Determination of the Energy Gap of LiD by Small-Angle Compton Scattering*

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X rays incoherently scattered by electrons at angles of a few degrees transfer energies to them which amount to only a few eV. If the electrons have binding energies of the same order of magnitude, interesting effects are expected which will change the usual form of the Compton spectrum. Theoretical considerations show that in the case of a conductor the spectrum starts from the position of the primary line with the form of a straight line and continues as an inverse parabola. In the case of an insulator the spectrum will show an abrupt limit on the side towards the primary radiation. The energy transfer corresponding to the edge is equal to the energy gap. The present paper describes experiments which allow the determination of the energy gap of LiD by this method. Cu $K\beta$ rays scattered by polycrystalline LiD at 18° were analyzed in a spectrometer employing a Soller slit and a $(22\bar{4}3)$ quartz crystal as an analyzer. At this scattering angle the intense diffraction peaks are avoided so that the spectrum of the scattered radiation consists only of thermal diffuse scattering and Compton scattering. By comparing it with the spectrum produced in copper by fluorescence, the two components were separated. The experiment was then repeated with metallic lithium, in which the Compton component starts exactly at the wavelength of the primary radiation. The two Compton profiles show a shift which is put equal to the energy gap. The resulting value is 5.4±0.8 eV.

1. INTRODUCTION

IN the Compton effect, energy is transferred to the electron with which the photon interacts. In the case of x rays scattered at angles of a few degrees, the energy transfer will amount to only a few eV. With such small values interesting effects are expected if the electron is a valence electron because its binding energy is of comparable magnitude. These effects consist in a change of the usual form of the Compton spectrum and allow, to some extent, the investigation of the state of the electrons involved in the scattering. We give here a short description of the results of the relevant theories and experiments.

A. Form of the Compton Spectrum

Let us consider the Compton spectrum in the idealized case of a strictly monochromatic primary radiation. If the scattering occurs at a certain angle φ from a free, stationary electron, the energy transferred to the electron is uniquely determined and the resulting spectrum is a line shifted towards longer wavelengths. We will call this energy shift W_c. If the electron is in a bound state, the energy transfer for a given scattering angle is not uniquely determined but may take various values with the result that the Compton line is broadened to a band. The profile of this Compton band depends on the type of binding of the electron. We will consider mainly weak binding.

(*a*) *Electron bound to a free atom.* If we consider an electron in a certain initial state, each different quantity of energy transferred will bring it to a different final state. In the present case the states can be either bound states or, for larger energy transfers, ionized states. The resulting spectrum $\sigma(\varphi,W)$ will consist of a number of lines and a band (Fig. 1). The lines are due to transitions to a final state which is also bound. They have been predicted for a long time and, lately, experimentally verified.[1] The band is produced by scattering processes in which the transition occurs to a final state in which the electron is free. It will have an abrupt limit towards the side of small energy transfers at a position at which the energy transfer W is equal to the binding energy A of the electron in the initial state. This limit, although observable,[2,3] has not been experimentally verified yet but may be the cause of the abrupt change of the background intensity seen in the scattering spectrum of graphite.[4] It has also been shown that the maximum of the intensity of the Compton band occurs[5] within a few percent of $W=W_c$.

(*b*) *Electron in the valence band of a conductor.* In a conductor all weakly bound electrons are in the unfilled valence band and the resulting Compton spectrum is an inverse parabola.[6] The parabola is symmetrical around W_c and reaches up to a point $W_{\max}$ which can be calculated from the momentum of the electrons at the Fermi surface. However, in scattering events involving small energy transfers, not all electrons can participate because, for many of them, the final state is occupied. The number of electrons contributing to the Compton scattering has been calculated for the case of a valence band in which the electrons behave as a free-electron gas.[7,8] The spectrum

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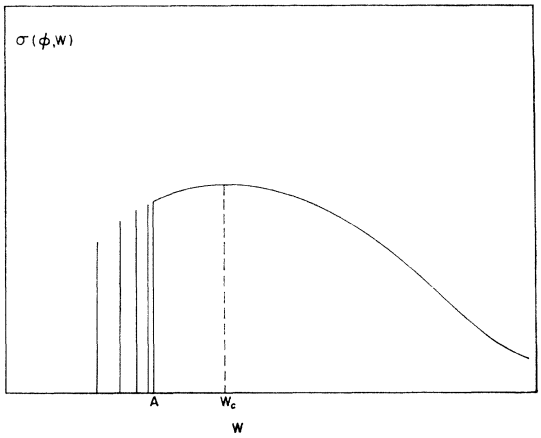

