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The Absolute Absorption Coefficient of Germanium and the Fine Structure in the K Edge of Some of its Compounds*

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The fine structure of the K absorption limit of Ge in GeH_4, Ge_2H_6, $GeCl_4$, and $GeBr_4$ has been obtained with absolute values under conditions of high resolution with a double crystal x-ray spectrometer. Results are compared with existent theory and previous measurements and discrepancies are pointed out. The question of the location of an absorption edge is considered along with the Kossel structure appearing in the germanium hydrides.

I. INTRODUCTION

UNDER high resolution the absorption edges of particular elements frequently exhibit a fine structure which depends not only on the element in question, but also on the compound of which the element may be a part, and on the physical state of the material.

Monatomic gases possess a Kossel structure[1] arising in transitions from inner levels to optical levels. Depending on the width of the inner level, the separation of the appropriate valence levels, and the resolving power of the spectrometer, a pronounced structure extending over a few volts may appear as in the case of argon,[2] or no structure whatever may be resolved as in the case of krypton.[3]

The Kossel structure may equally well exist in gaseous molecules, but the optical levels for the atom in question would be considerably modified by the molecular field. Moreover, such structure may be obscured by a more prominent type of structure of a different origin (see below).

When the absorbing element occurs in the solid state or is part of a solid compound, structure may extend over a few hundred volts. A theoretical explanation has been given by Kronig in terms of the Bragg reflection at the lattice planes.[4]

Interference effects may occur with gaseous molecules also to give rise to a fine structure to which we shall refer as "Kronig" structure. (The structure in crystals referred to above has generally been designated as Kronig structure.) Structure of this type has been studied in the diatomic molecules, bromine,[3,5–7] and chlorine,[7,8] and in the polyatomic molecules, arsenic trichloride[9,10] and germanium tetrachloride.[9–12] Bromine and chlorine display a single pronounced peak inasmuch as successive ones expected are too small to distinguish from experimental error. A number of maxima and minima occur in the polyatomic molecules $AsCl_3$, $GeCl_4$, $GeBr_4$, and similar compounds where the structure remains quite detectable even beyond the seventh peak. A theoretical calculation of the fine structure to be expected in a gaseous molecule has been carried out most completely[13] for $GeCl_4$. The electron wave originating in the photoelectric absorption process will be scattered by the other atoms in the molecule giving rise to a reflected wave superimposed on the outgoing wave. The probability of transition between the bound K state of the electron and the free state where it has kinetic energy, w, is proportional to $|P|^2$ where $P=\int \varphi_K e\dot{r}\varphi_w d\tau$.

In the case of an isolated atom this probability (as a function of energy) would decrease smoothly from some maximum value, but in a molecule it may oscillate. The wave function, φ_w, is the sum of the wave function of an escaping free electron with energy, w, and the scattered waves which cause the value of φ_w and of the integral to oscillate as the various waves interfere constructively or destructively. The absorption coefficient will therefore show an oscillation with frequency. Roughly speaking, this picture is the basis for the Kronig structure in a gaseous molecule.

While it is difficult to develop a quantitative theory for the Kronig structure in crystals, it has been possible to obtain an explicit expression for the ratio, χ, of the absorption coefficient of an atom, A, bound in a diatomic molecule, AB, to that of the isolated atom as a function of the energy of the ejected electron.[14] Moreover, if the absorbing atom, A, is contained in a polyatomic molecule, $AB_1\cdots B_i$, it can be shown[15] that the ratio, χ, is given to a good approximation by

$$\chi-1=\sum_i(\chi_i-1), \tag{1}$$

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[1] W. Kossel, Z. Physik **1**, 119 (1920).

[2] Lyman G. Parratt, Phys. Rev. **56**, 295 (1939).

[3] C. H. Shaw, Phys. Rev. **57**, 877 (1940).

[4] R. de L. Kronig, Z. Physik **70**, 317 (1931); **75**, 191 (1932).

[5] Bernard Cioffari, Phys. Rev. **51**, 630 (1937).

[6] S. T. Stephenson, Phys. Rev. **50**, 790 (1936).

[7] T. M. Snyder and C. H. Shaw, Phys. Rev. **57**, 882 (1940).

[8] A. E. Lindh, Compt. rend. **172**, 1175 (1921); dissertation, Lund (1923).

