

K X-Ray Absorption Spectra of Germanium in Crystalline and in Amorphous GeO₂

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The Ge K x-ray absorption spectrum was measured in three forms of GeO₂: hexagonal crystalline, tetragonal crystalline, and amorphous. From the measured results it is concluded that either the Kronig explanation of the extended fine structure observed in the spectra needs to be modified or the "glassy" GeO₂ is actually crystalline in character over small regions, i.e., the amorphous GeO₂ has a high degree of short-range order identical to that of the hexagonal crystalline form.

INTRODUCTION

THE Kronig¹ explanation of the fluctuations in the x-ray absorption coefficient observed on the high-energy (short wavelength) side of a major absorption discontinuity is dependent upon the crystalline character (periodicity) of the absorber. In this approach, the electron ejected in the absorption process is considered to be essentially "free," i.e., it is treated as a conduction electron whose motion is only slightly affected by the potential field of individual atoms inside the crystal. Using this concept, Kronig solved the Schrödinger equation for an electron moving in a periodic potential field (whose period is that of the crystal lattice) by a perturbation calculation. The calculation indicates the energies "forbidden" to the ejected electron and, for a simple cubic lattice, these energies are given by the familiar expression

$$E = \hbar^2(\alpha^2 + \beta^2 + \gamma^2) / 8md^2 \cos^2\theta,$$

where \hbar is Planck's constant, m is the electronic mass, (α, β, γ) characterize a crystallographic plane, d is the interplanar spacing of planes (α, β, γ) , and θ is the angle between the electron momentum vector and the normal to the planes (α, β, γ) .

Although the Kronig theory gives a plausible qualitative explanation for some of the observed coefficient fluctuations, particularly for fluctuations which are energetically some distance (~ 100 eV) from the main discontinuity, it is inadequate in many respects as has been discussed in the literature. Several modifications or alternatives have been proposed to account for the observed fluctuations.²⁻⁴ Of these, the most interesting is that due to Shiraiwa, *et al.*⁴

In this modification, the ejected electron is considered to be scattered by the adjacent atoms in the solid, i.e., the phenomenon is treated as a collision scattering problem. The electron is again represented by a plane wave function which is, however, multiplied by an attenuating factor to take account of the energy losses incurred in the inelastic collisions of the electron with neighboring atoms. One of the consequences of this treatment is that the fine structure observed may be dependent only on the atoms in the neighborhood of the absorbing atom. This would be true if the interactions between the ejected electron and the adjacent scattering atoms were largely inelastic, i.e., if the electron is never really very "free" in the lattice as is required by the Kronig assumption.

The most direct way to test the validity of the Kronig theory would be to use polarized x rays and a single-crystal absorber. This has been tried without much success to date.⁵⁻⁹ As an alternative way to test the Kronig theory, the authors decided to measure the absorption coefficient fluctuations in a glass and compare these with measurements on the same material in crystalline form since any fluctuations which depend directly upon long-range order should not appear for the amorphous form. This would enable one to identify the energy region over which the Kronig assumption is valid. The GeO₂ system was chosen since there are two crystalline forms (hexagonal and tetragonal) and pure GeO₂ can also be made into a glass.

EXPERIMENTAL PROCEDURE

The measurements were made at room temperature using a G.E. XRD-3 diffractometer with a NaCl single crystal as the monochromator and with a 1° takeoff slit

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¹ R. de L. Kronig, *Z. Physik* **75**, 191 (1932).

² T. Hayashi, *Sci. Repts. Tôhoku Univ. Ser. 1*, **33**, 123, 183 (1949); **34**, 185 (1950).

³ A. L. Kostarev, *Zhur. Eksp. i Teoret. Fiz.* **11**, 60 (1941); **19**, 413 (1949); **21**, 917 (1951).

⁴ T. Shiraiwa, T. Ishimura, and M. Sawada, *J. Phys. Soc. Japan* **13**, 847 (1958); T. Shiraiwa, *ibid.* **15**, 240 (1960).

⁵ S. T. Stephenson, *Phys. Rev.* **44**, 349 (1933).

⁶ R. Krogstad, W. Nelson, and S. T. Stephenson, *Phys. Rev.* **92**, 1394 (1953).

⁷ W. F. Nelson, Ph.D. thesis, Washington State College, 1956 (unpublished); available from University Microfilms, Ann Arbor, Michigan.

⁸ J. M. El-Hussaini and S. T. Stephenson, *Phys. Rev.* **109**, 51 (1958).

⁹ J. N. Singh, *Phys. Rev.* **123**, 1724 (1961).