FIG. 1. Compton spectrum of an electron bound to a free atom.

in this case has been calculated[9,10] to have the form of an inverse parabola with a linear start (Fig. 2). The linear part reaches the parabola at

$$W_0=(2E^2/mc^2)[(c/E)p_F\sin(\varphi/2)-\sin^2(\varphi/2)],$$

where E is the energy of the primary photon and p_F is the Fermi momentum. Theoretical calculations show that the Coulomb correlation between the electrons should deform the profile[10] described previously. Recent measurements[11] on metallic Li seem to coincide better with the profile of Fig. 2 than with the deformed profile.

(*c*) *Electrons in the valence band of an insulator.* As in the case of a conductor, not all electrons in the valence band of an insulator can participate in the scattering act. If we consider diminishing energy transfers, the number of electrons participating will decrease

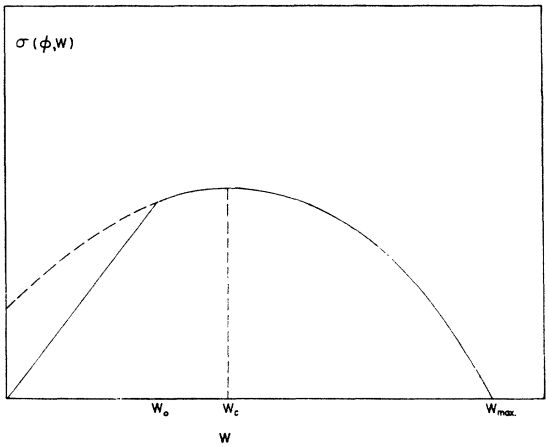

FIG. 2. Compton spectrum of valence electrons of a conductor.

and will become equal to zero when $W=E_g$ where E_g is the energy gap.

Hence the spectrum should show a limit at $W_{\min}=E_g$. If the conduction band does not overlap the higher bands, the spectrum should show also a limit towards large energy shifts at $W_{\max}=E_g+E_v+E_c$, where E_v and E_c are the widths of the valence band and conduction band, respectively (Fig. 3). No shift of the boundaries should occur with changing scattering angle. The low-energy limit $W_{\min}$ has been detected in the case of diamond.[12] The ordinate $\sigma(\varphi,W)$ for a given value of W will depend on the densities of all pairs of states (i.e., initial and final) that are compatible with the energy shift W. No calculation of the form of the Compton band for insulators exists. It is expected[1] that in the case of both conductors and insulators, if the conduction band overlaps higher bands, the Compton

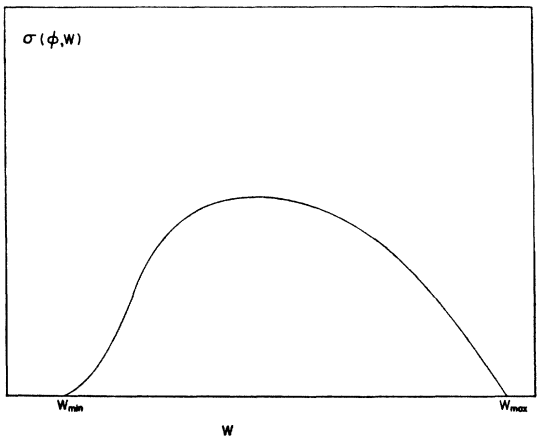

FIG. 3. Schematic Compton spectrum of valence electrons of an insulator.

spectrum will extend beyond the value mentioned for $W_{\max}$ and will show a structure corresponding to the "Kronig structure" in x-ray absorption.

B. Spectrum of the Total Diffuse Scattering

The radiation scattered on a crystalline body contains three components:

(a) The coherently scattered radiation with a spectrum identical to that of the primary radiation. Because of interference this component is intense only in certain directions in which it gives sharp maxima, and is zero in all other directions.

(b) The thermal diffuse scattering (TDS) which for all practical purposes has the same spectrum as the primary radiation. Because of interference it shows maxima in the same directions as (a), but the scattering also extends over all directions.

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(c) The Compton scattering which is incoherent and does not give any interference effects. By avoiding the scattering angles for which the maxima appear, only the last two components are obtained.

In the above consideration, the primary radiation was assumed to be monochromatic. In reality the spectrum of the primary radiation consists of a general background on which a spectral line with a natural width of a few eV is superposed.