[9] D. Coster and G. H. Klamer, Physica **1**, 889 (1934).

[10] S. T. Stephenson, Phys. Rev. **71**, 84 (1947).

[11] T. D. Drynski and R. Smoluchowski, Physica **6**, 929 (1939).

[12] C. H. Shaw, Phys. Rev. **70**, 643 (1946).

[13] Hartree, Kronig, and Petersen, Physica **1**, 889 (1934).

[14] R. de L. Kronig, Z. Physik **75**, 468 (1932).

[15] H. Petersen, dissertation, Groningen; Arch. Néerland. sci. **14**, 165 (1933).

where χ_i is the value of χ to which the atom, B, would give rise if it formed a diatomic molecule with A. The fine structures are therefore additive.

The theory[14] has been applied to $GeCl_4$ because of several favorable circumstances: the scattering atoms are sufficiently massive to scatter the photoelectrons strongly; the absorption edge of the Ge atom falls in a spectral region of sufficient resolution to delineate the fine structure; the molecule is symmetrical, all four Cl atoms contributing equally; the interatomic distance of Ge–Cl is known[16] from electron diffraction experiments to be 2.10A; the atomic field of the chlorine atom has been solved; an adequate vapor density can be obtained at low enough temperatures; the gas is stable.

If one chooses the K absorption edge and restricts himself to the nonvacuum region and to regions of dispersion greater than about 3 seconds of arc per volt, the elements available are Cr ($Z=24$) to Sr ($Z=38$). Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, and Sr compounds are not easily vaporized. Kr does not ordinarily form compounds. Ga, Ge, As, Se, and Br remain to be considered. Kronig structure has been reported for $GeCl_4$, $AsCl_3$, and Br_2; gallium halides are convenient for this type of study, but the selenium compounds tend to decompose at temperatures required for suitable vapor pressures. The compounds of Ga, Ge, and As are not equally desirable. Ge compounds are preferred because they yield the most pronounced structure with four scatterers instead of three; its halides have lower boiling points; it is less dangerous to handle than arsenic; Ga seems to form no gaseous compound with hydrogen comparable to AsH_3 or GeH_4. The existence of such a gaseous hydrogen compound is required to answer the question which originally suggested this investigation.

If for $GeCl_4$ one averages the absorption coefficient through the structure on the high frequency side of the K edge one would expect intuitively that the average mass absorption coefficient would be the same as that of isolated germanium. The ideal solution to this question would involve the use of an absorption cell of monatomic germanium vapor. An evaporated film of germanium would be inadmissible because it would exhibit its own Kronig structure peculiar to its crystalline state. A close approximation to the idealized case of a monatomic vapor of germanium is germane, GeH_4, since the H atoms would not be expected to scatter by a measurable amount. One would anticipate, therefore, a structureless absorption edge with which the structure-rich germanium halides could be compared. The present work obtains the ratio of the average absolute absorption coefficient of Ge in the germanium halides to that of Ge in germane, which, as far as Kronig structure is concerned, behaves like an isolated Ge atom. The theory gives for this ratio a value between 1.1 and 1.15 on the basis of certain convenient assumptions and the omission of certain terms difficult to evaluate but which are estimated to be small in their effect. Physically, one expects this ratio to be unity and so these simplifications may need to be re-examined. The existent theoretical predictions with regard to both position and number of the maxima and minima are also compared with experiment, and the question of an absorption edge position and width considered.

II. EXPERIMENTAL

The spectrometer used was a Societé Génevoise double crystal instrument.[17] Many sets of calcites were rejected before a set giving satisfactory rocking curve and line widths was found. In each case the crystals were aligned in both the $(1, -1)$ and $(1, +1)$ positions by visual observation of the copper K_α lines on a fluorescent screen, the criterion for adjustment being the sharp appearance and disappearance of the copper lines as the second crystal was rotated. Measurements were then made on the rocking curve and $\mathrm{Cu}K_{\alpha_1}$ line widths. The set of crystals finally selected gave rocking curve widths of 10.5″ and 8.7″ at 1.54 and 1.11A, respectively, and a $(1, +1)$ $\mathrm{Cu}K_{\alpha_1}$ width of 41″, values which are within a second of the best reported values.[18]

The high voltage and x-ray tube current were electronically regulated to within 0.01 and 0.1 percent, respectively, over 4-minute intervals.[19] At a power of 22 kv and 30 ma as used, the direct intensity was about 5000 counts per two-minute interval from the continuous radiation of the tungsten target, and higher in the neighborhood of some weak tungsten emission lines. The voltage was purposely kept as low as 22 kv in order not to excite second-order radiation of 0.557A.

