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X-Ray Absorption Fine Structure with Polarized X-Rays*

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The fine structure on the short wavelength side of the K x-ray absorption edge of Cl in single crystals of NaCl and KCl has been studied with polarized x-rays in a vacuum double-crystal spectrometer. The structure was obtained when the main direction of ejection of photoelectrons was perpendicular to a set of 100 planes and again when perpendicular to 110 planes. One significant difference in structure was noted for the two different directions of ejection in the case of NaCl.

INTRODUCTION

A SECONDARY fine structure on the short wavelength side of x-ray absorption edges has been observed in many crystalline materials. This structure, when within a few volts of the main edge, is quite dependent upon the character of the parent atom or ion concerned. An extended structure may be found further from the edge which is primarily dependent upon the number and arrangement of the neighbors of the atom or ion from which the photoelectron was ejected. Kronig[1] has suggested that the extended structure in solids is primarily due to the periodic potential lattice of the crystal. The ejected electron is treated as a free electron perturbed by the periodic potential of the lattice. Then the forbidden energies W_0 are found to be given by the expression,

$$W_0=\frac{h^2(\alpha^2+\beta^2+\gamma^2)}{8md^2\cos^2\theta_0},$$

for any plane of indices $\alpha\beta\gamma$ in a cubic crystal of grating space d, where θ_0 is the angle between the normal to the plane α, β, γ and the direction of motion of the electron. For the usual case of unpolarized x-rays and polycrystalline absorbers, the effect of integration over all planes and all angles is to smooth out the discontinuities to some degree so that a rather broad structure results. Many investigations have been carried out for this case. However, as Kronig points out, if one could use a single-crystal absorber and polarized x-rays, one would expect to find a more pronounced structure. Furthermore, by varying the orientation of the single crystal with respect to the electric vector of the polarized x-rays the angle θ_0 should shift for each plane, and a shift in the position of the structure should result. It is the purpose of the present work to study the fine structure resulting when polarized x-rays fall on a single-crystal absorber using different orientations of that absorber. One would expect the effects which are sought to be somewhat reduced in magnitude for the reason that, although the main direction of ejection of photoelectrons is parallel to the electric vector in a plane polarized x-ray beam, all of the electrons are not ejected in this direction.

As far as the authors are aware, only one previous investigation of this type has been made.[2] The K x-ray absorption edge of Br in a single crystal of KBr was studied using partially polarized (total deviation of 57° and 75 percent polarization) x-rays. A pronounced structure was obtained, and there was some evidence of dependence of structure on crystal orientation; but the partial polarization left much to be desired. The present availability of a vacuum x-ray spectrometer makes it possible to do a similar experiment at longer wavelengths so that the deviation in the first order is nearly 90° and the polarization is essentially complete.

EXPERIMENTAL

The vacuum double-crystal spectrometer together with the power supply and Geiger-counter means of intensity registration have been described previously.[3,4] Crystal A was a good calcite which had previously given $(1, -1)$ rocking curves (with another calcite as Crystal B) having a full width at half-maximum of 50 seconds at 4.38A. Crystal A gave a total deviation of 92.5° for the wavelength of the K-edge of chlorine. Crystal B was used both as the absorber and as the second crystal in the double-crystal scheme; measurements were made with a single crystal of NaCl as Crystal B and later with a crystal of KCl. These crystals were obtained from the Harshaw Chemical Company. The mount for Crystal B was made so that it could be rotated about an axis, perpendicular to the 100 face used as the reflecting face, by means of a solenoid arrangement operated from outside the bell jar. Crystal B was rotated 45° between runs so that the main direction of ejection of the photoelectrons was either perpendicular to a set of 100 planes or perpendicular to a set of 110 planes. The sequence of runs was as follows: a complete set of points involving 10 000 counts per point was run for an absorption curve with photoelectric ejection mainly perpendicular to 100 planes, a