C. Present Experimental Method

In the present paper an attempt is made to obtain experimentally the energy gap E_g of the insulator LiD (lithium deuteride) by determining the short-wavelength limit of the Compton band. The choice of a hydrogen compound was indicated because of its small absorption. LiD was preferred to LiH because it was obtainable in a pure form (99% versus 95%). Cu $K\beta$

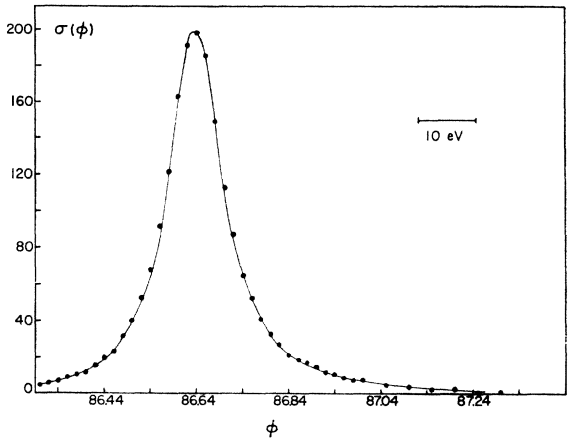

FIG. 4. Profile of the primary radiation.

rays were scattered from a very pure specimen of polycrystalline LiD[13] at an angle of 18°. Under these conditions the Compton radiation and TDS overlap. We have already noted that TDS and the primary radiation have practically the same spectrum. Hence a dummy experiment has to be devised which will allow the subtraction of the primary from the total spectrum. The Compton spectrum, thus obtained, is distorted because the primary radiation is not strictly monochromatic and because of profile errors introduced by the spectrometer. The experimental curve should hence be corrected by convolution techniques before its limit towards small energy shifts can be determined. Instead of this the energy gap was determined by comparing the uncorrected curve for LiD with a similar curve for metallic lithium taken with the same primary spectrum and with the same profile errors. In metallic

[13] Courtesy of F. Pretzel, Los Alamos Scientific Laboratory of the University of California.

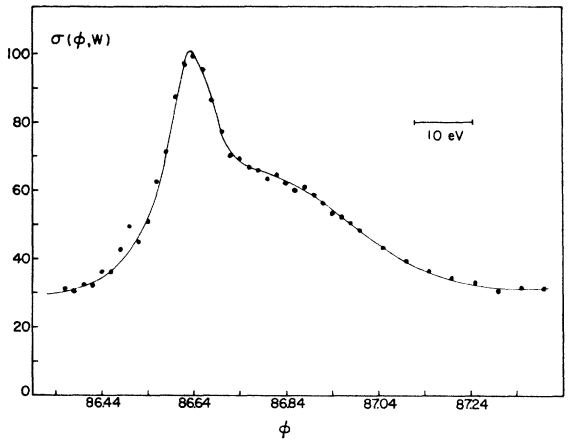

FIG. 5. Profile of the radiation scattered on LiD.

lithium the Compton spectrum starts at the position of the primary line (see Fig. 2) so that the shift of the limits of the two curves should correspond to the desired energy gap.

2. EXPERIMENTS AND RESULTS

A copper x-ray tube (24 mA, 40 kV, both stabilized) irradiated a slab of scatterer covered with a 5-μ Mylar foil from a distance of 10 cm. The scattered radiation entered a Soller system (length 25 cm, 100 channels of 100-μ width) and left with a divergence of 46 mdeg. The scattered radiation was analyzed on a Philips diffractometer with a finely ground (2243) quartz crystal and a Geiger counter. At each setting of the diffractometer a preset number of counts was measured. After recording the time, the diffractometer was turned to a new setting. The scattering angle between consecutive measurements differed by 0.02°. The recording of the time and the setting to the new position were automatic. The scattering experiments were carried out with the Cu $K\beta$ line. This line, although less

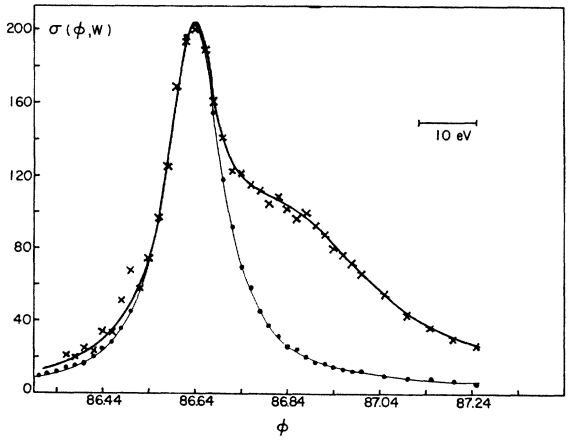

FIG. 6. Comparison of primary radiation and radiation scattered on LiD.