X-ray intensities were measured with a 30-cm chlorine-quenched argon counter (with scale of 64 and mechanical counter) over two minute intervals timed by a synchronous, motor-driven switch.

The absorption cells were of the in-blown glass window type, of soft glass, and generally with 10-cm absorption path lengths. The latter were measured accurately by means of a traveling microscope. Two fingerlike extensions were provided, the upper for attaching to a glass system for the purpose of filling the cell and the lower for freezing out the material with liquid N_2 during the sealing-off process. A mercury manometer as part of the glass system was used to read pressures for all the absorption cells except $GeBr_4$, whose vapor pressure was too low at room temperature. The purified $GeBr_4$ was added to its cell by means of an eye dropper. In all cases air was removed from the cells before sealing off. The cells were all filled at known room

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[16] R. Wierl, Ann. Physik **8**, 521 (1931).

[17] We are greatly indebted to the University of Chicago for making this instrument available to us for this work. The assistance of Professor Zachariasen in making the loan possible is highly appreciated.

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

[19] The planning and construction of the high voltage power supply were done largely by Mr. Earl H. Byerly.

temperatures to relatively low pressures:[20] GeH_4, 128.9 mm and 145.2 mm; $GeCl_4$, 99.14 mm; Ge_2H_6, 79.73 mm; Cl_2, 298.2 mm; HBr, 550.0 and 403.8 mm. (A knowledge of the mass absorption coefficients of chlorine and bromine was required in the calculations on the germanium halides.) The $GeBr_4$ cell was used at 156 mm at a temperature of approximately 145°C. The actual masses of material are in the range of 10 to 60 mg, and except for $GeBr_4$, densities were always calculated by means of the van der waals equation.

The densities represented by these conditions of temperature and pressure were so selected that all of the absorption cells except that of $GeBr_4$ would give rise to satisfactory counting rates while used at room temperature. Such low densities are preferred in maintaining counting rates far above background and in eliminating the necessity of temperature controlled ovens which other investigators have used.[9–12] For $GeBr_4$, however, with a vapor pressure of only 4 mm at room temperature, an oven had to be provided. The $GeBr_4$ cell was covered with thin asbestos paper, wound with nichrome wire and heat-insulated with glass cloth. The temperature was maintained at an estimated 20° above that required for complete evaporation of the $GeBr_4$ liquid so that temperature control was not critical. In fact, by the proper choice of the density of material in each cell no liquid phase existed, and hence there was no temperature control problem.

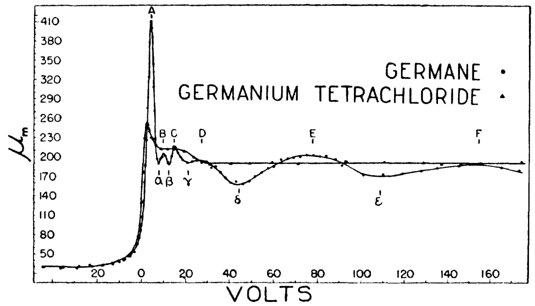

FIG. 1. Superposed graphs of the absolute absorption coefficient of Ge in GeH_4 and $GeCl_4$ as a function of energy separation from the K edge.

To insure that the cell was accurately returnable to its absorbing position in the x-ray beam, a cell holder was mounted on a platform which could translate on a track with V-shaped runways. A stop was provided and the whole structure was attached rigidly to the spectrometer posts. The cell holder had a number of degrees of freedom sufficient for optimum adjustment of the cell in the x-ray beam.

The background correction was determined by measuring the intensity while the second crystal was rotated beyond the position at which it passed diffracted radiation at both the longer and shorter wavelengths. As the second crystal was rotated beyond this position (at 1 to 1.5 Bragg angle degrees away from the Ge absorption edge setting), the background was found to be fairly constant. This extrapolated average count was taken as the background and determined similarly for I and I_0.

