2457 (1970).

[11] In Appendix C we analyze the one-dimensional case and prove that there is no phase transition in that case. This is not a surprising result since the model is very similar to a certain spin Ising model.

[12] T. A. Kaplan, Bull. Am. Phys. Soc. 13, 386 (1968); Ref. 10.

[13] D. Adler, Rev. Mod. Phys. 40, 714 (1968).

[14] See, for example, J. M. Ziman, *Electrons and Phonons* (Oxford U. P., London, 1960), Chap. V.

[15] A recent treatment of this problem has been given by H. Wagner, Phys. Rev. Letters 25, 31 (1970).

[16] For a discussion of this technique, see K. Huang, *Statistical Mechanics* (Wiley, New York, 1965), p. 346.

[17] We quote from G. A. Korn and T. M. Korn, *Mathematical Handbook for Scientists and Engineers* (McGraw-Hill, New York, 1961), p. 23: "The cubic equation has one real root and two conjugate complex roots, three real roots of which at least two are equal, or three different real roots if Q is positive, zero, or negative, respectively."

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Observed Fine Structure in X Rays Incoherently Scattered by Alkali Halides: Contribution from Color Centers. II

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The spectra of Cu $K\alpha_1$, $K\alpha_2$ and Cr $K\alpha_1$, $K\alpha_2$ radiations scattered by LiF and NaCl single crystals and powders at several angles have been investigated. The spectra of Cr $K\alpha_1$, $K\alpha_2$ scattered radiation were studied for two different color-center concentrations. The spectra of scattered radiation by samples of high color-center concentrations include a new line on the long-wavelength side of the primary spectrum. The line is located at a distance of 5 eV from the primary for LiF, and 2 eV for NaCl. These distances of the new line from the coherent line are independent of the incident radiation energy and scattering angles, and are equal to the F-center excitation energies in the respective crystals. Judging from the position of the new line, and its absence from spectra in which the scatterer had lower F-center concentration, it is concluded that the new line is caused by "x-ray discrete Raman" scattering from the F center. However, because the F-center concentration is at least three orders of magnitude lower than the concentration of the valence electrons, the observed intensity of the line cannot be explained by a simple model in which the isolated F center behaves as a scatterer.

INTRODUCTION; SCOPE OF INVESTIGATION

Previously,[1,2] the author reported on the existence of a new incoherent component in the Cu $K\alpha_1$, $K\alpha_2$ x-ray radiation scattered by LiF which he attributed to x-ray Raman components of F centers. The present investigation has several purposes: (a) to verify the initial observation by extending the research to different radiation and different samples; (b) to demonstrate that the new line can be attributed to the F center by comparing two sets of spectra for two different F-center concentrations; and (c) to study quantitatively the differential cross section of the new incoherent component.

In the present research, the initial observation of a new line in Cu radiation scattered by LiF is verified for the same radiation on NaCl, and for Cr radiation, scattered by LiF and NaCl single crystals and powders at several scattering angles ($\phi = 16°$, $25°$, $40°$, $70°$, $84°$). Cr radiation was chosen because the slow rate of production of F centers permits measurements from samples with low F-center concentrations. The measurement using Cr radiation was then repeated with samples previously irradiated to a saturation concentration of F centers. It is then possible to demonstrate that the fine structure of the spectra depends on color centers by the comparison of Cr $K\alpha_1$, $K\alpha_2$ radiation scattered by samples with two different F-center concentrations. Such a comparison shows that for a concentration one order of magnitude less than the saturation concentration the new line is not observable. The determination of the exact concentration during the measurement is not feasible for several reasons: The spectrum of the incident radiation is not monochromatic; the production rate depends on the energy of the x-ray beam, the F-center lifetime, and the temperature dependence of the lifetime; the perfection of the crystal, etc.

