the magnetic field, will cause much larger admixtures when the direction of the field is not parallel to the symmetry axis of the site. The fact that the $(g_N)_{||}$ values for both isotopes are close to the expected values, while $(g_N)_\perp$ for ^{153}Eu is greatly different, confirms this expectation. If good values for the nuclear g values can be obtained, it should be possible to calculate a rough value

of the separation of the $|\pm\frac{1}{2}\rangle$ doublet from the next nearest $|\pm\frac{3}{2}\rangle$ doublet.

Fine Structure Observed in Modified X-Ray Scattering by Boron

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Using a double-crystal spectrometer, two portions of the spectrum of Cu $K\alpha_1$, $K\alpha_2$ radiation scattered by boron have been recorded. One portion is near the Rayleigh peaks; the other portion is at a distance of about 180 eV from the Rayleigh peaks. Several discontinuities have been noted in the first region. A definite double line has been observed in the second region at a distance from the Rayleigh lines which corresponds closely to the energy required for a $1s$-$2p$ electron transition. The widths of the observed lines are in agreement with the K boron emission lines. No conclusive results have yet been obtained with regard to the selection rules. It is not clear that the process under investigation is a three-level transition process.

INTRODUCTION: CURRENT STATUS OF PROBLEM

SINCE the discovery of the Compton effect, physicists have expected this phenomenon to be useful in the study of the solid state. Early experimental data encouraged their hopes. However, little success is evident as yet in the application of modified x-ray scattering to the study of solids. Recent advances in instrumentation have improved the possibility of progress in this direction.

The fine structure of the Compton spectrum was first reported in a series of articles by Davis[1,2] and his co-workers, and by Mitchell[3] in 1929. Their results were challenged by Bearden[4] a year later. DuMond[5] discussed theoretically the existence of an x-ray Raman effect in terms of a series of sharp lines related to electron transitions to unfilled energy levels in the atom. He considered the contradictions in the literature to be due to the very low intensity of the effect. In 1936, Sommerfeld[6] studied inelastic scattering of x rays by bound electrons and predicted the existence of discrete Raman lines. He did not discuss the associated selection rules, but he did confirm theoretical studies by Schnaidt[7] on the relative intensities of the Rayleigh and Raman lines. According to Schnaidt, the first Raman line

(corresponding to the $n=1$ to $n=2$ transition) in the most favorable case (when the Compton shift is equal to the binding energy) has an intensity of $\frac{1}{5}$ of the Rayleigh line. Successive Raman lines diminish rapidly in intensity in proportion to $1/n^3$.

In recent years, the story has been one of repeated observation of Smekel-Raman-type lines and challenges to these observations. Das Gupta,[8] in 1959, using a bent Mica Cauchois spectrograph and a photographic exposure method, reported the existence of Raman-type modified lines for graphite, aluminum, and beryllium. Weiss,[9] in 1965, repeated the Das Gupta measurements on graphite, beryllium, and lithium fluoride with a Norelco fluorescence spectrometer and did not confirm Das Gupta's findings. It should be noted that the spectrometer used by Weiss did not appear to provide the resolution necessary to observe a fine structure in Compton spectra. Work by Faessler and Mühle,[10] in 1966, carried out with an experimental arrangement similar to that of Das Gupta, confirmed Das Gupta's results. Suzuki[11] studied the x-ray Raman effect in 1967 with a single flat-crystal spectrometer and Cu $K\alpha$ radiation from a high-intensity rotating anode tube. His results, with respect to the position of the Raman lines, are in agreement with theoretical predictions of Mizuno and Ohmura.[12] Mizuno and Ohmura predicted that the Raman spectrum should have

[1] B. Davis and D. P. Mitchell, Phys. Rev. **32**, 331 (1928).
[2] B. Davis and H. Purks, Phys. Rev. **34**, 1 (1929).
[3] D. P. Mitchell, Phys. Rev. **33**, 871 (1929).
[4] J. A. Bearden, Phys. Rev. **36**, 791 (1930).
[5] J. W. M. DuMond, Rev. Mod. Phys. **5**, 1 (1933).
[6] A. Sommerfeld, Phys. Rev. **50**, 38 (1936).
[7] F. Schnaidt, Ann. Phys. (Paris) **21**, 89 (1936).