The determination of the absolute absorption coefficient necessarily involved a correction for the absorption of the glass windows, for the change in air path by approximately 10 cm as the cell was placed in the beam and for absorption by other atoms in the molecule. The calculation for $GeCl_4$, for example, yielded for the absolute absorption coefficient of Ge

$$\mu_{Ge}=[1/(\rho x)_{Ge}][\log(I_0/I)+\log f]-(\mu\rho x)_{Cl}/(\rho x)_{Ge},$$

where ρ denotes density, x the absorption path length, I_0 the intensity recorded by the Geiger counter without absorption cell in position, I the intensity with the cell in position, and

$$f=\exp(10\mu\rho)_{air}/\exp(\mu\rho x)_{glass}=I_1/I_0.$$

I_1 denotes the value of I with $GeCl_4$ frozen out. The ratio $(\rho x)_{Cl}/(\rho x)_{Ge}=\rho_{Cl}/\rho_{Ge}$ is determinable from the atomic weights, while the absorption coefficient of Cl (or of Br) was separately determined.

The procedure used in taking data was to measure for two minutes at each point the direct intensity, I_0, and then the intensity, I, after absorption through the cell, and to repeat a number of times until the desired accuracy could be obtained. Ten to twenty thousand counts were registered for each point on the high frequency side of the edge, and twenty-five to fifty thousand on the low frequency side. For the direct intensity forty to sixty thousand counts were recorded. Points were taken at 2″ intervals on the high peaks, and at 3″, 5″, 10″, or larger intervals elsewhere. The counts were corrected for scattered radiation, the absorption of the glass windows and of Cl, Br, or H atoms was determined, and the absorption coefficient of Ge was calculated as above. The probable error in μ arising from statistical fluctuation in counts is less than 2 percent. The relative values of μ are thus considered to be accurate to 2 percent. The absolute values, which depend on measured pressures, lengths of cells, background, absorption of glass and of other atoms in the compounds are considered to be accurate to within 3 percent.

III. RESULTS AND DISCUSSION

In Figs. 1, 2, and 3 the absolute absorption coefficient of Ge at its K edge is plotted as a function of energy for the gaseous molecules GeH_4, $GeCl_4$ (superposed with GeH_4 in order to facilitate a comparison of the magnitudes of the absorption coefficient), Ge_2H_6, and $GeBr_4$. The original data for these germanium compounds extend to about 45 v on the low frequency side and 175 v on the high frequency side of the edge. For digermane, only the significant region near the edge

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[20] Dr. Gordon K. Teal of the Bell Telephone Laboratories very kindly supplied the GeH_4 and the Ge_2H_6 needed for this investigation.

has been plotted, inasmuch as the absorption coefficient levels off to a constant value on either side.

Consider first the question of the location of an absorption edge and the determination of its width. Definite conclusions concerning the position and width of an absorption edge can be drawn, in some cases, for monatomic gases. An absorption edge of a monatomic gas is customarily established at the energy position at which transitions to the optical continuum begin. The location of this point on the energy scale requires an analysis of the absorption edge whether structure be apparent or not, the structure being designated as Kossel structure. The *K* edge of argon, for example, exhibits a pronounced absorption peak followed by some smaller maxima and minima. Paratt[2] resolved the structure into its components using the optical *p*-terms of potassium, for when a 1*s* electron is ejected into the optical levels it will find itself in a field approximating that of the element $Z+1$. Hence, all of the energy intervals between the resonance absorption lines $1s\rightarrow np$, $n>3$, are known. These absorption lines are characterized by the same width, which, since the widths of the optical levels are negligible, is also the width of the inner *K* state according to the theory of line widths.[21] From the main resonance line that width is 0.58 ev. In view of the definition of the edge position, that of argon is 2.71 ev (the ionization limit of potassium minus the energy interval between the terms 4*s* and 4*p*) from the peak of the main resonance line and to shorter wavelengths. Since the width of the main edge is essentially that of the *K* state, its width is 0.58 ev. The shape of the main edge is, moreover, an arctangent curve.[22] With position, shape, and width known, the main edge can be drawn in readily, and as a result of the resolution it is found to be located at 3.5 to 4 X.U. less than was assumed previously. (The edge was usually placed at the center of the main rise.)

