryst. 36, 1342-1347 (2003).

[4] S. J. L. Billinge and M. G. Kanatzidis, *Chem. Commun.*, 749-760 (2004).

[5] A. P. Hammersley, S. O. Svenson, M. Hanfland, and D. Hauserman, High Pressure Research 14, 235 (1996).

[6] A. P. Hammersley, FIT2D. Internal Report ESRF98HA01T European Synchrotron Radiation Facility, Grenoble, France (1998).

[7] Xiangyun Qiu, Jeroen W. Thompson and Simon J. L. Billinge, *J. Appl. Crystallogr.* 37, 678 (2004).

[8] Th. Proffen, S. J. L. Billinge, J. Appl. Cryst. 32, 572-575 (1999).

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