[8] K. Das Gupta, Phys. Rev. Letters **3**, 38 (1959).
[9] R. J. Weiss, Phys. Rev. **140**, A1867 (1965).
[10] A. Faessler and P. Mühle, Phys. Rev. Letters **17**, 4 (1966).
[11] T. Suzuki, J. Phys. Soc. Japan **22**, 134 (1967).
[12] Y. Mizuno and Y. Ohmura, J. Phys. Soc. Japan **22**, 445 (1967).

essentially the same shape as the mirror image of the K absorption spectrum. They reached several conclusions about the angular behavior of Raman scatter-

ing: at large scattering angles, the Compton scattering and the Raman scattering overlap, making it difficult to discern the Raman; at small scattering angles, the
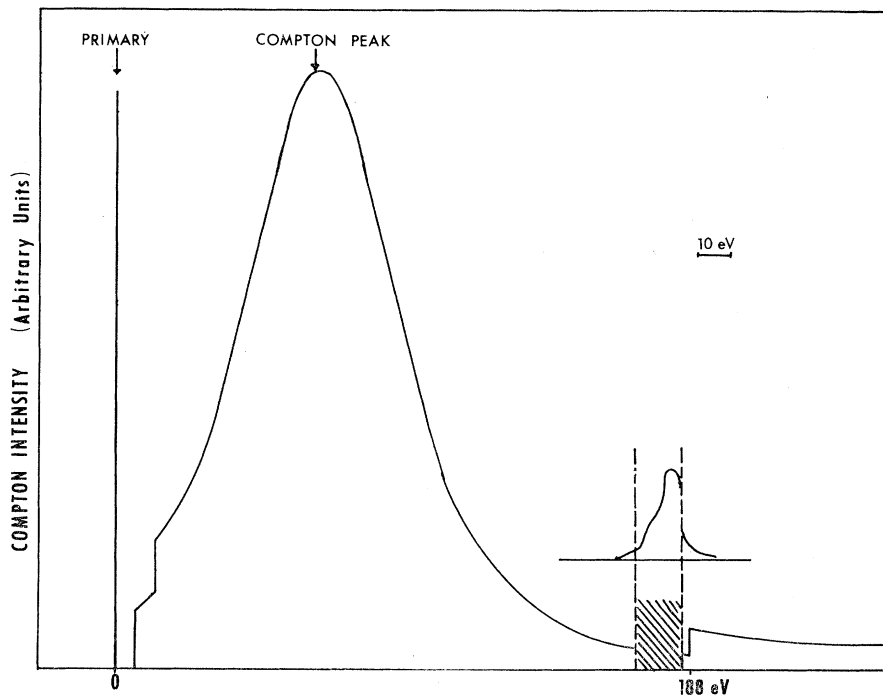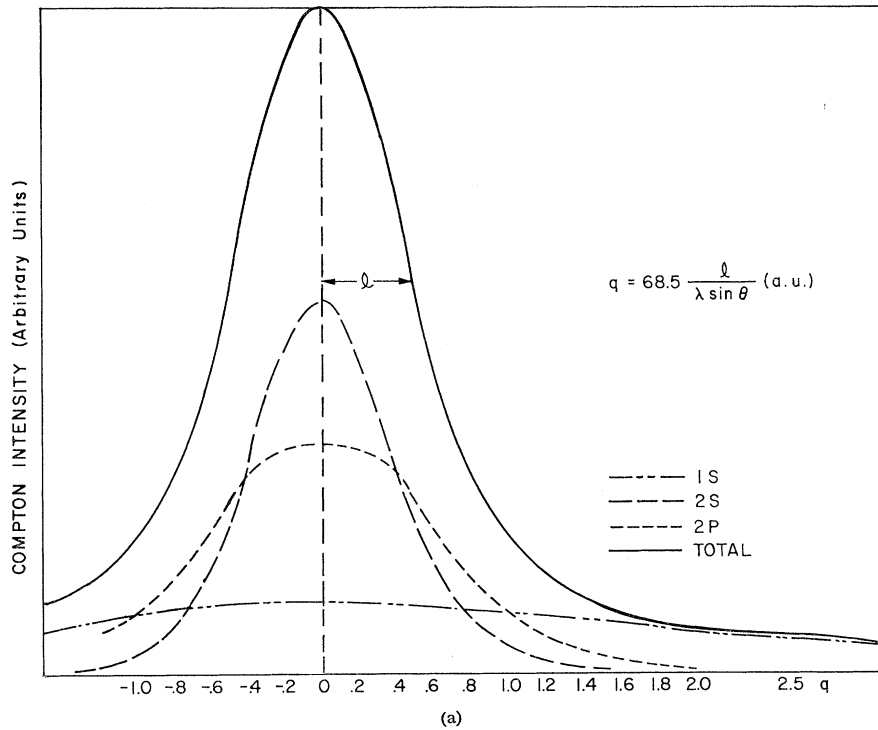

