Structure in the X-Ray K Absorption Edges of Solid Potassium Chloride

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A two crystal vacuum spectrometer was used to investigate the x-ray absorption spectrum of solid potassium chloride over a fifty-volt range in the vicinity of the K edges of both potassium and chlorine. Absorbers were prepared by vacuum evaporation of the salt onto thin, taut Kodapak films. High precision of intensity measurement was made possible by the use of fortuitously located $L\alpha_1$ radiations from targets of antimony and palladium. No corrections to observed intensities were made for the finite resolving power of the instrument. Results are expressed by graphs of relative absorption coefficient as a function of relative photon energy, and are summarized in a table of relative energy separations of prominent absorption maxima and minima.

INTRODUCTION

THE study of fine structure in the x-ray absorption edges of solids has long been considered important for an understanding of their electronic states. Recently, successful correlations between theory and experiment have been made for some of the simpler metals.[1,2] However, both theoretical and quantitative experimental work on non-conductors is meager and unsatisfactory. The present experimental work, using the most precise techniques known, was undertaken in order to provide information about the x-ray absorption fine structure of potassium chloride, an ionic crystal which is presumably one of the simplest from a theoretical standpoint.[3]

The experimental equipment consisted of a high voltage d.c. power supply, an x-ray tube, a set of potassium chloride absorbing films, a two crystal vacuum x-ray monochromator, an ionization chamber for detecting the x-rays, and a d.c. amplifier with galvanometer output for measuring ion currents. Several runs of absorber opacity *versus* monochromator setting were made for each absorption edge. The natural logarithms of the opacities for each run were then suitably corrected and the values for separate runs adjusted and matched so as to yield results conveniently represented as graphs of relative absorption coefficients as a function of relative photon energy.

EXPERIMENTAL DETAILS

Apparatus

The high voltage power supply was of the full-wave rectifier type with filtered and electronically stabilized output.[4] The x-ray tube voltmeter, consisting of a galvanometer in series with two 1000-megohm resistors could be read with a precision of ± 0.1 percent and with an accuracy of ± 0.5 percent at 10,000 volts. The tube current was read with a 0–100 milliammeter with a precision of ± 0.2 percent. The majority of measurements were made with a tube voltage of 10,000 volts and current of 100 ma.

Details of the x-ray tube construction have been given elsewhere.[5] The target used for the study of the potassium edge was an alloy of 12 percent antimony and 88 percent lead tinned to the copper target carriage,[2] while the target used for the study of the chlorine edge was a 10-mil sheet of palladium soldered to the carriage. These target materials were selected because the $L\alpha_1$ lines of antimony and palladium provided both high x-ray intensity in the regions of the edges and standards for wave-length measurement.

The absorbing films were prepared by vacuum evaporation of chemically pure potassium chloride from a furnace, similar to one described by Schneider and O'Bryan,[6] onto tautly stretched Kodapak films 0.001 inch thick. The thickness of

[1] W. W. Beeman and H. Friedman, Phys. Rev. 56, 392 (1939).

[2] J. B. Platt, Phys. Rev. To be published.

[3] Salient features of the fine structure of potassium chloride have been reported by J. M. Nuttall, Phys. Rev. 31, 742 (1928); and G. P. Brewington, Phys. Rev. 46, 861 (1934).

[4] L. G. Parratt and J. W. Trischka, Rev. Sci. Inst. 13, 17 (1942).

[5] L. G. Parratt, Phys. Rev. 54, 99 (1938).

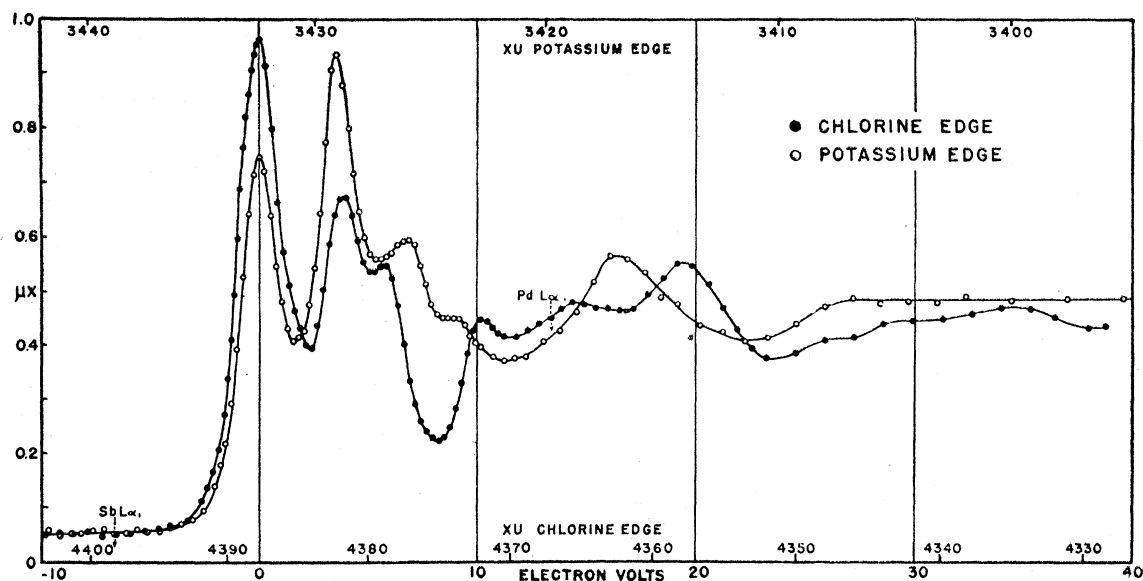[6] E. G. Schneider and H. M. O'Bryan, Phys. Rev. 51, 293 (1937).

