within the experimental precision. This, however, does not rule out the possibility of its existence which could only be established by more precise measurements.

The comparison of the present data with that of Schein, Jesse, and Wollan[2] shows that the curves A and B at 22° North magnetic latitude are consistently lower at the higher elevations, thus exhibiting a definite latitude effect on mesotrons passing through 8 cm of lead. This is in agreement with recent measurements of Bhabha and his collaborators[3] who also found a latitude effect of the same order of magnitude on the mesotron component.

The author acknowledges with thanks the valuable suggestions and criticism given by Professor Marcel Schein. The author also wishes to express his thanks to the R.A.F. for putting at his disposal one of their Mosquito aircraft in which the flights were made.

[3] H. J. Bhabha, S. V. Chandrashekhar Aiya, H. E. Hoteko, and R. C. Saxena, Phys. Rev. **68**, 147 (1945).

PHYSICAL REVIEW VOLUME 71, NUMBER 2 JANUARY 15, 1947

X-Ray Absorption Structure of $GeCl_4$ and $AsCl_3$*

S. T. STEPHENSON
State College of Washington, Pullman, Washington
(Received October 31, 1946)

The fine structure on the short wave-length side of the K x-ray absorption edges of Ge and As in $GeCl_4$ and $AsCl_3$ has been measured with a double crystal spectrometer having resolution sufficient to resolve all structure predicted by theory. The results are compared with the theory and with previous measurements made with spectrographs of lower resolving power. Structure is obtained closer to the edge than that resolved heretofore, which structure is not altogether in agreement with the theory.

INTRODUCTION

THE fine structure to be found on the short wave-length side of the x-ray absorption edge of a molecular gas was explained by Kronig[1] in terms of the scattering of the ejected electron by neighboring atoms in the molecule. The probability of the ejection of the electron, and consequently the absorption coefficient, is found to be dependent upon the energy with which the electron leaves the parent atom. Kronig's general arguments have been summarized by Snyder and Shaw[2] and applied to the Br_2 molecule which had been shown to have a pronounced structure.[3–5] The theory was in agreement with the experimental structure near the edge in so far as position was concerned but not as regards the intensity. Structure which was predicted for positions further from the edge was not observed.

Perhaps the most detailed theoretical calculation of the fine structure for a gaseous molecule is that made for the germanium edge in $GeCl_4$ by Hartree, Kronig, and Petersen.[6] $GeCl_4$ has been studied experimentally by Coster and Klamer[7] and by Drynski and Smoluchowski.[8] Agreement between theory and experiment was acceptable at an energy separation of 50 volts and more from the main edge. Unfortunately, the experiments were carried out using a photographic spectrograph of low resolving power; consequently, the several pronounced structures nearer to the edge than 50 volts which were predicted by theory could not be checked experimentally. $AsCl_3$ was also considered by Hartree,

* This work was carried out as part of Contract N6ori-167, Task Order II with the U. S. Navy Office of Naval Research.

[1] R. de L. Kronig, Zeits. f. Physik **75**, 468 (1932).
[2] T. M. Snyder and C. H. Shaw, Phys. Rev. **57**, 882 (1940).
[3] S. T. Stephenson, Phys. Rev. **50**, 790 (1936).
[4] B. Cioffari, Phys. Rev. **51**, 630 (1937).
[5] C. H. Shaw, Phys. Rev. **57**, 877 (1940).
[6] D. R. Hartree, R. de L. Kronig, and H. Petersen, Physica **1**, 895 (1934).
[7] D. Coster and G. H. Klamer, Physica **1**, 889 (1934).
[8] T. Drynski and R. Smoluchowski, Physica **6**, 929 (1939).

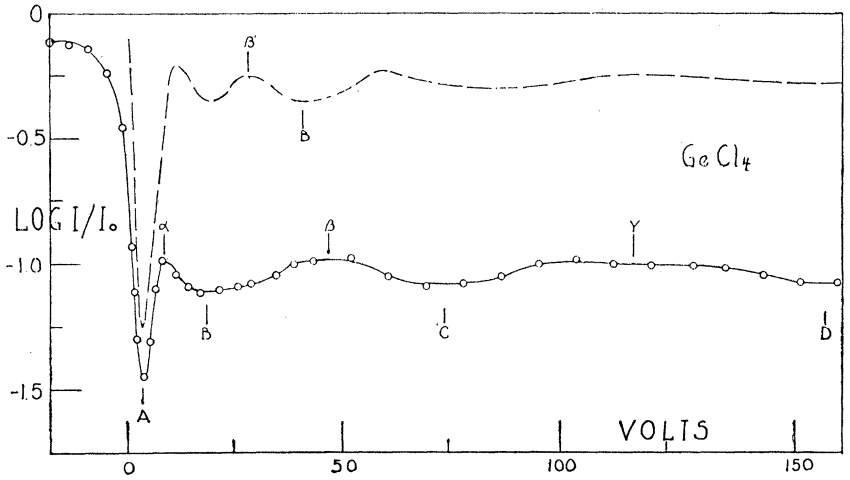

FIG. 1. K x-ray absorption edge of Ge in $GeCl_4$. The circles on the solid line are experimental points. The broken line represents theory drawn to an arbitrary and displaced $\log I/I_0$ scale.