The F-center concentration, as estimated from optical-absorption measurements, was found to be of the order of 10^{17} F centers per cm^3. Since the line characteristic energy loss is equal to the F-center excitation energies in the respective crys-

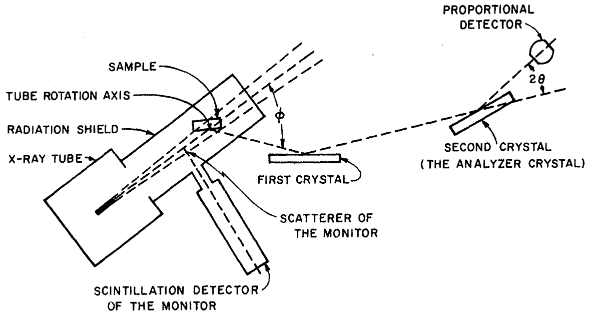

FIG. 1. Experimental arrangement.

tals, the new line is considered to be due to "x-ray discrete Raman" scattering from F centers. However, using the existing theoretical relations for the Compton differential cross section, as derived for large energy transfer and the available F-center wave functions, seems to lead to a disagreement between theory and experiment. A possible explanation for this is that some type of resonance effect is present which has been neglected throughout the several approximations of the differential cross section. The spectrum of the incoherently scattered x-ray radiation by LiF and other alkali halides has been studied by other investigators for the purpose of deriving the electron momentum distribution for the valence electrons. None of them, however, has observed a similar fine structure, mainly because their interest was in the high energy transfer side of the spectrum. In their case, no high resolution was required in the experimental set up and large scattering angles were used.

EXPERIMENT

In the present research, a triple-crystal geometry was used with the scattering sample placed in the first crystal holder (Fig. 1). The resulting instrument is a basic double-crystal spectrometer. In the investigation for fine structure near the primary radiation, two cleaved calcite crystals [(104) reflection] were used. A resolution, $E/\Delta E = 3500$, was achieved for Cr $K\alpha_1$, $K\alpha_2$ radiations and $E/\Delta E = 5000$ for Cu radiation. The analyzer crystal and the detector were moved by a stepping device in steps of 0.30 eV for Cr and 0.35 eV for Cu. The focal point of the Norelco diffraction tube was used. The scattering angle was defined by the sample size to within $\pm 1\frac{1}{2}°$.

The characteristic spectrum of the incident x-ray beam was monitored using a rotating polycrystalline sample and a scintillation counter with the associated electronics. A proportional counter was used in connection with a single-channel pulse-height analyzer circuit to record the scattered radiation, in order to minimize the background. (The background was found to be about 2 counts/min.)

Single crystals of LiF and NaCl with cleaved surfaces were used as scatterers, as well as LiF and NaCl powder. In the case of Cr radiation, measurements were made on the same samples before and after irradiation by harder radiation.

The tubes were checked for impurities by obtaining the emission spectra of the area under investigation. The samples were checked by fluorescence analysis using the same instrument and Mo radiation. The copper and the chromium fluorescence spectra were obtained to get Compton-free spectra with the same astigmatic errors as those in the spectra under investigation. This permitted the use of the method described and applied previously.[1,3]

Because of the reported disagreements between x-ray dosage and F-center concentration, optical measurements were required to determine the rate of production of F centers by the x rays under the present experimental conditions. These measurements were carried out on a Leiss spectrometer with an IP 28 photomultiplier and a Sylvania hydrogen arc lamp (HAK 50). The relative absorption was measured for time intervals of 30 min. During this time the sample was irradiated by x rays coming from the spectrometer tube. The Cr tube was operated at 30 kV, 10 mA, and the Cu tube at 45 kV, 25 mA.

The rate of production of F centers by the Cr tube is approximately one-tenth the production rate by the Cu tube. During the time required to collect the data on the spectrum of the Cu $K\alpha_1$, $K\alpha_2$ radiation reported earlier for the LiF and presently for NaCl, the F-center concentration was of the order of 10^{17} F centers per cm^3. The Cr measurements were repeated after the samples were irradiated to reach the above-mentioned concentration.

In order to avoid production of centers from the continuum part of the x-ray tube radiation, an effort was made to monochromatize the radiation before scattering. This was unsuccessful because of the very low resulting intensity.