(a)

(b)

FIG. 1. (a) Theoretical Compton line shape, of boron, showing individual electron contributions. (b) Calculated Compton line shape for monochromatic primary radiation, using a scattering angle of 60°, and taking binding effects into consideration.

intensity of the Raman lines decreases. Another experimental observation of Raman lines came from Cooper and Leake[13] in 1967.

It is clear from the preceding discussion that there are reasons to doubt the observability of fine structure in modified x-ray scattering, mainly because of the low intensity of the effect and because of stipulations regarding the experimental resolution. Theoretical predictions, however, are quite strong. Reasons for the existence of fine structure include: allowed electron transitions between energy levels; normally forbidden electron transitions between energy levels for which there exists a higher allowed level to serve as an intermediate step; electron transitions via a virtual level; and the plasma excitation effect. The selection-rule problem is not yet solved; it is not generally accepted that the x-ray Raman effect has the same selection rules as the Raman effect in the visible region. It appears that the data in the literature represent a two-level transition rather than a three-level Raman jump.

Thus far, experimental results have been inconclusive because of relatively poor resolution. The uncertainty has been larger than the energy distance between the outer levels of elements with small atomic number. Some information can be obtained concerning the positions of the observed lines, but little can be said quantitatively about their shape. Conclusive results could easily be obtained using a very high-resolution instrument if the intensity of the effect under consideration permitted such a luxury. Polarized x rays may be needed to study virtual states, but at the moment this also is out of the question because of low intensity.

APPROACH TO PROBLEM

Some of the discrepancies in the literature can be resolved with a careful choice of experimental components: selecting an advantageous combination of scattering sample and angle, type of radiation and instrumentation. Assuming that the Mizuno-Ohmura[12] theory (that Compton and Raman lines can be calculated from the same expression) is correct, one should choose a scattering element which has a large Compton cross section for the initial electron configuration. Interpretation of the scattered spectrum is facilitated if the scattering element has a reasonably simple energy configuration (as in the low-Z elements) and if the element is in the amorphous phase.

For our experiment, commercially purified amorphous boron[14] was used. Figure 1(a) is the Compton line shape

of boron showing individual electron contributions, according to Weiss et al.[15] Figure 1(b) is the expected Compton line shape due to strictly monochromatic primary radiation, scattering at an angle of 60°, and taking binding effects into consideration. Assuming that a Raman line has the same width and shape as the corresponding emission line[16] then the shaded area in the insert to Fig. 1(b) indicates where the Raman line, with an intensity at least equal to that of the 1s Compton band, is expected.

A scattering angle near $\phi = 60°$ was chosen in order to obtain as much intensity as possible together with little overlapping with the Compton band of the outer electrons. Near $\phi = 60°$, the contributions of the 2s and 2p boron electrons to the Compton spectrum have died out, and the 1s electron contribution (which is nearly flat) is still near its maximum.