Kronig, and Petersen and was measured by Coster and Klamer. It is the purpose of this paper to present experimental results on $GeCl_4$ and $AsCl_3$ as obtained with a double crystal spectrometer having resolving power adequate to check all predictions of the theory. A better understanding of the relatively simple case of absorption structure for molecules is perhaps necessary before one can expect quantitative agreement between theory and experiment on absorption structure for the more complicated case of the solid state.

EXPERIMENTAL

The double crystal spectrometer is of the type described by Ross[9] constructed from a good Societé Genevoise optical spectrometer. The circular scale on the table for crystal B could be read to a second of arc by means of microscopes with micrometer eyepieces. The ways on which crystal A was mounted were part of a comparator. The crystals were split from one piece of optical quality calcite and were the same pair used previously.[3] Since that time they have been etched with HCl.[10] As finally used the crystals gave a $(1, -1)$ curve at ca. 1116 x.u. of 13 seconds full width at half-maximum. X-ray intensities were measured with a Geiger-Mueller counter of the type sold commercially by the Cyclotron Specialties Company. Counting rates ranged from as high as ten counts per second on the low absorption side to as low as four counts per second on the high absorption side including a natural count of 2.3 counts per second. The x-ray background and natural count together were about 2.9 counts per second with crystal B turned some 10° away from the position for reflection. From four to ten thousand counts were registered for each point in a run. A total of six runs were made for $GeCl_4$ and four runs for $AsCl_3$. In order to make certain that the incident intensity was constant throughout the region covered by a run, blank runs were made without any absorber in the beam.

The $GeCl_4$ and $AsCl_3$ were sealed in glass absorption cells 10 cm long and 3 cm in diameter with thin windows blown on each end. The cells were placed in a small electric furnace. The furnace windows were of double walled Cellophane and the furnace windings were placed near the windows in such a fashion that no condensation of vapor was noted on the thin glass walls of the cell. The temperature in the furnace was taken with a thermocouple and kept nearly constant with a Variac control. The temperature of the vapor was about 45°C for $GeCl_4$ and 75°C for $AsCl_3$. The absorption cells were placed between crystals A and B. In order to make sure that variations in the thin windows were not contributing to the structure the cells were moved slightly between runs or moved end for end.

The source of x-rays was a commercial General Electric CA-6 x-ray tube, with molybdenum target and beryllium window, run at 23,000 volts and 35 milliamperes. The voltage

[9] P. A. Ross, Rev. Sci. Inst. **3**, 253 (1932).
[10] K. V. Manning, Rev. Sci. Inst. **5**, 316 (1934).

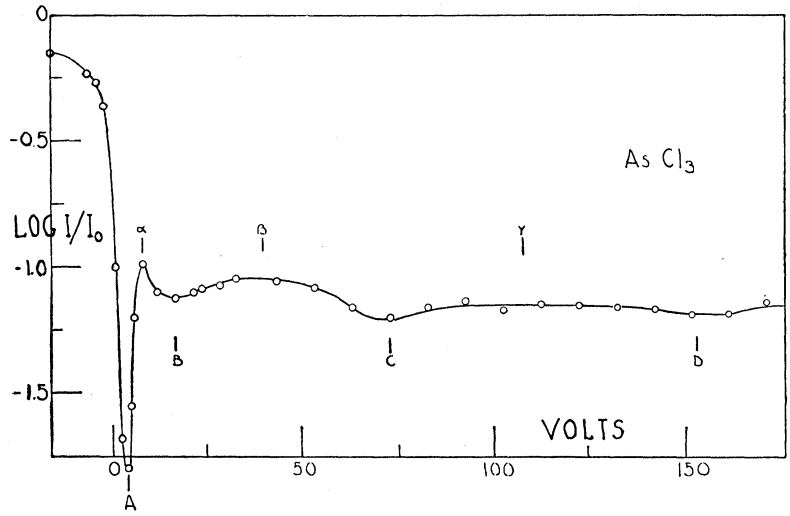

FIG. 2. K x-ray absorption edge of As in $AsCl_3$. The circles on the solid line are experimental points.

was read on a microammeter in series with a resistor of 10^9 ohms. The power supply was a conventional full wave rectifier with 0.2 mf capacity for smoothing. The control was by means of a Variac supplied through a commercial voltage stabilizer so that voltage variations were less than one percent.