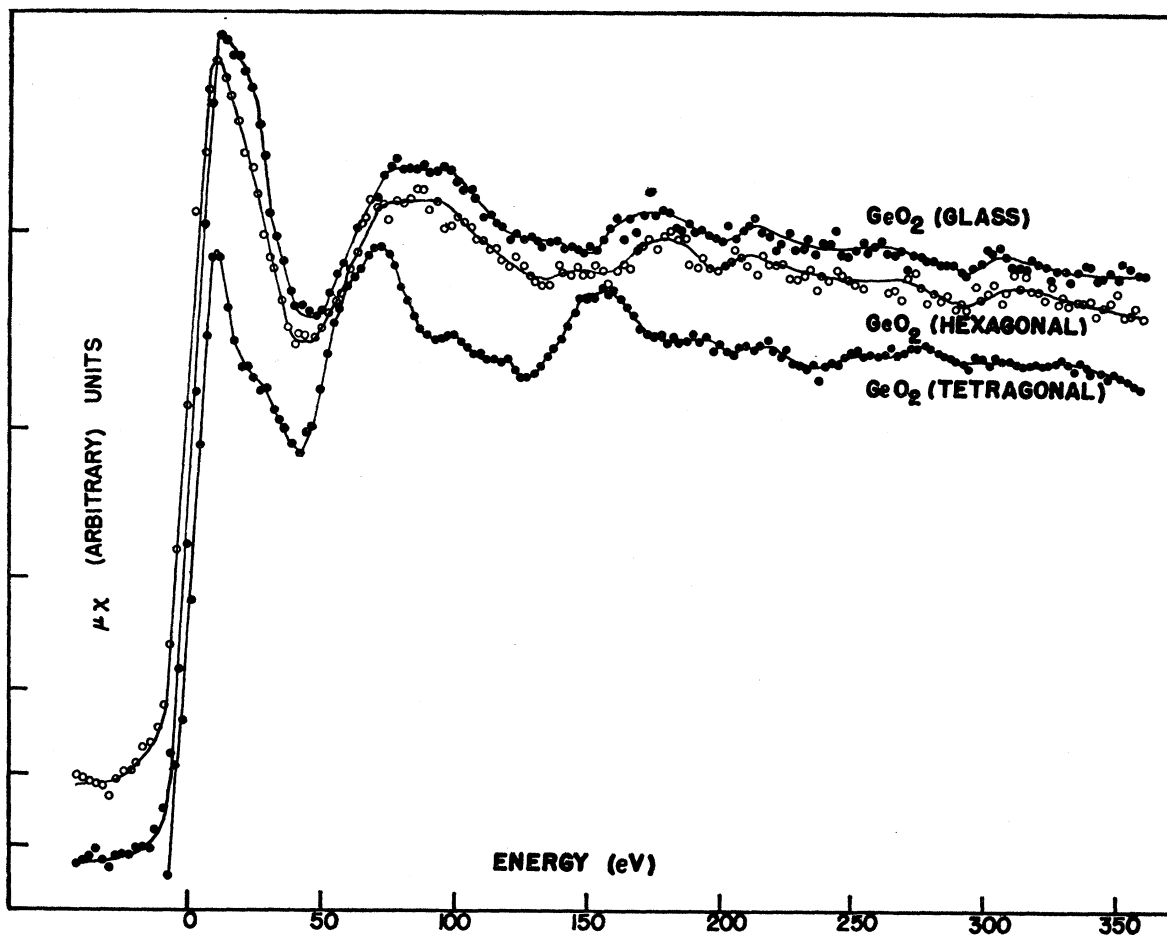


FIG. 1. K x-ray absorption spectra of Ge in crystalline and in amorphous GeO_2 . The ordinate is μx , where μ is the linear absorption coefficient and x is the sample thickness measured normally to the incident x-ray beam. The abscissa is the energy of the incident x rays. The zero of energy is taken at the midpoint (half-height value) of the initial discontinuity. The positions of the midpoints for the three curves coincide within the experimental accuracy of the data.

and a 0.02° detector slit. Data were taken manually by alternately recording the time for 10^4 counts with the sample in the x-ray beam and out of the beam at each angular setting. The angular increments used were $2\theta = 0.005$ deg.

The samples were prepared in the form of a powder which was uniformly spread over the adhesive side of cellophane tape. A GeO_2 thickness of approximately 0.003 in. was used. The uniformity of samples prepared in this fashion was checked in earlier measurements on the Fe edge in Fe-containing glasses by grinding a piece of the glass to the same thickness as the powder samples. The results from the ground-glass sample and the equivalent powder sample were identical within the accuracy of our measurements.

The GeO_2 used was Eagle-Picher electronic grade which is 0.99999+ pure. This material is supplied in the form of the hexagonal crystalline powder. The tetragonal GeO_2 was made by converting the hexagonal form to the tetragonal form in a hydrothermal bomb in the

manner described by Laubengayer and Morton.¹⁰ The glass was made by melting and quenching the hexagonal form. All three forms were identified by x-ray diffraction.

