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Secondary Structure in the K Absorption Limit of Germanium Tetrachloride

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An experimental determination of the fine structure of the K absorption limit of $GeCl_4$ has been made under conditions of high resolving power with the two-crystal spectrometer. Both position and magnitude of the structure were obtained for comparison with the theory of Hartree, Kronig, and Petersen and with their theory as modified by Corson (following paper).

CONSIDERABLE secondary structure appears in the x-ray absorption edges of solids, liquids, and gases within a few volts of the edge. In the spectral region in which work on gases has been done the resolving power on an energy scale must be high if the experiments are to show the natural structure. The photographic spectrometers used for studies of gases have had rather low resolving power, with the result that data have not been gathered near the absorption limit with this equipment.[1,2]

With the development of accurate means of low x-ray intensity measurement, the application of the two-crystal spectrometer became practicable and it was possible not only to determine the position of the fine structure, but to measure its intensity through the absorption limit.[3–5]

The theory of the fine structure as developed by Kronig[6] and Petersen[7] has been applied most rigorously to gaseous $GeCl_4$.[8] This gas was chosen by these authors for several reasons: The absorption limit of germanium is in a convenient x-ray region, the gas is stable and easily handled, the chlorines are sufficiently massive to provide good scattering of the ejected photoelectrons, the molecule is symmetrical, and the Hartree field has been calculated accurately for chlorine.

The present work is a study of the fine structure of the germanium K absorption limit in gaseous $GeCl_4$, and a comparison with theory of both the position and intensity of the fine structure.

EXPERIMENTAL

The double-crystal spectrometer and G-M counter intensity recorder are described in former communications.[4,9] A slight change, however, was made in recording the data. Repeated tests have shown the x-ray intensity to be constant to about two percent over a period of several hours. The remainder of the equipment likewise is stable enough that the spectral distribution curve with absorber in may be obtained and then a determination of the incident radiation made with absorber out. The necessity for moving the rather bulky absorption cell between each reading is thereby eliminated.

A gold target electroplated on a copper target base served as the source of continuous radiation. With the "perfect" calcite crystals of Class I[10] used in these experiments the continuous spectrum at 35 kv and 20 ma gave about 15,000 counts per minute in the G-M counter.

The absorption cell was the in-blown glass window type, with an absorption path of some 7 cm. It was mounted in a thermally insulated envelope in such a way that its temperature could be maintained at about 65°C by a stream of thermostatically regulated air. At this temperature, the vapor pressure of $GeCl_4$ is about 390 mm.[11] To insure that no droplets of liquid were gathered on the cell windows, streams of the warm air were made to play directly on the windows. The temperature of the cell was measured by a thermocouple placed in contact with the cell itself.

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[9] J. A. Bearden and C. H. Shaw, Phys. Rev. **48**, 18 (1935).
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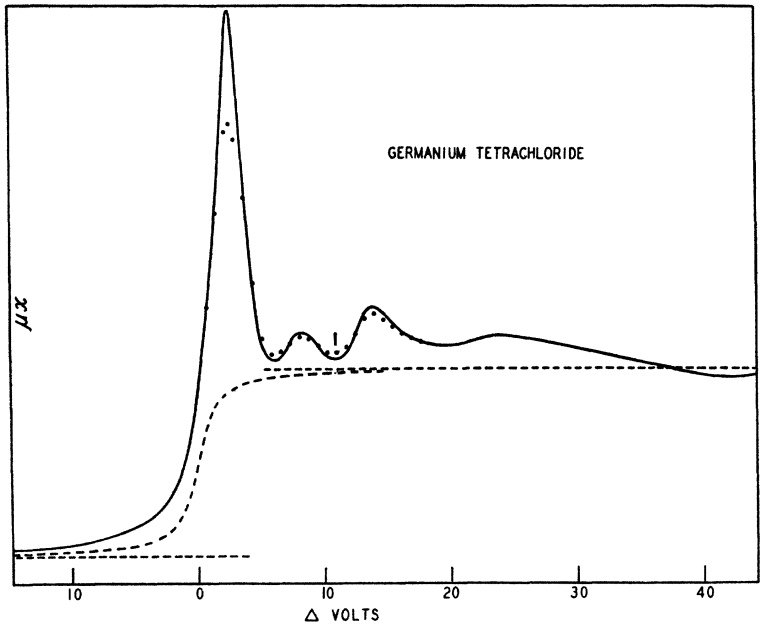

FIG. 1. The absorption coefficient in arbitrary units for the K absorption limits of the free germanium atom (dashed line) and of the germanium atom in $GeCl_4$ (solid line) as a function of energy separation from the edge.