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similar complete curve for the 110 direction at 45° from the first, a similar curve for the 100 planes at 90° from the first, and so on. Spurious structure caused by imperfections in the reflecting face of the crystal would have been shown up by such a procedure. Three or more complete curves were run for the 100 and the 110 positions. A complication in taking data arose from the fact that at the long wavelengths concerned and with crystal faces of the order of 4 cm in extent it was not possible to leave Crystal *A* fixed while covering an adequate wavelength range with Crystal *B*; consequently, it was necessary to maximize Crystal *A* for each new setting position of Crystal *B* by taking the time for three or four 10 000-count points with different positions of *A* to determine the maximum. Intensities were of the order of 60 counts per second on the long wave side of the edge and 35 counts per second on the short wavelength side. All measurements were made at 5.5 kilovolts and 250 milliamperes with an x-ray tube having a tungsten target.

RESULTS

Typical curves are presented in Figs. 1 and 2. An absorption curve for the main direction of ejection of photoelectrons perpendicular to a set of 100 planes is labeled (100) and appears as the upper curve in each case. The lower curve is for ejection perpendicular to a set of 110 planes and is labeled (110). The ordinates of the curves are arbitrarily displaced. No displacement of the main absorption edge was observed, although the absolute accuracy of measurement would not have allowed detection of such a shift, if it had been less than about a volt. The distances in volts from the center of the main edge of the structure observed are given in Table I. The differences in position and in general shape for the feature β between the 100 curve for NaCl and the 110 curve for NaCl are considered to be significant. No other variations of significance between 100 and 110 curves were found. A search made out to 100 volts from the main edge failed to yield any repeatable structure beyond 25 volts from the edge.

TABLE I. Distances of structure features measured in volts from the center of the main edge.

Crystal	Orientation	*A*	α	*B*	β	*C*	γ
NaCl	(100)	3.6	9.1	15.0	21.5	···	···
NaCl	(110)	3.6	8.8	15.0	17.8	···	···
KCl	(100)	2.5	4.9	6.8	10.5	16.8	25
KCl	(110)	2.5	4.9	6.6	9.9	16.8	25

DISCUSSION

Measurements with polycrystalline absorbers and non-polarized x-rays have been made on KCl and NaCl in other laboratories.[5–7] Because of the different conditions for the present experiment one would not expect to obtain a one-to-one correspondence in structure with previous work; however, a comparison shows that the general features are similar.

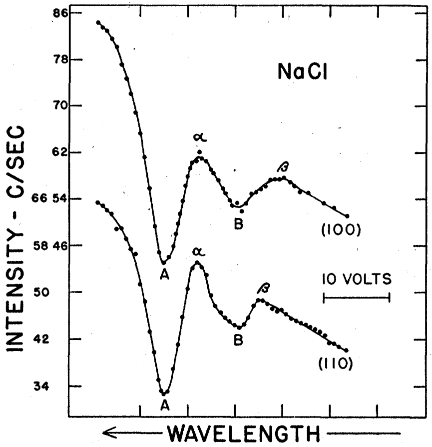

FIG. 1. *K* x-ray absorption edge of Cl in NaCl with main direction of photoelectron ejection perpendicular to 100 (top curve) and 110 planes (bottom curve).

A major disappointment with respect to the main objective of the present work is that no structure was found beyond 25 volts; Kronig's theory is expected to be more nearly valid at such energy distances from the edge since it concerns a small perturbation to the free electron problem. Local fields are more important as the energy becomes less until finally the energies are largely governed by semi-optical level considerations. It is currently planned to repeat the present polarization experiment with metal single crystals for which extended

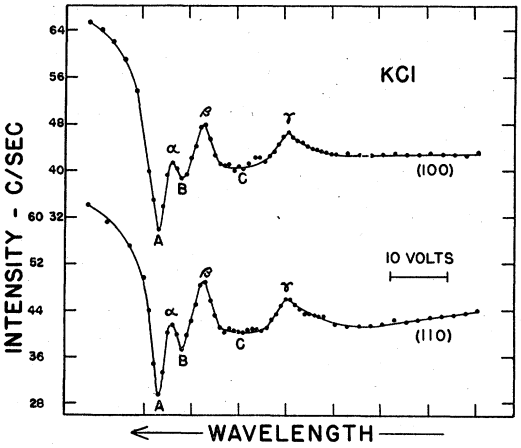

FIG. 2. *K* x-ray absorption edge of Cl in KCl with main direction of photoelectron ejection perpendicular to 100 (top curve) and 110 planes (bottom curve).

