First XAFS spectra with a YB_{66} monochromator

We have employed a YB_{66} double-crystal monochromator to measure high resolution XAFS spectra of Mg (K-edge, 1303 eV), Al (1559 eV) and Si (1839 eV) in a number of compounds and minerals. The successful use of this unique cubic boride material (a = 23.44 Å) as a monochromatic dispersing element in the soft X-ray range of 1–2 keV (1) stems from a number of critical events in the course of an international, collaborative development: (a) growth of large, single crystals of YB_{66} by Tanaka et al. (2,3); (b) systematic material characterization with rocking curve measurements, and X-ray topography to map out grain structure and growth-induced defects (4,5); and (c) synchrotron reflectivity measurements (6) as a function of crystal growth parameters and position in a grown crystal. Data derived from these property characterizations, especially those from (b), were used as feedback information to improve and attain growth of large and perfect enough crystals for monochromator usage.

The XAFS measurements were performed on the JUMBO beamline (7) at SSRL during a recent run in January 1993, with SPEAR operating at an electron energy of 3 GeV, injection current of ~100 mA and a lifetime of over 20 hr. A YB_{66} boule was grown using an indirectly heated float zone technique described elsewhere (2,3). A sister pair of (400)-oriented crystals (2d = 11.72Å), 18 mm × 10 mm × 0.7 mm thick each, was cut and polished from this boule. Areas of high homogeneity as revealed by white light synchrotron radiation topography and by single peak in rocking curve measurements were carefully mapped out for each crystal. These areas were found to be located along the growth axis of the crystal closer to the zone end. The crystal pair was configured in a non-dispersive mode and with a fixed exit beam height, sending a monochromatic beam from the UHV monochromator chamber to a vacuum sample chamber (10^{-5} Torr or better) through a 0.4 mm thick CVD diamond window. The energy position of the monochromator was initially calibrated using its own transmission curve from the position of the L_3 and L_2 edges of Y at 2080 eV and 2156 eV (8) respectively, assuming no chemical shift in YB_{66} from the metal values. X-ray absorption spectra were recorded by monitoring total electron yield with a channeltron.

In Figure 1, the full width at half maximum of the YB_{66} double-crystal rocking curve is plotted as a function of photon energy in the range 1100–2500 eV under various beam size and divergence conditions. Typically, the crystal resolution is ~0.25 eV at 1100 eV and increases monotonically to ~1 eV at 2000 eV, above which the Y $L_{3,2,1}$-edges set in at 2080, 2156 and 2373 eV respectively, and lower the transmission function of the monochromator substantially, making it less attractive when compared with InSb(111) and Ge(111) at high energy (9).

In Figure 2, the "raw" experimental EXAFS spectrum of Al metal is shown. This spectrum, the first EXAFS scan ever made with YB_{66}, was recorded with a SPEAR current of ~50 mA. The integration time from each data point was 1 sec. Traditionally, Al K-edge XAFS spectra have been recorded with quartz ($10\bar{1}0$) monochromator crystals, which undergo radiation damage in a synchrotron beam in a matter of hours (10), thus degrading the resolution. The use of a quartz monochromator would yield an upper energy limit to just below the Si K-edge at 1839 eV. With YB_{66}, Al EXAFS spectra can now be routinely recorded to 2060 eV, some 500 eV above its K-edge to give a much more useful and usable EXAFS data range to k = 11 $Å^{-1}$.

Figure 3 is an experimental EXAFS scan of sillimanite, an aluminosilicate mineral having a chemical composition of Al_2SiO_5, from 1525 to 2060 eV. This spectrum was recorded at a SPEAR current of ~79 mA. A fine step-size of 0.2 eV/point was used over both the Al and Si edges to register the high resolu-

