K X-Ray Absorption Spectrum of a Single Crystal of Germanium*

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The extended fine structure on the short wavelength side of the K x-ray absorption edge of Ge in a thin single crystal of Ge has been studied by using a double-crystal spectrometer. Extended structure was obtained out to 300 ev from the main edge. Positions of the structure observed are given.

INTRODUCTION

ACCORDING to the Kronig theory[1] of extended structure in x-ray absorption edges of crystalline solids, a study using polarized x-rays incident on a single-crystal absorber should be more meaningful than the usual procedure using unpolarized x-rays and a polycrystalline absorber. Attempts at such measurements have met with limited success.[2,3]

Nelson, in this laboratory, recently attempted to study the germanium K edge with a double-crystal spectrometer utilizing a germanium single crystal both as the absorber and as the second analyzer. He found no extended structure. This same experimental technique was also used in the previously cited investigations and suffers from several important disadvantages: (1) Few crystals are perfect enough to give optimum resolution. (2) The experimenter has no control over absorber thickness. (3) The incident intensity I_0 cannot be measured. The appearance of a plot of transmitted intensity I *vs* wavelength λ is strongly dependent on the absorber thickness. To correctly indicate the variation of absorption coefficient with wavelength, $\ln(I_0/I)$ should be plotted *vs* λ. Because of the advantages of a transmission-type experiment, in which the absorber can be removed from the beam at will, it was decided to prepare a single crystal of germanium thin enough for transmission absorption measurements and to investigate the fine structure observed with this arrangment. Results reported here are for unpolarized x-rays. A later experiment with polarized x-rays is projected.

EXPERIMENTAL

Various means of preparing a single-crystal germanium absorber of the desired thickness (about 20 μ) were investigated. Vacuum evaporation, electrodeposition, and thermal dissociation were considered and discarded in favor of thinning a bulk single crystal. The original crystal was 15×15×1 mm, of p-type (indium concentration 0.16 ppm), and had been cut with faces parallel within a few degrees to the (111) planes.[4] The crystal was waxed to a brass plate and lapped to a thickness of about 100 μ. It was then removed from the plug and waxed over a hole in a glass microscope slide and chemically etched to the desired thickness. A modified CP-4 etch was used, consisting of 25 parts nitric acid, 15 parts hydrofluoric acid, 25 parts acetic acid, and 2–3 drops of bromine. The etching was done by dipping the crystal into the etch solution contained in a shallow Teflon dish. The thickness was checked periodically by placing the foil in a monochromatic x-ray beam.

The double-crystal spectrometer employing Geiger counter registration was of the Ross type and has been described elsewhere.[5] For the wavelength of the Ge K edge, the spectrometer was used in air without a bell jar. A Machlett (AEG-50-T)W target tube was used as source. Cleavage faces of calcite were used in the (1,+1) position. They gave a (1,−1) rocking curve at 1.54 A which had a full width at half maximum of 15 sec.

This arrangement, of course, did not yield polarized x-rays. It was considered desirable to run the simpler nonpolarized experiment first to determine the extent of the structure in the germanium K edge of a single-crystal absorber.

The x-ray tube with tungsten target was operated at 21 kv and 46 ma. The tungsten $L\gamma_1$ line served as a convenient reference line about 177 electron volts from the edge. In passing over the line, aluminum absorbers were introduced to keep the counting rate below 100 counts/sec, making a dead time correction unnecessary. For a typical run, I_0 was about 50 counts/sec including 1.6 counts/sec background; I varied from 26 to 5 counts/sec on the long- and short-wavelength sides, respectively, including a background of 0.9 count/sec. At each angular setting, 5000 counts were taken for I_0, 5000 for I, and another 5000 for I_0. This gave a standard deviation of about 1% for points on the short-

TABLE I. Structure positions in electron volts relative to the center of the main edge.

	A	α	B	β	C	γ	D	δ	E	ϵ	F	ζ
Present work	6.7	15.7	25.2	31.7	48	61	79	114	147	186	223	271
Hulubei and Cauchois	5.7	14.6	20	28	39	47	77	108	157	193	225	287
Beeman and Friedman	4.3	16										

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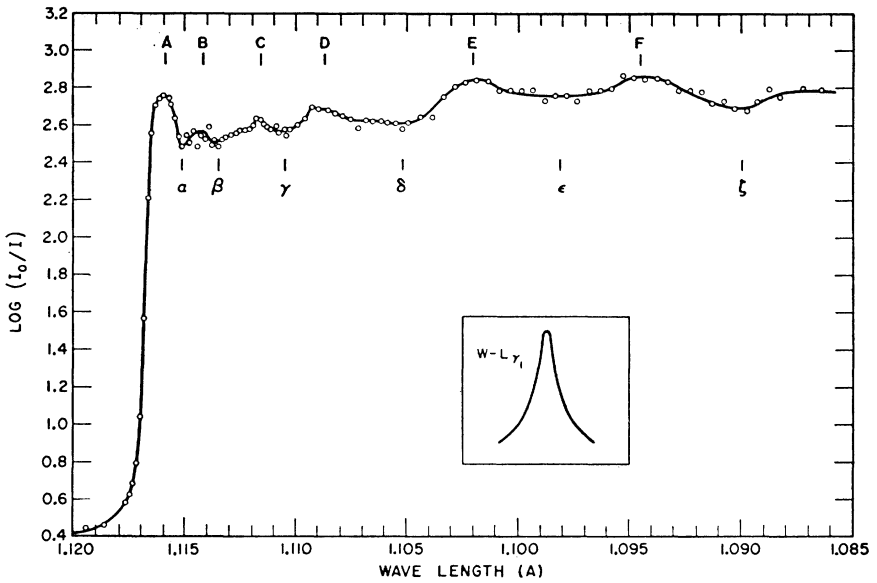

FIG. 1. Fine structure of the Ge *K* edge. Logarithm of the ratio of incident to transmitted intensity as a function of wavelength.

wavelength side of the edge. Three runs were made to 300 ev and one to 60 ev. Shifting the general area of the absorber covered by the beam between two runs had no effect on the results.

RESULTS

The germanium *K* edge shows structure extending 300 ev from the edge. The curve in Fig. 1 is a composite of all runs; the points are from run II. The maxima and minima of absorption are labeled with capital letters and small Greek letters, respectively. Their positions in electron volts, relative to the inflection point of the main edge, are given in Table I. Also given for comparison are the values reported by Hulubei and Cauchois.[6] The closest structure only was covered by Beeman and Friedman[7] and the positions listed in Table I, deemed comparable to our *A* and α, are estimated from their curve.

DISCUSSION

To the writers' knowledge, the only investigations of the germanium *K* edge are those by Beeman and Friedman[7] and Hulubei and Cauchois.[6] The former made a study of the shape of the edge itself (out to only 20 ev) using a double-crystal spectrometer and an absorber in the form of powder. Hulubei and Cauchois worked with a curved-crystal spectrometer, photographic registration, and (presumably) a polycrystalline absorber. Their observed structure was given in tabulated form only and no curves or intensity data were presented. The agreement between the present work and that of Hulubei and Cauchois, beyond 80 ev, is considered quite good in so far as the position of the structure is concerned. The different methods used in the two investigations might introduce some discrepancies especially since a single crystal absorber was used in the present work. Agreement with the work of Beeman and Friedman is inconclusive since their results did not extend very far beyond the edge.

Of particular interest is the absorption maximum *A*. This maximum, while not so pronounced as is observed in some insulators, is more pronounced than that observed for such metals as copper. The extended structure ($D-\zeta$) beyond 80 ev is quite broad in its general aspects compared to copper.

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