RESULTS

In the present research 50 spectra were analyzed. Ten of these were the spectra of Cu $K\alpha_1$, $K\alpha_2$ radiation scattered by single crystals of LiF and NaCl (100) at scattering angles ($\phi = 16°$, $25°$, $40°$, $70°$, $84°$). Another ten spectra were from LiF and NaCl powder. The rest were the spectra of Cr $K\alpha_1$, $K\alpha_2$ radiation scattered at the same set of scattering angles from the powder, and from the single crystals before and after irradiation by harder radiation. The F-center concentration in the samples of single crystals used in the case of Cu $K\alpha_1$, $K\alpha_2$ and Cr $K\alpha_1$, $K\alpha_2$ after irradiation

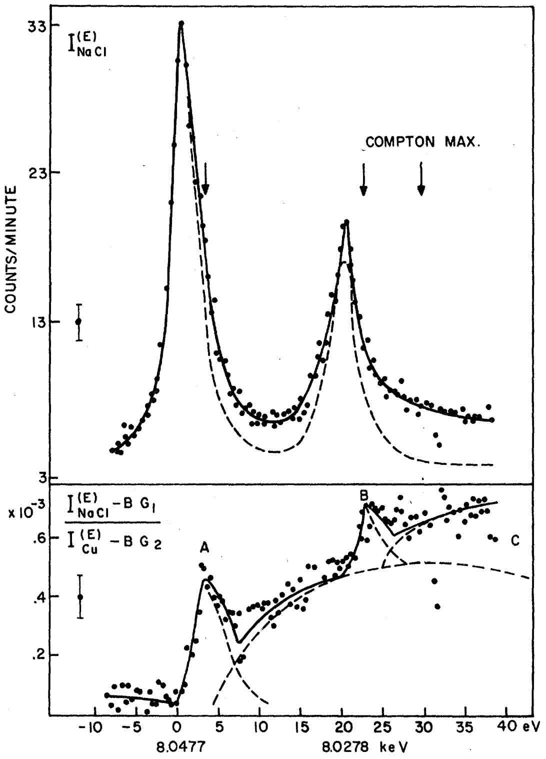

FIG. 2. Top: spectrum of Cu $K\alpha_1$, $K\alpha_2$ scattered by NaCl (100) at 40° angle. The arrows indicate the discontinuities; the dotted line is the shape of the Cu $K\alpha_1$, $K\alpha_2$ spectrum. Bottom: normalized incoherently scattered components. Line A is the new incoherent component of Cu $K\alpha_1$ scattered radiation; line B is that of the Cu $K\alpha_2$ superimposed on Cu$K\alpha_1$ Compton band C.

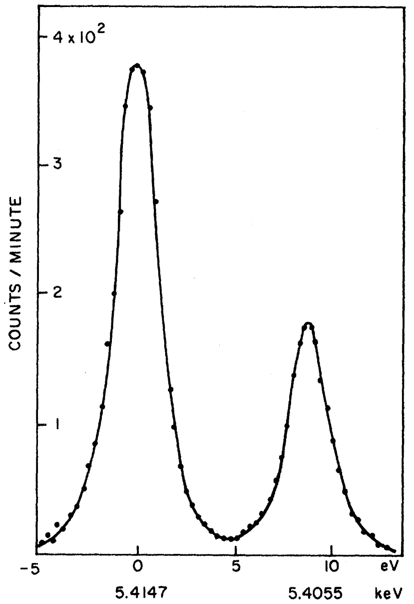

FIG. 3. Chromium fluorescence spectrum, obtained using the double-crystal spectrometer.

was estimated optically to be 10^{17} F centers per cm^3. This estimation can be wrong by up to one order of magnitude. With the crystals used for Cr $K\alpha_1$, $K\alpha_2$, the concentration before irradiation is one order of magnitude less than the above.