Krypton does not allow such fortunate and definite conclusions. The width of its *K* state is about 2.1 ev, the optical levels of rubidium are more closely spaced, and the physical resolving power about 78 percent less. The *K* edge of krypton therefore appears as structureless. Shaw[3] made a "reasonable" resolution into components presumably from a knowledge of the optical levels and ionization potential of rubidium, with the aid of which he was able to place the main edge of krypton to perhaps within half a volt. It is important to bear in mind that the optical energy scheme of ionized krypton was fairly well known from the terms of element $Z+1$.

Another favorable circumstance sometimes occurs in the case of metals where bands of energy replace simple optical levels. If certain assumptions are approximately satisfied, one can obtain both the position and the width of the edge from the experimental absorption curve with the help of the theory of Richtmyer, Barnes, and Ramberg.[22]

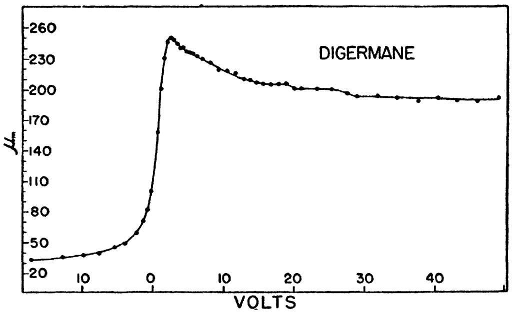

FIG. 2. The absolute absorption coefficient of Ge in Ge_2H_6 as a function of energy separation from the *K* edge.

In contrast to the examples above the germanium compounds here studied present a different picture, for in none of these cases does the electronic energy scheme appear to be known and each molecule becomes an individual problem. Nor can the theory of Richtmyer, Barnes, and Ramberg be applied. As a result no definitive statement can be made concerning the position of the Ge edge or its width, nor can a quantitative interpretation be given of the associated Kossel structure. The picture is complicated further by the presence of both Kossel and Kronig structure in some of the compounds.

In a personal communication, Professor Kronig compares the molecule GeH_4 with the krypton atom by thinking of GeH_4 as Ge^{IV-} ion in the electron shell of which four hydrogen nuclei are embedded. The absorption maximum could then be associated with the transition of the *K* electron to the 5*p*-orbit of the krypton-like system. The peak thus represents Kossel structure.

Physically, the Kossel structure exists for the four molecules of germanium studied; but, since the molecular field varies from compound to compound, it is difficult to state whether or not the spectrometer would resolve Kossel structure for all four, even in the absence of Kronig structure. The prominent Kronig structure in the halides in any case has obscured any Kossel structure that would otherwise have manifested itself. For the reasons cited above, a comparison of the

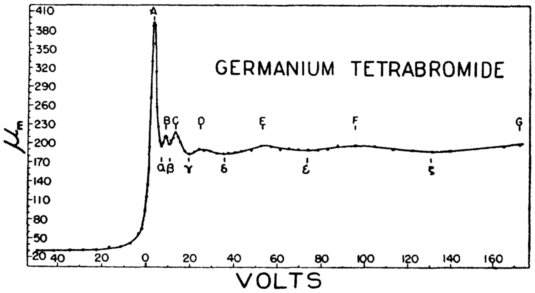

FIG. 3. The absolute absorption coefficient of Ge in $GeBr_4$ as a function of energy separation from the *K* edge.

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[21] V. Weisskopf and E. Wigner, Z. Physik **63**, 54 (1930).

[22] Richtmyer, Barnes, and Ramberg, Phys. Rev. **46**, 843 (1934).

TABLE I. Shift of arbitrarily defined edge position relative to that of GeH_4.

Substance	Shift
GeH_4	0
Ge_2H_6	0.5±0.2 volt
$GeCl_4$	0.8±0.2 volt
$GeBr_4$	0.9±0.2 volt

position of the edge in the four molecules cannot be carried out properly. However, to compare the positions of the Kronig structure with theory and previous experiment some scheme had to be adopted. It was decided for the sake of convenience to select the point representing the average absorption coefficient between the mean on the high frequency side and on the low. This point is roughly at $\mu=110$ for all the germanium compounds (and would be the point of the edge if the theory of Richtmyer, Barnes, and Ramberg applied). While this choice is arbitrary, it should be pointed out that the methods previously used to locate the edge were equally arbitrary.[9–12] Table I lists the shift to shorter wavelengths of the particular point selected using that of GeH_4 as reference.

