

15.2-4 TOPOGRAPHIC EXAFS. By D.K. Bowen<sup>1,2</sup>, S.R. Stock<sup>3,4</sup>, S.T. Davies<sup>1</sup>, E. Pantos<sup>2</sup>, H.K. Birnbaum<sup>3</sup> and Haydn Chen<sup>3</sup>.

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Contrast near an absorption edge has been observed in synchrotron radiation topographs obtained with white radiation due to the variation of wavelength across an image. Variations in absorption, due to the fluctuations in the EXAFS spectrum, appear as fringes parallel to the edge. The contrast has been measured densitometrically for a Nb specimen and excellent agreement obtained with a conventional EXAFS spectrum. The exposure time for the topograph was 25 s. The spectral characteristics of this technique are analysed and shown to be comparable with standard EXAFS spectroscopy. The method provides a means of extracting microstructural and spectroscopic information simultaneously and point-by-point on one sample. Possible applications are discussed.

15.3-1 ABSORPTION MEASUREMENTS OF Pb/Bi-SULFIDES CLOSE TO L-EDGES WITH SYNCHROTRON RADIATION. By V. Kupcik, M. Wendschuh-Josties, A. Wolf, R. Wulf, Mineralogisch-Kristallographisches Institut der Universität Göttingen, V.M. Goldschmidt-Str. 1, D-3400 Göttingen, Germany, FRG.

A common problem in crystal structure analysis is the distinction of atoms with similar scattering power i.e. atomic number. Only in some special cases the different sites of the atoms can be derived from chemical arguments or examination of the coordination polyhedra. To overcome this principal difficulty a method called "Delta-Synthesis" is derived based on a difference Fourier synthesis calculated from two data sets measured at two different wavelengths. These two wavelengths have to be properly chosen on both sides of the absorption edge of the anomalous scatterer.

In connection with one of the research projects of our institute [structure analysis and physical properties of sulfosalts,  $(Me_x^1 Me_y^2 S_z)$ ,  $Me^1 = Pb, Cu, etc.$ ;  $Me^2 = As, Sb, Bi$ ], we are essentially interested in de-

termination of the Pb/Bi distribution in these compounds. Recent theoretical calculations on Lillianite ( $Pb_3Bi_2S_6$ ) and Galenobismuthite ( $PbBi_2S_4$ ) (V. Kupcik, M. Wendschuh-Josties, A. Wolf, R. Wulf, HASYLAB Jahresbericht 1983) indicate that the method mentioned above is only valid if the correct values of the  $f'$  and  $f''$  components of the anomalous scatterers are known. So absorption-measurements at the  $L_{III}$ -edge of Pb and Bi as well as on various Pb/Bi containing compounds have been carried out in order to study the change of the absorption curves due to the chemical composition. Knowing these wavelength dependences the proper wavelengths for data collection can be chosen.

The measurements have been carried out on the 5-circle-diffractometer (V. Kupcik, P. Wulf, M. Wendschuh, A. Wolf and A. Paehler, Nucl. Instr. and Methods (1983) 208, 519 pp) in the Hamburg Synchrotron Radiation Laboratory at DESY.

15.3-2 RECONCILIATION OF VALENCY AMBIGUITY IN  $V_2TiO_5$  USING XANES SPECTROSCOPY. By S. Åsbrink<sup>1</sup>, G.N. Greaves<sup>2</sup>, P. Hatton<sup>2</sup> and K. Garg<sup>2</sup>.

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The crystal structure of  $V_2TiO_5$ , which is of  $V_3O_5$  type (Åsbrink, Acta.Cryst.(1980) B36, 1332; Hong and Åsbrink, Acta.Cryst.(1982) B38, 713), was determined from neutron powder diffraction data (Åsbrink and Säuborg, to be published). The 4-fold metal atom position between the shear planes was occupied by  $V^{3+}$  ions, judging from the observed V-O bond lengths, while the corresponding 8-fold position at the shear planes was taken by a 50/50 mixture of V and Ti ions, the charges of which however could not be determined unequivocally. We have therefore turned to XANES spectroscopy at the V (5465.1 eV) and the Ti (4966.4 eV) K-edges to explore chemical shifts and local symmetry. Edge positions for  $V_2TiO_5$  were measured relative to V and Ti metals and the following model compounds:  $VO_2$ ,  $V_2O_5$ ,  $TiO_2$  and  $Ti_2O_3$ . Strong similarities are observed, both in position and fine structure, between the V K-edges in  $V_2TiO_5$  and  $V_2O_5$  and between the Ti K-edges in  $V_2TiO_5$  and  $TiO_2$ . These demonstrate that  $V^{3+}$  ions occupy both the 4-fold site and the 8-fold site in  $V_3O_5$  type structure whilst  $Ti^{4+}$  ions occupy the 8-fold site. The potential usefulness of XANES spectroscopy for solving similar valency ambiguities seems evident. Furthermore this approach might also prove useful for studying phase transitions involving valency redistributions.