Copper $K\alpha_1$, $K\alpha_2$ radiation was used because of its relatively high intensity and its small half-width (2.31 eV for $K\alpha_1$ and 3.21 eV for $K\alpha_2$). Thus it is a narrow probe yielding good resolution for studying energy structure.

Although the focusing geometry spectrometer has adequate resolution for the problem at hand, and higher efficiency than any other system, its lack of stability is a serious drawback. The bent crystal is extremely sensitive to temperature variation. Since the effect under study is of very low intensity, a rather long exposure time is required, during which slight temperature changes could produce spurious results.

A one-flat-crystal instrument with two Soller-slit assemblies was also found to be unacceptable for the present investigation. A misalignment could result in the creation of additional peaks.[17] Also, in order to reach adequate resolution, higher-order reflections should be used. Even in the case of optimum positioning, an appreciable amount of radiation is absorbed by the foils. If the resolution is determined by the rocking curve of the analyzer crystal, a double-crystal instrument (with two similar crystals) with equal resolution to the single-crystal instrument will have higher efficiency.

A double-plane-crystal instrument was selected for the present work. Although the configuration of this system has a lower efficiency than a bent crystal system, it has the advantage of being relatively insensitive to temperature variation while maintaining a high resolution.

[13] M. Cooper and J. A. Leake, Phil. Mag. **15**, 1201 (1967).

[14] The boron scattering sample we used was prepared by American Potash and Chemical Corp., and was said by them to be 95–97% pure. We checked our sample by fluorescence analysis. and no impurities in the region under study were detected. Elements which could possibly have contributed between the energies 7880 and 7820 eV are [J. A. Bearden, Rev. Mod. Phys. **39**, 78 (1967)]: First order: 71 Lu, $L\eta$, 7.8575 keV; 65 Tb, $L\gamma_5$,

7.8535 keV; 75 Re, Ll, 7.8525 keV; 72 Hf, $L\alpha_2$, 7.8446 keV; 76 Os, Ll, 7.8222 keV. Second order: 82 Pb, $L\gamma_4$, 15.777 keV; 40 Zr, $K\alpha_1$, 15.7751 keV; 82 Pb, $L\gamma_4'$, 15.752 keV; 84 Po, $L\gamma_1$, 15.744 keV; 92 U, $L\beta_6$, 15.7260 keV; 82 Pb, 15.725 keV; 84 Ac, $L\beta_1$, 15.713 keV; 83 Bi, $L\gamma_3$, 15.7102 keV; 70 Zr, $K\alpha_2$, 15.6909 keV; 83 Bi, $L\gamma_6$, 15.6853 keV. Third order: none.

[15] R. J. Weiss, A. Harvey, and W. Phillips, Phil. Mag. **17**, 241 (1968).

[16] H. W. B. Skinner, Phil. Trans. Roy. Soc. London **A239**, 95 (1940).

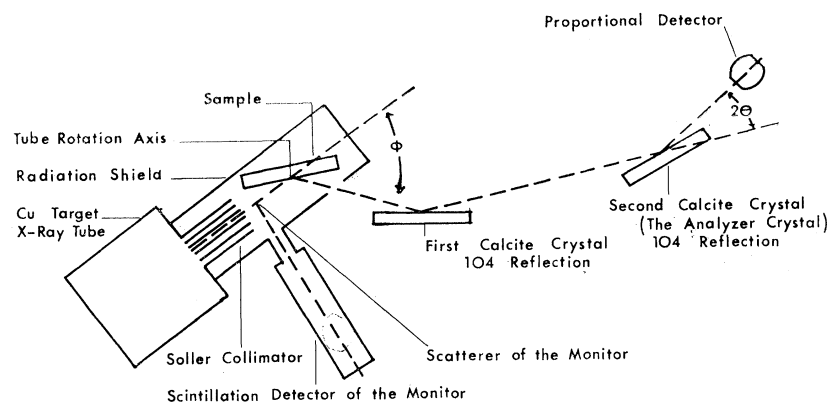[17] N. Spielberg, W. Parrish, and K. Lowitzsch, Spectrochem. Acta **8**, 564 (1959).