Judging from the positions of the fine structure of the $GeCl_4$, serious discrepancies appear to exist between theory and experiment (both of which exist for this halide only). These disagreements are demonstrated under the high resolution of the double crystal x-ray spectrometer, but they escaped notice in the early experiments performed under relatively poor resolution. Table II compares the positions of the structure predicted by the theory, the present measurements, and the tabulated results of other investigators.

From Table II it is clear why it was believed earlier that experiment supported theory. Above 50 volts, experiment and theory appeared to agree quite well, but the serious disagreements occur near the edge for the most part. (Uncertainty in edge position would be a maximum of 3 volts.) If one of the first few peaks and valleys of the present work were eliminated, the same sort of agreement would arise, i.e., if peak *E* were placed in the row for peak *D*, etc. Then agreement would exist at energies in excess of 50 v (as previously found[9–11]) but still not at smaller energies. The early single crystal photographic work simply could not resolve narrow structure (the peaks *A*, *B*, *C*, and *D* extending through about 27 v tended to coalesce into a single peak), while in the double crystal work[10] several factors operated against proper detection of structure: (1) a rocking curve width of as much as 13″ (the predominant factor), (2) probable temperature fluctuations due to the use of a Variac-controlled oven, (3) moving the absorption position of the cell slightly between runs. The rocking curve width should be in the neighborhood of 8″ for best results, an oven need not be used, and the cell is best not disturbed during runs.

TABLE II. Comparison with theory and previous experiments of energy positions in volts of the fine structure maxima and minima for $GeCl_4$; and present values for $GeBr_4$.

Structure[a]	Present work[b]	Theory[c]	Ref.[d]	Ref.[e]	Ref.[f]	$GeBr_4$ present work
A	3.85	2.8			3.4	3.26
α	7.41	10.5			8.5	6.82
B	9.48	19		16	18	8.75
β	11.8	27				10.6
C	14.4	40				13.2
γ	20.8	59	50	48	46	19.3
D	26.9	85	86	79	74	24.6
δ	43.8	117	120	110	117	35.6
E	77.3	155	160	160	157	53.0
ϵ	108	196	203	208		73.7
F	154		257	258		95.8
ζ						131
G						172

[a] *A*, *B*, *C*, etc. refer to absorption maxima; α, β, γ, etc., refer to absorption minima.

[b] The values were calculated using a dispersion of 6.95 seconds/volt at 1114 X.U. and 6.72 seconds/volt at 1096 X.U., being based upon the newest physical constants listed by J. W. M. DuMond and E. R. Cohen, Revs. Modern Phys. 20, 82 (1948).

[c] Reference 13.

[d] Reference 9.

[e] Reference 11.

[f] Reference 10.

Shaw[12] has also obtained the curve for $GeCl_4$ and with very fine resolution, but not with the absolute absorption coefficient. As did Stephenson, Shaw used for the jump of the absorption coefficient at the edge a value interpolated from adjacent atomic numbers, but that value (7.95) now appears to be in error (see below). He did not tabulate the positions of the structure, but from inspection his maxima and minima agree fairly well in position with those reported here for $GeCl_4$.

TABLE III. Experimental values of mass absorption coefficients at Ge *K* edge.

Substance	Value
Ge, low frequency side	30.5±3%
Ge, high frequency side	191.0±3%
Chlorine	42.6±1%
Rate of change approximately	0.23% per 8.6 volts
Bromine	36.1±1%
Rate of change approximately	0.21% per 8.6 volts

The discrepancy between theory and experiment goes beyond the positions of the maxima and minima and their numbers, for as stated earlier the average χ has a theoretical value of 1.1 to 1.15. As one averages out the structure over a sufficient energy interval, one expects physically a value of unity for χ and Fig. 1 shows the average value of χ to be unity within experimental error. The same conclusion holds in comparing $GeBr_4$ with GeH_4 or Ge_2H_6 with GeH_4. The magnitudes found for the mass absorption coefficients of Ge, Cl, and Br at the wave length of the Ge *K* edge (1114 X.U.) are shown in Table III. The mass absorption coefficient of Ge at its *K* edge jumps by a factor of 6.3 instead of 8 as previously assumed.