The spectrum of the Cu $K\alpha_1$, $K\alpha_2$ radiation scattered by a single NaCl crystal (100) at 40° is shown in Fig. 2 (top) as a typical example of the spectra obtained. Both lines ($K\alpha_1$, $K\alpha_2$) are asymmetrical on the long-wavelength side, the arrow indicating the starting of the asymmetry. Figure 2 (bottom) is a plot of the ratio $[I_{NaCl}(E) - BG_1]/[I_{Cu}(E) - BG_2]$. This figure is similar to $[I_{LiF}(E) - BG_1]/[I_{Cu}(E) - BG_2]$ as given in Ref. 1. BG_1 and BG_2 are the backgrounds for the LiF and Cu measurements, respectively. The only difference between the two graphs is the position of the peaks. In the case of NaCl the distance between the primary and the new incoherent component is 2 eV, the excitation energy of the F center in NaCl.

A Cr fluorescence spectrum is reproduced in Fig. 3. The spectra of Cr $K\alpha_1$, $K\alpha_2$ scattered by NaCl and LiF at different scattering angles are very similar to that shown in Fig. 3. A plot of the

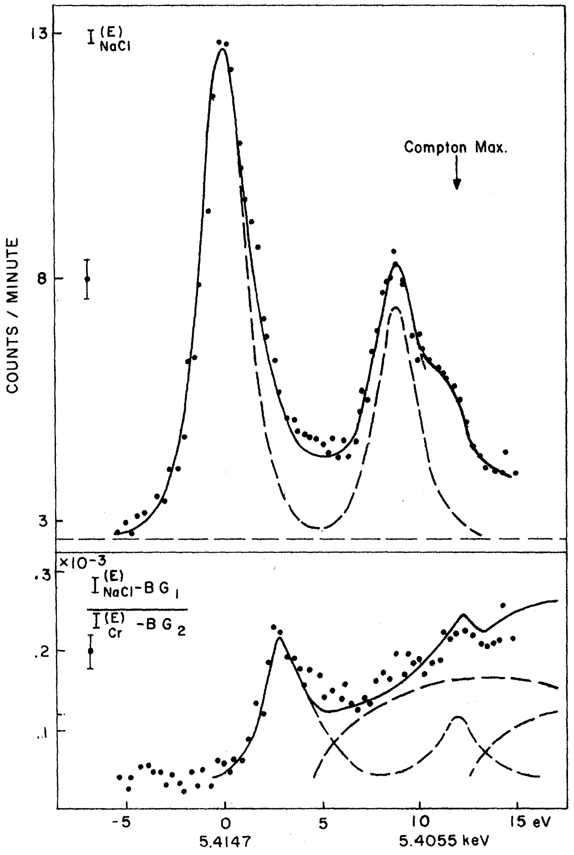

FIG. 4. Top: spectrum of Cr $K\alpha_1$, $K\alpha_2$ scattered by irradiated NaCl, scattering angle of 40°. Bottom: normalized incoherently scattered components.

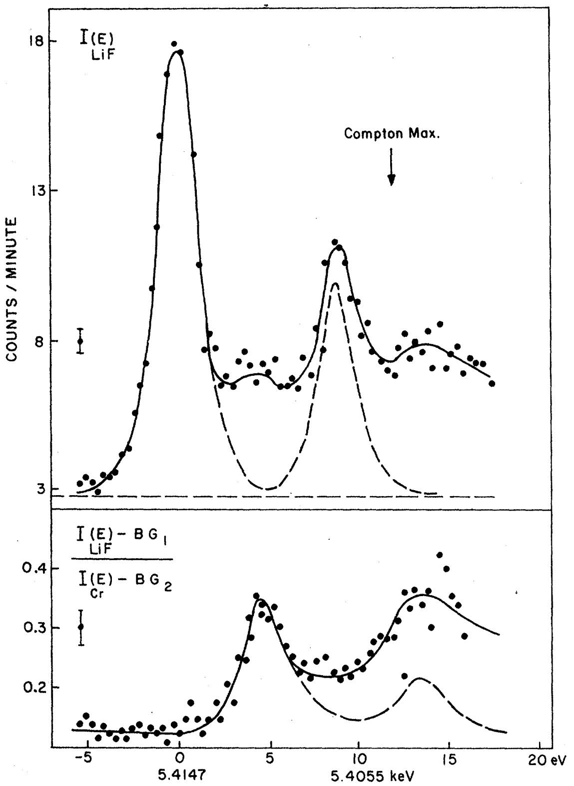

FIG. 5. Top: spectrum of Cr $K\alpha_1$, $K\alpha_2$ scattered by irradiated LiF, scattering angle of 40°. Bottom: normalized incoherently scattered components.

ratio $[I_{LiF}(E) - BG_1]/[I_{Cr}(E) - BG_2]$ or $[I_{NaCl}(E) - BG_1]/[I_{Cr}(E) - BG_2]$ does not show evidence of fine structure. The fine structure in the curves of those ratios appeared only after the crystals were irradiated for 10 h by Cu radiation.