FIG. 2. Experimental arrangement.

EXPERIMENTAL ARRANGEMENT

The triple-crystal geometry described by Dumond[18] was used in constructing our experimental arrangement. We put the scattering sample in the first crystal holder and cleaved calcite crystals [(104) reflection] in the holders of the second and third crystals. Thus, we had a basic double-crystal-spectrometer setup.[19] (Fig. 2) Several modifications concerning the crystal holders have been made in order to facilitate the alignment of the instrument and to permit its use for other purposes in the future. These modifications permit each of the crystals a gross rotation around the vertical axis, a rotation about the horizontal axis, and a translational motion. The last crystal (the analyzer crystal) has an additional fine rotation around the vertical axis which the first and second crystals lack.

A stepping device moves the analyzer crystal and the detector in steps of 0.35 eV. The x-ray tube can be rotated around the axis of the first crystal for a scattering-angle range of 1°–84°. The tube is a Norelco diffrac-

tion tube,[20] the line focus of which has been used with a Soller-slit system to define the scattering angle to $\pm 1\frac{1}{2}°$.

Special attention was given to the monitoring system in order to allow statistical evaluation of the data and to have an immediate check on the variation of the incident radiation. The monitor consisted of a poly-crystalline sample rotating at 15 rpm on the edge of the incident x-ray beam. The Bragg reflection of the characteristic spectrum of the radiation was recorded by a scintillation counter.

The scattered spectrum was recorded by a proportional counter using a fixed count of 500. A single-channel pulse-height-analyzer circuit was associated with each counter in order to minimize the background. Background for the proportional counter was 2 counts/min.

Even with the stable flat-crystal system, long-time long-range temperature variation did not permit us to run the experiment for many successive days. It was necessary to run only portions of the complete spectrum in order not to sacrifice the accuracy obtainable through small steps and large fixed counts.

RESULTS AND DISCUSSION

The copper fluorescence spectrum (Fig. 3) was obtained in order to check the instrument and to make sure that no peaks exist in the area where the Raman lines are expected. This dummy experiment was performed with a piece of copper in the scattering sample position. From Fig. 3, the resolution is calculated to be $E/\Delta E = 5000$.

Two portions of the spectrum of Cu $K\alpha_1$, $K\alpha_2$ radiation scattered by amorphous boron were recorded for scattering angle, $\phi = 60°$. In the portion of the scattered radiation near the Rayleigh line there are several discontinuities in the flank of the longer wavelengths. The discontinuity at 6 eV is interpreted as being due to the binding energy of the $2p$ electron.[21]

The portion of the recorded spectrum beginning at a distance of about 170 eV from the Rayleigh peaks (the
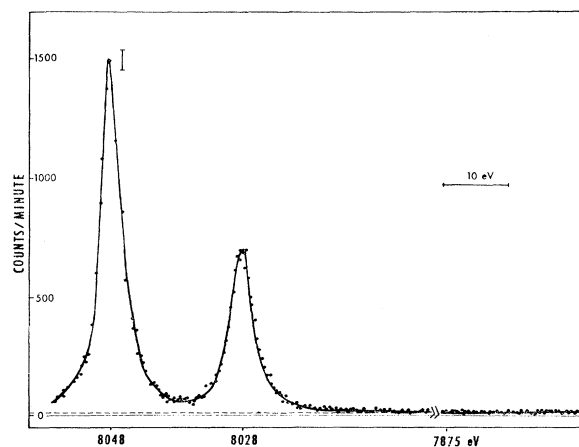

FIG. 3. Copper fluorescence spectrum obtained using the double-crystal spectrometer.