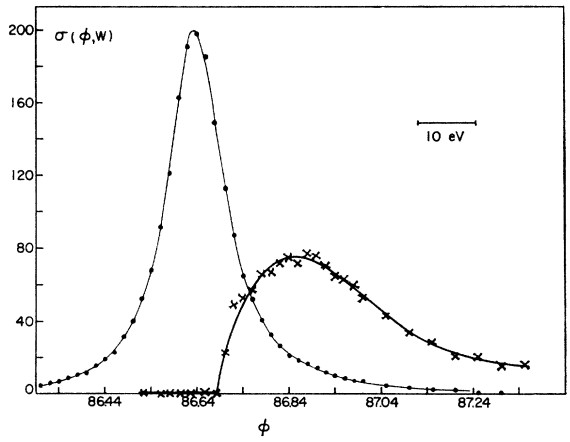

FIG. 7. Comparison of primary (i.e., TDS) and Compton radiation for LID.

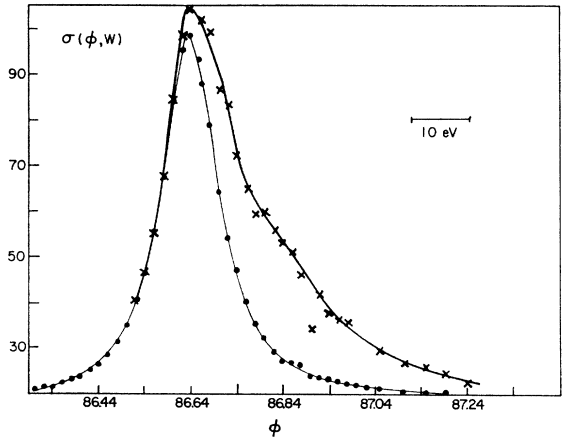

FIG. 9. Comparison of primary radiation and radiation scattered on Li.

intense than the Cu $K\alpha_1$ line, has the advantage of having no other line on the side of large wavelengths, that otherwise would coincide with the Compton band. The spectrum of the total scattered radiation was found to depend to some extent on the way the Soller system was illuminated. As the Compton spectrum is obtained by separating the primary from the total scattered radiation, it was imperative to illuminate the spectrometer in all experiments in exactly the same way. For this reason it was found advisable not to use the direct beam from the tube for the dummy experiment because this kind of source (line source) would give a different kind of profile error for the primary spectrum. The correct procedure was to use a source of primary radiation that would be at the same position as the scatterer and that would be distributed in space in the same way. For this purpose, we used a mixture of paraffin and very fine copper powder obtained electrolytically. The concentration was such as to imitate a material of the same absorption coefficient as the scatterer. Upon irradiation from a tungsten tube, the copper fluoresced and constituted a radiation source of the same spatial distribution as the scatterer had in the main experiment. The fluorescent radiation also had the advantage of being free of any Compton component. The result is given in Fig. 4. The width at half-value is 0.14°, corresponding to 11.9±0.6 eV which is larger than the natural width, 6.3 eV. As the divergence of the beam leaving the Soller system is only 46 mdeg, other factors (such as nonuniform illumination of the Soller system, etc.) must have deformed the spectrum.

The results from LiD are given in Figs. 5, 6, and 7. Each curve represents the result of six consecutive runs through the spectrum, each point corresponding to 6000 counts. The spectrum of the radiation scattered on LiD is given in Fig. 5. It is obvious that this spectrum consists of a TDS component similar to the primary radiation and a Compton component shifted towards larger angles. In order to separate the two components a suitable reduction of the scale of the ordinates of Fig. 4 is necessary so that it will fit the curve of Fig. 5 in the region where the Compton scattering is negligible. This evidently is true in the

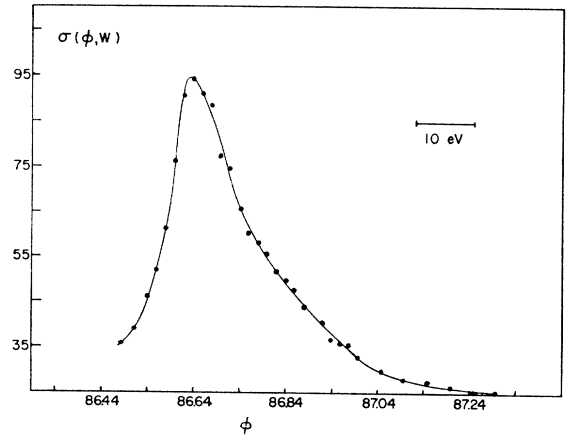

FIG. 8. Profile of radiation scattered on Li.