Among the factors contributing to the disagreement between theory and experiment, probably the most serious is the assumption that the ejected electron finds itself in the field of a purely neutral chlorine atom, or in reality, of four such atoms. Another potential source of error may occur in the approximation leading to the additive result in Eq. (1). It was estimated by Petersen[15] that a double summation, quite laborious to evaluate, which takes account of molecular configuration, could be neglected, leading to this additive result.

Digermane represents an interesting case in that one would expect to see results similar to the Kossel structure peak of GeH_4 and at the same time at least a single Kronig structure peak as found for Cl_2 or Br_2. The experimental curve shows a peak at the same energy position as found for GeH_4, but it is of greater width with two "steps" suggesting a washed out structure. Any Kronig structure contribution can only be a small, wide maximum.

Structure for the two germanium halides presents similar features; but the positions of the structure are closer together for the tetrabromide (Table II), and the amplitudes for the latter are in general smaller. While it is true that the more massive bromine atoms ought to scatter more effectively, the increase in internuclear distance leads to the reverse effect. Until the correct fields of the bromine atoms in $GeBr_4$ are known, the fine structure cannot be calculated and so the experimental results are not compared with theory.

In view of the results obtained, it appears that the theory needs revision before it can be relied upon for quantitative predictions. The theoretical value of the ratio of the average absorption coefficient of Ge in the polyatomic molecule, $GeCl_4$, to that of the isolated atom is too high; the number and positions of the theoretically predicted maxima and minima are not in agreement with experiment. In addition the correct location of the position of the Ge edge and the determination of its width require first a resolution and analysis of the experimental curve.

The author wishes to express his gratitude to Professor J. A. Bearden, under whose direction this work was carried out. It is a pleasure to acknowledge helpful discussions with Professor R. de L. Kronig, Dr. G. L. Rogosa, and Dr. G. Schwarz. Thanks are also due to Dr. T. H. Berlin for valuable suggestions regarding the manuscript.

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Particle Spin and Rotation

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It is proposed to treat the spin of a particle phenomenologically by considering the particle as a small rotating sphere, the rotation of which is described by euler parameters. If the rotation is quantized in the space of the euler parameters, one obtains both integral and half-integral values for the spin. In this way one arrives at a formalism in which the spin components can be represented as differential operators in the Schroedinger representation.

FROM the standpoint of group theory, the spin of an electron is connected with the two-valued representations of the rotation group in three dimensions. In the present paper an attempt is made to investigate some properties of a model in which this connection is used.

1. ROTATION PARAMETERS

Let us consider a free particle with spin as a small rotating rigid sphere. Let us take two cartesian coordinate systems with origins at the center of the sphere, one, XYZ, with axes having fixed directions in space, the other, $X'Y'Z'$, rigidly attached to the sphere. To describe the rotation of the sphere one can make use of the euler angles θ, φ, ψ, where θ is the angle between the Z and Z' axes, φ is the angle between the Y axis and the intersection of the XY and $X'Y'$ planes, and ψ is the angle between the latter and the Y' axis. However, for the present purpose we shall introduce instead the euler parameters[1] defined by the relations

$$\begin{aligned}\xi&=\sin\tfrac{1}{2}\theta\,\sin\tfrac{1}{2}(\psi-\varphi),\\ \eta&=\sin\tfrac{1}{2}\theta\,\cos\tfrac{1}{2}(\psi-\varphi),\\ \zeta&=\cos\tfrac{1}{2}\theta\,\sin\tfrac{1}{2}(\psi+\varphi),\\ \chi&=\cos\tfrac{1}{2}\theta\,\cos\tfrac{1}{2}(\psi+\varphi),\end{aligned}\tag{1}$$

so that

$$\xi^2+\eta^2+\zeta^2+\chi^2=1.\tag{2}$$

In terms of these parameters, the direction cosines of the $X'Y'Z'$ axes relative to the XYZ axes are homogeneous quadratic functions,[1] so that changing the signs of all the parameters leaves the orientation of the sphere unchanged.

For the sake of greater generality and convenience, let us now take four new parameters ξ_k ($k=1$, 2, 3, 4)

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[1] E. T. Whittaker, *Analytical Dynamics* (Cambridge University Press, London, 1937, or New York, 1944), pp. 8–16.