[18] J. W. M. DuMond, Phys. Rev. **52**, 872 (1937).
[19] A. H. Compton and S. K. Allison, *X-rays in Theory and Experiment* (D. Van Nostrand Co., Inc., Princeton, N. J., 1935), 2nd ed.

[20] We checked the tube for impurities in the region under investigation. For a list of possible impurities see Ref. 14.
[21] We are in the process of investigating this region of the spectrum in greater detail.

FIG. 4. Portion of the Cu $K\alpha_1$, $K\alpha_2$, spectrum scattered by boron beginning at a distance of 170 eV from the Rayleigh lines: A background equals approximately 5 counts/min, B line due to $1s$-$2p$ electron transition in boron (resulting from Cu $K\alpha_1$ incident radiation), C band due to $1s$-ionization electron transition in boron (Cu $K\alpha_1$ incident radiation), D line due to $1s$-$2p$ electron transition in boron (Cu $K\alpha_2$ incident radiation), and E band due to $1s$-ionization electron transition in boron (Cu $K\alpha_2$ incident radiation).
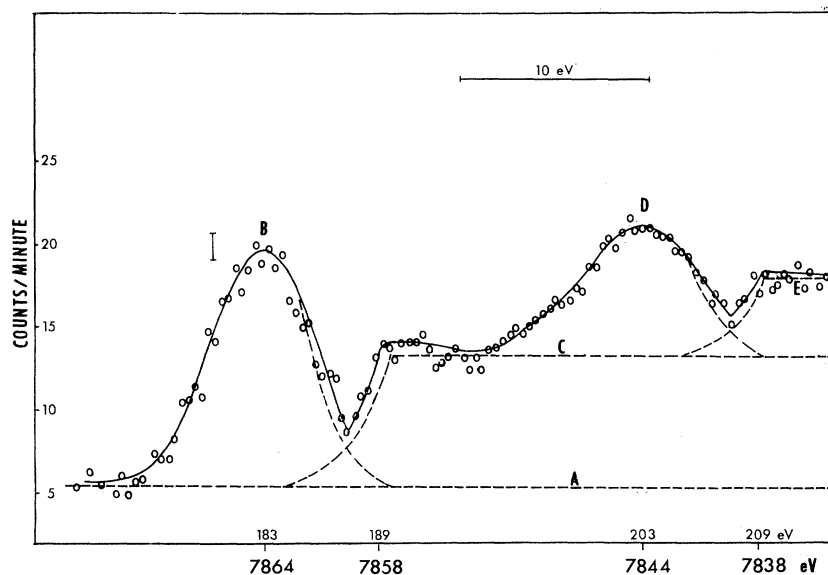
area where fine structure is predicted) is shown in Fig. 4. The energy transferred to the electron at maximum Compton intensity is 63 eV for $\phi = 60°$. A comparison of this energy with 188 eV,[22] the boron K electron binding energy, shows that the maximum of the Compton band is at a much lower energy than the expected binding energy discontinuity. The fine structure and the discontinuity appear twice in the spectrum because of the $K\alpha_1$ and $K\alpha_2$ initial radiation, but the fine structure due to $K\alpha_2$ is superimposed on the Compton band due to $K\alpha_1$. The observed line corresponds to the energy required for a $1s - 2p$ transition. The discontinuity corresponds to the binding energy of the K electron. Values obtained for the inner level transition and the binding energy were 183 and 188 eV, respectively. The width of the observed line is related to the width of the corresponding emission line (B $K\alpha$). The shape of the line compares qualitatively with the K emission spectrum, although deconvolution procedures must be carried out before offering a quantitative discussion of the transition probability.

The reported spectra are evidence of the existence of fine structure, the position and shape of which are similar to the K emission spectra. The effect can be interpreted simply as being due to partial absorption of an x-ray photon by the electron in an atomic excitation process. This last is not the only possible conclusion since a process involving a virtual state should yield the same spectrum.

ACKNOWLEDGMENTS

[22] J. A. Bearden and A. F. Burr, Rev. Mod. Phys. **39**, 125 (1967).