Figure 4 (top) is the spectrum of Cr $K\alpha_1$, $K\alpha_2$ radiation scattered by irradiated NaCl at a scattering angle of 40°. Figure 4 (bottom) shows the ratio $[I_{NaCl}(E) - BG_1]/[I_{Cr}(E) - BG_2]$, giving the normalized incoherently scattered components. This has the same features as Fig. 2 (bottom). Figure 5 (top and bottom) is the spectra and the normalized incoherent components for LiF single crystal (100) and scattering angle of 40°. A study of Figs. 2, 4, and 5 (top) indicates that the lines are asymmetrical on the longer-wavelength side. It can be seen from those figures that the asymmetry in the spectra is found always at the F-center excitation energies of the respective crystals. Examination of Figs. 2, 4, and 5 (bottom) and Fig. 1, Ref. 1, indicates that the incoherent part of the spectrum of the scattered x radiation consists of one discrete line and one band. The distance between the peak of the primary line and the peak of the new line is independent of the types of incident radiations, and found to be 5 eV for LiF and 2 eV for NaCl. These values are very close to the F-center excitation energy. The band starts sharply at a distance which corresponds to the crystal energy gap.

DISCUSSION

A. General

The expected Compton-Raman profile from a noninteracting "gas" of N F-center electrons will be the superposition of the N identical profiles from each of the N F-center electrons. Neglecting the $\vec{p}\cdot\vec{A}$ terms, the profile is given by[4]

$$\frac{d\sigma}{d\omega\, d\Omega}=\frac{2\pi\rho_n(2\pi)^2 n}{137\,\omega_1\omega_2}\sum_f\sum_i |\langle f|\, e^{i\vec{k}\cdot\vec{r}}|i\rangle|^2\delta(\epsilon_f-\epsilon_i-\omega)\,, \tag{1}$$

where ρ_n is the density of the final state, $\vec{k}=\vec{k}_1-\vec{k}_2$, $\omega=\omega_1-\omega_2$, and $|i\rangle$ is the initial and $|f\rangle$ is the final state of the electron.[5]

Figure 6 is a diagram of such a spectrum, originally shown by Sommerfeld.[6] The lines are due to transitions from the ground state $|i\rangle$ to an $|f\rangle$ discrete F-center state. The band is caused by transitions to an $|f\rangle$ in the conduction band. For energy transfer $\omega > E_g$ additional contributions to the band come from transition where $|i\rangle$ is a valance electron state.

However, computations using Eq. (1) have not yet been carried out for this type of transition because of the lack of precise wave functions. Therefore only an order-of-magnitude comparison will be attempted. In such a comparison the F centers will be approximated by hydrogenlike structure.

B. Conclusions

Although the intensities obtained are low, and thus the statistics are poor, the results are evidence of the existence of the new incoherent component. Figure 7 gives the position of this compo-

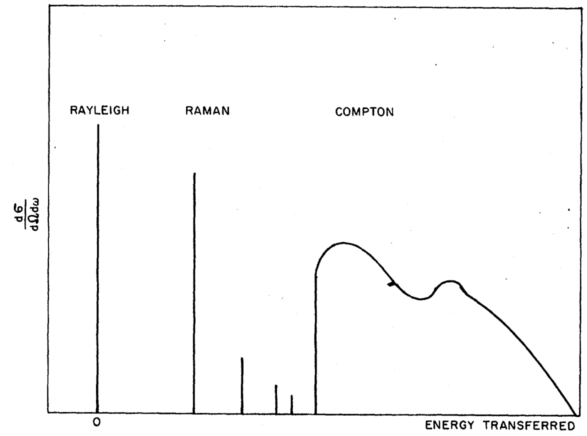

FIG. 6. Schematic of the expected shape of the x-ray scattered radiation by a "gas" of F centers.