DISCUSSION OF RESULTS

The results of our measurements are shown in Fig. 1. The data are not corrected for the "thickness effect"¹¹ and other corrections usually made when analyzing data obtained with a two-crystal spectrometer. The curves have been normalized in the manner of Van Nordstrand¹² to facilitate comparisons.

From the figure, we see that the two crystalline forms of GeO_2 give fluctuations in the absorption coefficient which are markedly different from each other. This

¹⁰ A. W. Laubengayer and D. S. Morton, *J. Am. Chem. Soc.* **54**, 2303 (1932).

¹¹ L. G. Parratt, C. F. Hempstead, and E. L. Jossem, *Phys. Rev.* **105**, 1228 (1957).

¹² R. A. Van Nordstrand, in *Non-Crystalline Solids*, edited by V. D. Fréchet (John Wiley & Sons, Inc., New York, 1960), p. 168.

result can be expected from the viewpoint of either the original Kronig theory or from its modifications due to Shiraiwa *et al.*⁴ The most interesting result is the fluctuation pattern for the GeO₂ glass or amorphous form. From the figure, we see that, within the limits of the measurements, the pattern is identical to that for the hexagonal crystalline modification. A similar result was found for "amorphous" and crystalline Ge by Shiraiwa.⁴

On the basis of the Kronig theory, this is a somewhat surprising result since the GeO₂ glass was distinctly amorphous as determined by ordinary x-ray diffraction while the hexagonal crystalline modification was indeed crystalline. Thus, although it may not be surprising that there are fluctuations for the amorphous GeO₂ out to 300 eV in energy, it is surprising that the fluctuations are identical with those for the crystalline form since electrons of this energy should begin to be affected by the differences in long-range order between the two materials if the "free" electron approximation of Kronig is valid.

On the other hand, on the basis of the Shiraiwa modification of Kronig's theory, which allows for all of the fine structure to be caused by nearest or next-nearest neighbors, the result is reasonable. But even here, the fact that the results are identical is still a little surprising because this would seem to indicate a requirement for not only the same coordination but, in fact, exactly the same symmetry and spacing for at least the first or second configuration shells in both the crystalline GeO₂ and the GeO₂ glass. In other words, a truly random network concept of the Zachariasen-Warren type¹³ does not seem applicable to the GeO₂ glass, at least as far as can be determined from a measurement of this type. At the same time, the ordinary x-ray diffraction measurements indicate that there is really no extensive long-range order in the amorphous sample.

Although we do not make the unequivocal claim that the GeO₂ glass is "crystalline" when examined on a sufficiently localized scale, the present results do suggest such a possibility. Furthermore, infrared measurements

¹³ W. H. Zachariasen, *J. Am. Chem. Soc.* **54**, 3841 (1932); B. E. Warren, *J. Appl. Phys.* **8**, 645 (1937).

made on the two crystalline forms and on the amorphous form of GeO₂ by Obukhov-Denisov *et al.*¹⁴ give similar results, i.e., both the infrared and Raman spectra of the glass and the hexagonal form are quite similar while the spectrum for the tetragonal form is completely different.

Recent measurements by Lytle¹⁵ of the x-ray absorption spectra of Cu and Ni at cryogenic temperatures lead him to the conclusion that if the Kronig explanation is correct, it is necessary to consider the Bragg reflection of the ejected electron to occur at planes of extremely high Miller indices, i.e., very small interplanar spacings and therefore rather short distances from the absorbing atom. If the GeO₂ glass is, in fact, crystalline on a localized scale, the Kronig explanation might still be valid if one accepts Lytle's interpretation since reflection from higher-index planes would not require any long-range order in the sample. Furthermore, utilizing the higher-order planes makes the Kronig and Shiraiwa theories essentially equivalent since diffraction is only a special type of scattering.

CONCLUSIONS

Our results suggest that the study of x-ray absorption spectra in glasses offers a new way to check the validity of theories of the observed fine structure which require long-range order and also might help characterize what is termed the "amorphous" or "glassy" state of matter.

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¹⁴ V. V. Obukhov-Denisov, N. N. Sobolev, and V. P. Chermisinov, *Optics and Spectroscopy* **8**, 267 (1960). See also E. R. Lippincott, A. Van Valkenburg, C. C. Weir, and E. N. Bunting, *J. Research Natl. Bur. Standards* **61**, 61 (1958).

¹⁵ F. W. Lytle, Boeing Scientific Research Laboratories Report DL-82-0164, Seattle, Washington, 1961 (unpublished); See also *Developments of Applied Spectroscopy* (Plenum Press, New York, to be published), Vol. 2.