FIG. 1. X-ray *K* absorption edge of chlorine and potassium in solid potassium chloride.

the potassium chloride films so prepared was calculated to be approximately 35,000 Angstroms. Transmission of x-rays through each of several areas of each absorber showed that they were sufficiently uniform to make the exponential absorption law valid within 0.1 percent or better.

The two-crystal vacuum spectrometer has been described elsewhere.[5] Results of measurements of the (1, −1), (1, +1), (2, −2) widths and (1, −1) percent reflection for Cu *Kα* radiation placed the crystals in Class I.[7] From the (1, −1) widths of the Sb *Lα*$_1$ and Pd *Lα*$_1$ radiations, the physical resolving power was estimated to be approximately 12,000, which was essentially the resolving power of the instrument, since the geometrical resolving power was of the order of 60,000.

To obtain 99 percent absorption of the x-ray beam the ionization chamber[2] was filled with krypton to a pressure of 20 cm of Hg for the study of the chlorine *K* edge and with argon to a pressure of 26 cm of Hg for the study of the potassium *K* edge. A modified Barth circuit,[8] utilizing a Western Electric D96475 tube, amplified the currents from the ionization chamber. Its sensitivity was 150,000 mm/volt on a scale two meters from the galvanometer.

[7] L. G. Parratt, Rev. Sci. Inst. 6, 387 (1935).
[8] D. B. Pennick, Rev. Sci. Inst. 6, 115 (1935).

X-Ray Intensities

In the region of the potassium edge the peak of the Sb *Lα*$_1$ line, at 10 kv and 100 ma, provided the greatest intensity, giving an ionization current of 1.2×10^{-12} ampere or a galvanometer deflection of 5620 cm on the highest sensitivity (grid resistor of 10^{12} ohms). The weakest direct beam used, continuous radiation, gave a current of 1.4×10^{-14} ampere or a 64-cm deflection at highest sensitivity. In the region of the chlorine edge the Pd *Lα*$_1$ line gave a peak intensity at 10 kv and 80 ma of 3.5×10^{-12} ampere, corresponding to a 16,700-cm galvanometer deflection at full sensitivity. The weakest direct beam gave a current of 2.5×10^{-14} ampere or a deflection of 112 cm at full sensitivity.

Procedure and Analysis of Data

Because of the rapidly varying intensity of the line radiation with crystal angle, data for a complete opacity measurement were taken at each wave-length setting of the monochromator according to the schedule outlined by Platt.[2] The time required for each opacity measurement varied from 10 to 14 minutes depending on the amplifier grid resistor used. Of the five absorbers prepared, two were used for recording both absorption edges. Eight runs with four different

TABLE I. Energy separations in electron volts of fine structure maxima and minima from initial absorption peak.

Feature	K−K edge	Cl−K edge
A	0.0	0.0
α	1.7	2.3
B	3.5	3.8
β	5.5	5.2
C	6.9	5.7
γ	?	8.2
D	9.0	10.1
δ	11.5	11.4
E	16.3	14.3
ε	22.4	?
F	27.5	19.2
ζ	—	23.4
G	—	29.9

absorbers were made in the region of the potassium edge. Of these runs three covered the entire region studied. In the region of the chlorine edge three runs, with three different absorbers, were made.

The general method of treating absorption measurements where more than one element is present in the absorber has been described by Platt.[2] The jump ratios of both potassium and chlorine were taken to be 10. Successive runs were matched at the peak of the first absorption line. The corrections for higher order radiation, made to the natural logarithm of the opacities, had a maximum value of 3 percent for the potassium measurements and 1 percent in the region of the chlorine edge. No correction for the resolving power was attempted since no reliable method has been developed for making such corrections to absorption spectra.

For purposes of absolute wave-length determination, separate runs were made to determine the position of the first absorption maximum relative to the $L\alpha_1$ radiation used for recording the fine structure.

RESULTS

Figure 1 is a graph of relative values of μx vs. relative photon energy in electron volts in the regions of the K absorption edges of chlorine and potassium in solid potassium chloride. The wave-length scale used in expressing the results is an X.U. scale rather than a Siegbahn scale. The standard wave-lengths used were 3431.8 Siegbahn units for Sb $L\alpha_1$ and 4358.5 Siegbahn units for Pd $L\alpha_1$.[9] The ratio of the grating and Siegbahn scales of wave-lengths was taken as 1.002034.[10] The wave-lengths of the peaks of the first absorption lines in the chlorine and potassium spectra were determined to be 4387.6 X.U. and 3432.5 X.U. respectively.[11] In establishing the voltage scale the wave-length associated with one absolute volt was taken to be $12{,}395 \times 10^{-8}$ cm absolute volt.[10]

For ease of comparison with other data and with theoretical results, which are likely to take the form of energy separations, Table I presents the energy separations from the initial maximum of the various maxima and minima in Fig. 1. Maxima and minima are referred to by letters of the Roman and Greek alphabets respectively.

It is estimated from the self and mutual consistencies of the various runs that variations in μx as small as 3 percent are significant. An addition of component errors gives a maximum uncertainty in absolute wave-length specification of ± 0.15 X.U. Relative wave-lengths are precise to ± 0.02 X.U., the error in matching different runs.

[9] H. Hjalmar, Zeits. f. Physik 3, 262 (1920).
[10] R. T. Birge, Rev. Mod. Phys. 13, 233 (1941).
[11] Or 4378.7 Siegbahn units and 3425.5 Siegbahn units respectively.