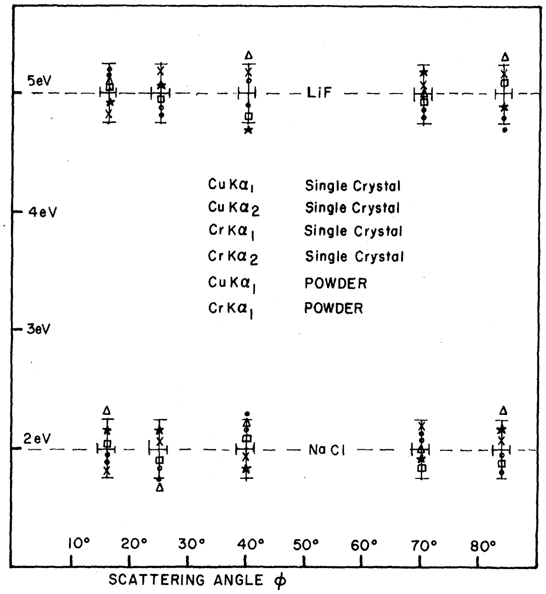

FIG. 7. Characteristic energy losses observed at recorded spectra.

nent for the recorded spectra. The characteristic energy loss necessitates the conclusion that the reported effect is an x-ray Raman scattering from *F* centers.[7] The fact that the fine structure is not detected in the case of low *F*-center concentration is a clear indication that the observed fine structure comes from the scattering by the *F*-center trapped electron. Experimental data and theoretical calculations give very little information about the shape of the new line.

The angular dependence of the Raman peak intensity is given by Mizuno and Ohmura.[8] Figure 8 gives the peak intensity as a function of the scattering angle.

Making the reasonable order-of-magnitude approximation that the differential cross section for the valance electron is given by the Klein-Nishina relation for large energy transfer, the conclusion is that the intensity of the new line should be at least two orders of magnitude less than that of the Compton band. Considering the spectra of Figs. 2, 4, and 5, it is obvious that such a low intensity should not be observable. No satisfactory explanation of this can be provided presently by the author.

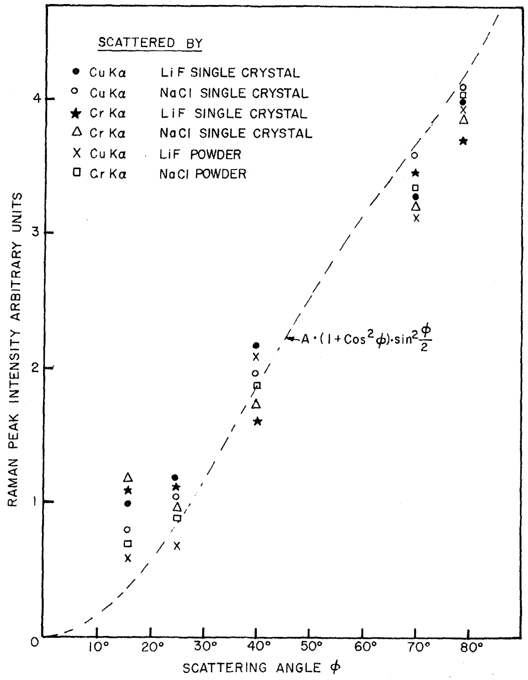

FIG. 8. Angular dependence of the Raman peak intensity.

Two speculations are (a) that some type of resonance effect is present which has been neglected in the derivation of relation (1) and, (b) that the $\vec{p}\cdot\vec{A}$ term may, in the present case, contribute considerably.

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[5] If $|f\rangle \neq |i\rangle$ the scattering is incoherent and the effect is called the "Raman-Compton effect." If $|f\rangle = |i\rangle$ the scattering is coherent and the effect is called "Rayleigh-Thomson scattering."

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