As a final check that the temperature and hence the gas pressure were constant throughout the run, the intensity at a chosen wave-length was observed periodically. Three runs were made with absorber in, and two with absorber out. The intensity of the incident radiation varied with wave-length considerably, because of emission lines from the gold target. Calibrated aluminum absorbers were used to reduce the intensity when the counting rate rose above the linear region of the counter.

Absorption of x-rays in the windows of the cell was measured with the $GeCl_4$ frozen out by air cooled to dry ice temperature.

Former work has shown that at this wave-length the correction for second-order radiation from the target is unnecessary.[12]

RESULTS

The absorption coefficient as a function of energy as shown in Fig. 1 was obtained as follows: The two experimental curves of incident intensity and transmitted intensity as a function of wave-length were plotted and the average curve in each case drawn through the experimental points. The necessary corrections for counter base line and absorption in windows were made on these curves, and the logarithm of the quotient of the curves was taken. The dots in Fig. 1 represent this curve where it differs from the solid line which was obtained after correction of the data for the diffraction pattern of the spectrometer crystals.[10] The short vertical line indicates the estimated experimental error. Figure 1 shows experimental results to 40 volts from the absorption edge. The remainder to 180 volts is shown in Fig. 1 of the succeeding paper by E. M. Corson.

Kronig's theory gives the relation between the absorption coefficient of an atom bound in a molecule to that of the free atom. In order to compare experiment with theory, correction must be made for the absorption by the chlorines in the $GeCl_4$. This is most readily accomplished by using the experimental values of the absorption jump as determined by S. J. M. Allen[13] to locate the germanium absorption base line. The absorption jump for germanium was interpolated to be 7.95 from the data given for adjacent

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atomic numbers. The base line for germanium absorption is the abscissa of Fig. 1.

Since no GeH_4 was available, it was not possible to determine the shape of the absorption edge for the germanium atom directly, but there is no reason to expect that it would be much different from that for the bromine or krypton atom. On the assumption that the true absorption edge width for the germanium atom is 2.10 volts, the average of those for bromine and krypton,[4] the dashed curve in Fig. 1 was constructed. The relative positions of the absorption edges were fixed arbitrarily. It is obvious that the large absorption peak introduces uncertainty in the position of the edge. In fact if a shift of the initial rise for the molecule of about 6 volts toward lower energies were assumed, the discrepancy between experiment and theory for the major peak intensity (following paper) disappears without very much affecting the remainder of the structure. Had GeH_4 been available, a measure of the shift would have been made experimentally.

Because of the high resolving power, structure appears which has not been detected previously. This structure, of finer detail than the remainder, appears within some 15 volts of the absorption edge.

The ratio of the absorption coefficient of the germanium atom in $GeCl_4$ to that of the free atom is given in Fig. 1 of the following paper to an ejection energy of 180 volts, together with the theoretical results of HKP and the theoretical modification of Corson. Experiment and theory agree for the position of the fine structure from 80 to 180 volts. In contrast with the results of Coster and Klamer[2] the experimental and predicted positions of the absorption minimum α fail to coincide by practically 20 volts. A decrease in resolving power would have the effect of shifting the observed absorption minimum α to larger voltages, which would account for these authors' better agreement with theory.

The following paper reconsiders the Kronig-Petersen theory in the light of different assumptions for the distribution of the chlorine atoms in the molecule.

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The Theory of the Fine Structure of X-Ray Absorption Limits in Polyatomic Molecules†

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The theory of the fine structure of x-ray absorption limits in polyatomic molecules is developed in a form which takes molecular configuration into account, and it is found that the Petersen formula represents a limiting case. The fine structure of the K-absorption limit is calculated for several molecular models, in particular that of Ge in $GeCl_4$, for which comparison is made with the previous calculation of Hartree, Kronig, and Petersen, and the newer experimental results obtained by Shaw.

INTRODUCTION

X-RAY fine structure, which in the case of polyatomic molecules may extend over a region of several hundred volts on the high frequency side of the edge, was first explained by Kronig[1] on the basis of the interference between the direct wave representing the ejected photoelectron, and the components scattered by the partner atoms. This interference modifies the amplitude of the wave, and thereby the transition

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