RESULTS

Figure 1 shows the averaged data obtained on the six runs for $GeCl_4$. The temperature of the furnace and the position of the absorbing tube were changed between runs; most of the scattering of points results from the difficulty in correcting for the former together with small variations caused by the latter. Similarly Fig. 2 presents data for four runs over $AsCl_3$. The scale of $\log I/I_0$ is arbitrary as follows: I was readily obtained by subtraction of the natural count and x-ray background from the recorded intensity. I_0, however, could not be obtained directly because of the absorption in the chlorine. A blank run with absorption tube and furnace windows alone would not yield I_0 because the chlorine, of course, goes with the germanium or arsenic. It was finally decided to choose I_0 so that the ratio of the average $\log I/I_0$ on the high absorption side of the edge to that on the low absorption side was about eight,[11] a value of the jump ratio characteristic of elements near Ge and As in the periodic table.

[11] J. B. Platt, Phys. Rev. 69, 337 (1946).

The distances (in volts) from the center (point of inflection) of the main edge of the structure observed are given in Table I together with the predictions of theory and previous experimental results.

The uncorrected edge widths, defined as the distance between points where the $\log I/I_0$ curve reaches $\frac{1}{4}$ and $\frac{3}{4}$ of the asymptotic values, are 2 volts in each case.

DISCUSSION

It is immediately apparent from an inspection of the figures and table that the double crystal spectrometer reveals several pronounced features of the fine structure which were not observed in earlier photographic studies. The first absorption minimum recorded heretofore nearly coincides with the feature β in the present work. The agreement with previous experimental results at distances of 45 volts and more from the edge is satisfactory when one considers that the structure is very broad in this region and can hardly be placed to closer than 10 volts. Structure beyond D is very weak and hardly exceeds experimental error. Also experimental error is larger beyond D because of slight tungsten filament evaporation which causes $WL\gamma_1$, to appear about 176 volts from the Ge edge and $WL\gamma_4$ about 195 volts from the As edge.

To aid in comparison of the experimental data with the theoretical predictions of Hartree, Kronig, and Petersen the theoretical curve (with an arbitrary and displaced $\log I/I_0$ scale) is

redrawn from their paper and appears in Fig. 1. Strictly speaking the theoretical curve is for the ratio of the absorption coefficient for Ge in $GeCl_4$ to the absorption coefficient for an isolated Ge atom. However, the absorption edge for an isolated Ge atom probably departs from a symmetrical curve only within a very few (about 5) volts of the short wave-length side of the edge and there only slightly because of the narrow atomic optical levels and the broad K state (compare krypton and bromine[5]). Consequently the features of the theoretical curve should be directly comparable with the experimental results except as regards some uncertainty concerning the magnitude of the first absorption maximum A. There is acceptable agreement between theory and experiment, 50 volts and more from the edge, as has been pointed out previously. The predicted structure within 50 volts could not be resolved in the earlier studies. The present experimental results are not in agreement with certain predictions of the theory in this range. In particular, the resolution is quite adequate to detect β^1 and B^1 but these features were not observed; instead these features are lumped together in a broad β. The agreement for A and α is perhaps as close as could be expected. According to theory the pronounced structure at A is caused by the behavior of δ_l, the phase constant expressing the phase shift of the electron wave of angular momentum l scattered by a Cl atom, for an l of 1. Theory predicts a value of π at zero energy instead of 2π and a deep sharp structure. The experiments do, in fact, show A to be the most pronounced feature of the fine structure; β^1 and B^1 have their theoretical origin chiefly in the behavior of δ_l for an l of 2 and it is here that the chief disagreement with experiment is noted.

TABLE I. Energy positions in volts of fine structure maxima and minima as measured from the point of inflection of the main edge.

Structure	Present work	Theory[a]	Previous experiment Ref.[b]	Previous experiment Ref.[c]	Present work	Previous experiment[b]
	$GeCl_4$				$AsCl_3$	
A	3.4	2.8			3.8	
α	8.5	10.5			7.5	
B	18	19		16	17	
β^1		27				
B^1		40				
β	46	59	50	48	39	48
C	74	85	86	79	72	73
γ	117	117	120	110	107	104
D	157	155	160	160	153	138
δ		196	203	208		181
E			257	258		224

[a] Reference 6.
[b] Reference 7.
[c] Reference 8.

The experimental results for $AsCl_3$ are quite similar to those for $GeCl_4$ except that the structures are a little closer to the edge. Hartree, Kronig, and Petersen[6] point out that the structure for $AsCl_3$ should be positioned the same as that for $GeCl_4$ if a factor involving the ratio of the squares of the nuclear separations is applied. Experiment indicates, therefore, that the distance from Ge to Cl atoms is somewhat less than from As to Cl atoms. It is further expected[6] that the fluctuations in absorption coefficient should be less for $AsCl_3$, with 3 chlorine atoms to scatter the ejected electron waves, than for $GeCl_4$ with 4 scattering chlorine atoms. It is not considered that the experimental data are sufficiently precise to test this point definitely although the structure seems weaker beyond B for $AsCl_3$. However, A appears more pronounced for $AsCl_3$ than $GeCl_4$ and this is regarded as a true effect larger than experimental variations.