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structure is expected some hundreds of volts beyond the main edge. A comparative study for different directions of ejection should then be more rewarding.

It would appear that the structure for both of these ionic crystals is unaffected by the direction of photoelectron ejection within 15 volts of the main edge. No significant difference between 100 and 110 occurs for KCl throughout the entire structure range. One such difference does occur for the structure β in the Cl edge of NaCl. β is closer to the edge for 110 than 100 which, if β is caused by the same planes in each case, means that $\cos\theta_0$ is greater so that the angle with the plane is smaller. The question arises as to why there is a difference for NaCl at 18–20 volts from the edge and not for the features which are as much as 25 volts from the edge for KCl when both are ionic cubic crystals. This result implies greater symmetry of the Brillouin zones in the case of KCl. The probable explanation is that the ionic lattice for KCl contains identical numbers of scattering elements at every lattice point whereas that is not true for NaCl. Consequently KCl may be considered as a true simple cubic whereas NaCl represents an interlacing face-centered lattice network.

CONCLUSION

Pronounced structure has been observed close to the main absorption edge of chlorine using single-crystal absorbers of NaCl and KCl and polarized x-rays.

When the main direction of photoelectric ejection was changed from 100 to 110 there was a definite difference in shape and position of the feature β in NaCl. There were no significant differences for any absorption features in KCl. Thus greater symmetry of the Brillouin zones is implied for KCl, which condition may be attributed to its pure cubic structure.

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Direct Measurement of the Dielectric Constants of Silicon and Germanium

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Direct measurements of dielectric constants of silicon and germanium between 500 cps and 30 Mc/sec have been made. Small parallel-plate condensers were made from samples of these elements after doping with gold so as to produce high-resistivity material ($\rho \sim 10^7$ ohm cm for germanium at 77°K, $>10^{10}$ ohm cm for silicon). The dielectric constant of silicon (at 1 Mc/sec) was taken to be 11.7±0.2, of germanium 15.8±0.2. The dielectric constant of silicon is constant to ±1 percent over the range 500 cps–30 Mc/sec, whereas germanium, because of its lower resistivity, has a much greater apparent variation of dielectric constant with frequency.

RECENTLY it has been found possible to produce germanium and silicon having high resistivity (above 10^6 ohm cm) at reasonable temperatures[1,2] (77°K and above). The technique of doping with the proper amount of gold leads, in the case of germanium, to samples of resistivity at 77°K, as high as 50 meg cm; in the case of silicon, greater than 10^4 meg cm. This makes it possible to do experiments on these substances that have been difficult, either because of the high conductivity or the impracticability of doing the experiment at temperatures at which ordinary germanium and silicon would have suitably high resistivity (liquid helium or hydrogen temperatures).

A case in point is the measurement of the dielectric constants. Until recently the only available precision measurements were made at infrared frequencies. Briggs,[3] working with wavelengths of the order 1–2μ found values of index of refraction that extrapolate at zero frequency to dielectric constant values of 16.1 for germanium, 11.7 for silicon. Benedict and Shockley[4] have recently determined the dielectric constant of germanium by means of a wave guide method. Their value was 16.0±0.5. An estimate of lesser precision has been recently made by Dacey.[5] He gives the value 16.0±10 percent obtained by measurement of the "punch-through" voltage of a "unipolar" transistor.

Small parallel-plate condensers have been made of both silicon and germanium single crystals (some of the silicon wafers contained twin boundaries). A coating of aluminum-gallium paste was applied as electrodes. Fixed holders clamping the samples in a suitable position within a Dewar flask were used so that accurate correction for lead capacities would be obtained. Areas were calculated from the weight and thickness, using a density of 5.325 g/cm^3 for germanium at 25°C, 2.328 for silicon.[6]

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