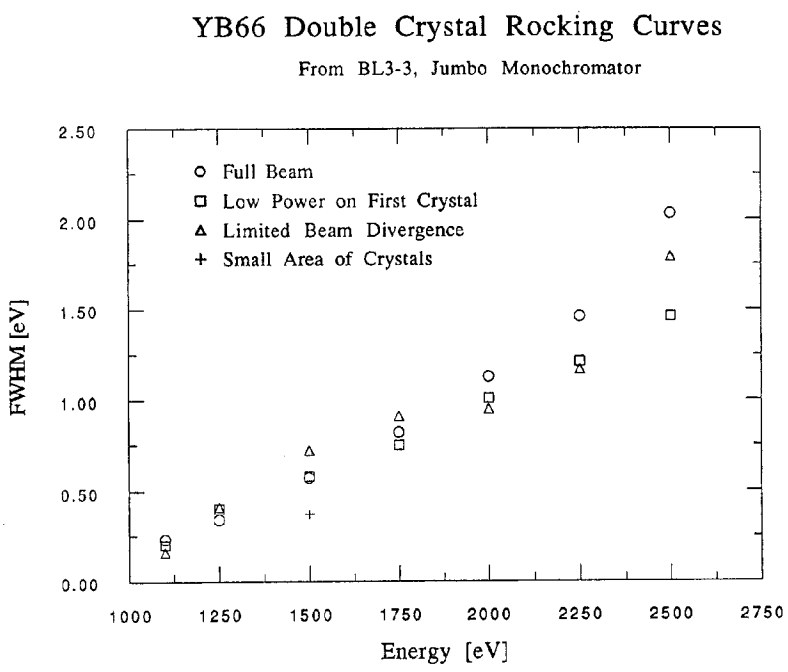

Figure 1. FWHM of YB_{66} double crystal rocking curves as a function of photon energy under various beam conditions.

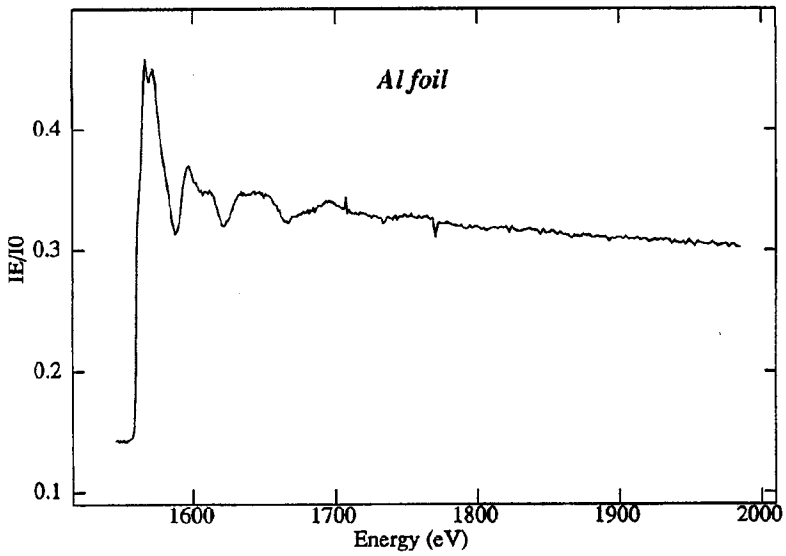

Figure 2. An experimental XAFS scan of Al metal—the first ever recorded with YB_{66}.

tion features in the XANES region. The integration time for each data point was two sec. The whole spectrum was recorded in just over an hour. Positive chemical shifts amounting to 6–9 eV from the corresponding Al metal and elemental Si values were measured in this and other aluminosilicate minerals and compounds.

In Figure 4, the XAFS spectrum of Mg in MgO, recorded in the range 1250–2000 eV, is shown. The scanning parameters used were similar to those used for the sillimanite sample discussed above. Note again the high resolution features in the XANES region. A positive edge shift of ~6 eV with respect to Mg metal (1303 eV) was observed. With this monochromator, EXAFS data can now be collected to over 700 eV above the Mg edge to yield a k_{max} value to ~13.5Å^{-1}, which is much greater than a k-range of ~8Å^{-1} available with a beryl monochromator, which limits data to just below the K-edge of its Al constituent (11).

The preliminary data presented here clearly establish the performance of YB_{66} as both a high resolution and *synchrotron radiation-stable* soft X-ray monochromator in the 1–2 keV region. Over a continuous experimental run of two weeks on the JUMBO line, the energy calibration of the monochromator was stable to within ~1.5 eV. The drift may largely be due to thermal effects on the first crystal at high SPEAR current in the beginning of each fill. This was anticipated since YB_{66} has a low thermal conductivity (12). More systematic characterization of the thermal load effects is being planned. As monitored periodically by rocking curve measurements, the monochromator resolution remained essentially unchanged during the two week run. This again had been speculated (1) since YB_{66}, a semiconductor like Si and Ge, is less prone to radiation damage in a synchrotron radiation beam than insulating materials such as quartz and beryl.