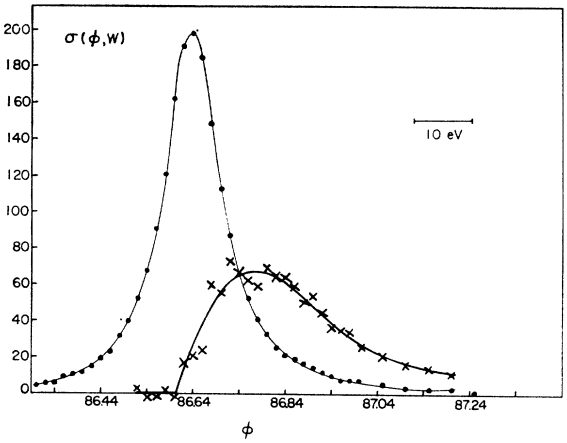

FIG. 10. Comparison of primary (i.e., TDS) and Compton radiation for Li.

region of the left flank of the curve where, according to theory, the Compton component will not yet have developed an important intensity. The existence of a region free of Compton scattering can be investigated by calculating the ratio of the ordinates of Figs. 4 and 5 after subtracting the continuous backgrounds. We found by this method that, in effect, the ratio was constant on a considerable region of the left flank. By using this constant value as a scale factor, Figs. 4 and 5 can be plotted together (Fig. 6). They show good fit on the left side of the picture and a Compton component on the right. On Fig. 7 the two components have been drawn separately. The Compton spectrum shows a rather well-defined limit on the side of the short wavelengths. Figures 8, 9, and 10 represent the corresponding results for metallic lithium. We notice that, also in this case, the Compton component shows a well-defined limit (Fig. 10), but it is shifted towards shorter wavelengths than in Fig. 7 by 0.065°. The difference between the two limits gives an energy gap of 5.4 eV. The error is evaluated to ±0.8 eV. The curves of the Compton component in Figs. 7 and 10 cannot be compared directly with any theoretical curve of the Compton spectrum because, as mentioned, they are distorted. We notice that their general forms are similar but their widths differ by 15%. As the distorting effects are the same in both cases, we conclude that the Compton profile of LiD is wider than that of Li.

The effects of distortion can be evaluated in an approximate way, by the method proposed by Lord Rayleigh.[14] The deconvolution will give a sharper cutoff, a steeper and more rectilinear flank on the left side, a sharper maximum and minor changes of the form on the right side. The general form, however, will not change much.

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Shapes of Impurity Absorption Bands in Solids*†

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Optical-absorption line shapes arising from interaction of the electronic states of impurities with the vibrational modes of the crystal are considered. It is shown that this line shape may be expressed as an N-fold convolution integral, where each element of the convolution is the line shape due to a single vibrational mode of the ground state of the system. Two types of vibrational modes, linear and quadratic, are considered in detail in both the semiclassical approximation and quantum mechanically. It is shown that the semiclassical approximation, although often of use for linear interactions, has limited validity for quadratic modes. Formal methods are developed for performing the convolution integral to obtain the line shape due to a number of vibrational modes. Explicit numerical examples are presented.

I. INTRODUCTION

PREVIOUS work on the influence of lattice vibrations on impurity absorption bands has centered largely on the simplest possible model of the lattice-impurity interaction, i.e., a linear interaction. Such a model was first considered by Muto,[1] Huang and Rhys,[2] and Pekar.[3] Their calculations were extended and formalized in an elegant paper by Lax[4] and later by O'Rourke.[5] This model has been successful in explaining the general features of the absorption line shape for several impurity centers.

For many impurity centers of interest, this simple model will not be wholly adequate. In particular, if the impurity site is a center of inversion, the linear interaction will vanish by symmetry for half of the vibrational modes (those of odd parity); and, for these modes, a quadratic interaction will dominate. Previously, such modes have been considered only in the so-called semiclassical approximation or in perturbation theory. In this work, the first thorough quantum treatment of line shapes due to quadratic modes is presented. The complications of quadratic modes are such that the

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