Thus, besides opening up new XAFS investigations of these three relatively spectroscopic "silent" elements, Mg, Al and Si, which are constituents in a large variety of important technological materials such as zeolites, silicate glasses, high performance alloys (to name a few), the YB_{66} monochromator also enables L-edge spectroscopy of some 4 p elements such as Ga to Sr and M-edge spectroscopy of elements from La, including all rare earths to Ir to be investigated. These L-edge and M-edge spectroscopic measurements will provide the needed data for understanding the electronic structure and, hence, chemical bonding of materials containing these elements, since the final states are associated with the valence levels of interest. Also, since the Bragg angle for the YB_{66}(400) reflection varies from 80 to 20 deg in the 1–2 keV range, this monochromator may be used to preserve circularly polarized light above and below the orbit plane to study magnetic dichroism in the soft X-ray

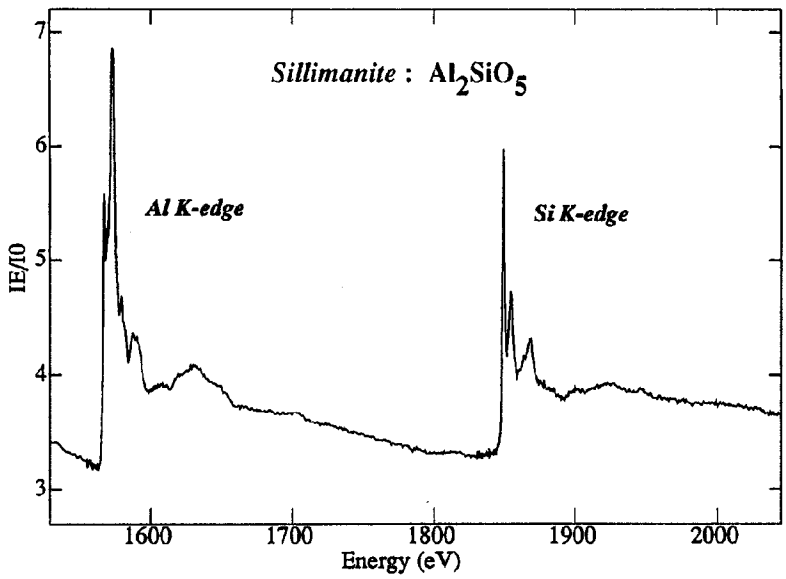

Figure 3. An experimental XAFS spectrum of Sillimanite, Al_2SiO_5.

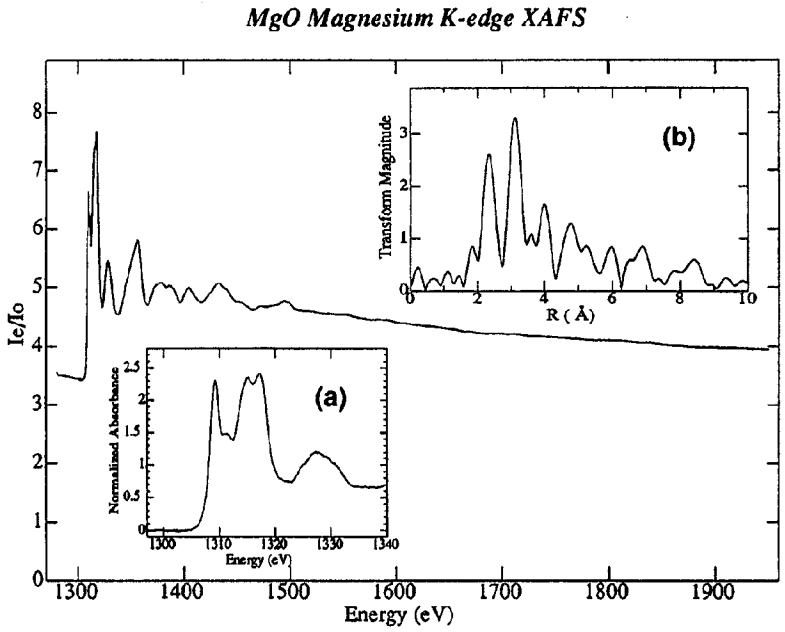

Figure 4. An experimental XAFS spectrum of MgO. Insets: (a) normalized XANES and (b) k-weighted Fourier transform of the extracted EXAFS signal showing radial structure to 6 Å.

above 1800 eV. Finally, YB_{66} may also have significant impact in catalysis, mineralogy and possibly environmental and biological sciences. ■

Acknowledgments

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