ions which possess the $3d^9$ configuration; that is, the band will become wider and its peak will shift toward higher frequencies. Hence, when the energy of the incident electrons is high, the observed band will reflect the combined emission from $3d^9$ and $3d^{10}$ configurations.

Similar effects might be expected in the case of the M_2 or M_3 band. Our study of the M bands shows one "satellite" peak whose spectral position cannot be correlated with a peak in the secondary structure of the M_3 absorption curve for which reliable measurements are available. In the present experiment it was not convenient to study the possible variation in the shape of the M_3 band as a function of the incident electron energy; so that we cannot state whether the effect noted in the case of the L_3 band is also present in the M_3 band. Under our experimental conditions, a calculation indicates there are about 60 incident electrons for every copper atom located in the volume effective in the production of photons. Unquestionably, "holes" are created by the incident electrons in the filled states of the valence band, but the equilibrium concentration of such vacancies depends not only on high production rates but also on the rate at which vacancies disappear. Owing to the highly mixed character of the valence states, it would be naive to expect that the lifetime of a $3d$ hole is long, though on the basis of atomic selection rules alone, such an expectation may be regarded as reasonable since the l value of a $4s$ electron must change by two units to bring about the contemplated $4s \rightarrow 3d$ transition.

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X-Ray *K*-Absorption Spectra of Solid Argon and Krypton*

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The x-ray K-absorption edge structures of argon (at 3.86 A) and of krypton (at 0.86 A) have been measured in the gaseous and solid states. The spectra of the gases confirm previous work. The spectra of the solids exhibit pronounced structure extending far to the short-wavelength side of the absorption edge. The broad absorption maxima observed can be correlated with the valence bands in the crystal, but the extremely sharp initial rise requires an unusual density of states in the bands, perhaps offering evidence for the existence of excitation states.

In the region of an absorption edge, the x-ray absorption spectrum of a given element in the solid state is inherently different from that of the same element in the gaseous state. The difference arises from the perturbation of the outer (unfilled) electronic states in the solid by the fields of neighboring atoms. The discrete atomic levels of the isolated atom are replaced by broad bands, overlapping one another and extending several hundred electron volts toward higher energies. Kronig[1] was able to explain the rather faint structure in the spectrum well to the high-energy side of the edge by considering the scattering of the de Broglie waves of the ejected electron by the absorbing crystal. Observed spectra agree well with his theory, especially for energies greater than some 30 electron volts from the edge. Such intensity structure is characteristic of the crystal structure of the absorber, rather than of the particular element of which it is composed. For energies near the absorption edge, on the other hand, one might expect that the spectrum would reveal the density of states in the conduction bands. It is the purpose of the work reported here to examine the absorption edge structure of gaseous and solid argon and of gaseous and solid krypton to gather some information on the influence of the crystal lattice on the electronic states and transition probabilities of these atoms.

The absorption spectra were obtained with a two-crystal vacuum x-ray spectrometer fitted with a cryostat for maintaining the absorption cell at low temperature.

The source of continuous radiation for the argon experiment was a gold-plated copper-target x-ray tube operated at 8.8 kv and 40 ma. The electron gun cathode arrangement permitted independent stabilization of voltage and current to within a few tenths of 1%. The target focal spot was about 3 mm in diameter.

Calcite crystals were used after preliminary experiments indicated that reflection of the continuous x-ray

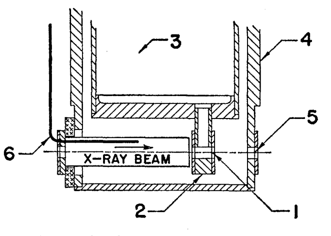

Fig. 1. Section through the low-temperature absorption cell.

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[1] R. Kronig, Z. Physik 75, 191 (1932).

spectrum from the (11·0) planes of quartz was too feeble to permit precise measurements in a reasonable time. The calcite crystals were cleaved and tested for quality by measuring the (1, −1), (1, +1), and (2, +2) rocking curves using the iron $K\alpha$ radiation at 1.93 A. The crystals were Class I at this wavelength, giving rocking curve widths in good agreement with those reported by Parratt.[2]

A xenon-methane side window proportional counter was used as detector. The pulse-height distribution was such as to separate clearly the first-order continuous radiation from the second order. A single channel pulse-height discriminator following the linear amplifier effectively removed all second order pulses, in addition to reducing the background count to a negligible value.

Figure 1 is a section through the absorption cell and cryostat. Two thin (3 mil) beryllium windows (1) were sealed with indium wire gaskets to the absorption cell chamber (2) which was soldered to the reservoir (3). The reservoir and absorption cell could be filled with the absorbing gas, or, for the experiments on the solidified gas, with liquid helium. The 1.1-cm path through liquid helium transmitted about 80% of the radiation at 3.9 A. The entire absorption apparatus was contained in a refrigerated housing (4) which acted as a radiation shield and which was cooled by thermal contact with a liquid nitrogen reservoir. Additional thin (2 mil) beryllium windows (5) were used to cover the apertures in this jacket to reduce radiant heat to the absorption cell. At 3.9 A the x-ray intensity through the various windows, but with no argon film, was about 3000 counts per minute for the continuous spectrum. A small bore nickel tube (6) was brought near the absorption cell to allow the absorber gas to diffuse onto the beryllium window to form a film of solid absorber approximately 0.002 mm thick.

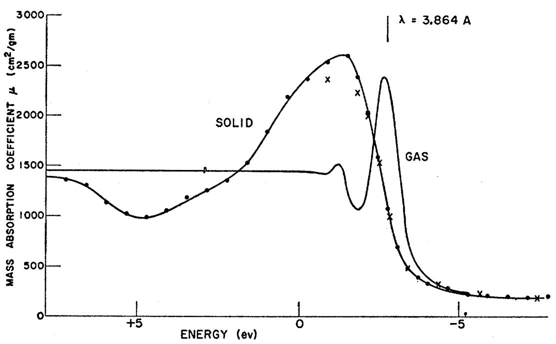

FIG. 2. Mass absorption coefficients of gaseous and solid argon in the region of the *K*-absorption edge at 3.86 A. Crosses are points on the arc tangent curve calculated to fit the observed absorption edge in the solid. The position of the iron $K\alpha_1$ emission line ($2\lambda = 3.864$ A) in the second order is shown for wavelength calibration.

The correct thickness for the argon film was determined by monitoring the x-ray intensity transmitted through the film as the gas condensed. The flow of argon from a low-pressure reservoir to the condensing surface was controlled by a high-vacuum valve which could be closed when an optimum absorber thickness had been reached. The absorption edge structure of solid argon was measured several times with no significant differences in the results, indicating that the films were of uniform density. The pressure in the main vacuum chamber was normally below 5×10^{-7} mm Hg during an experiment, although it was observed to rise slightly during the formation of the absorbing film.

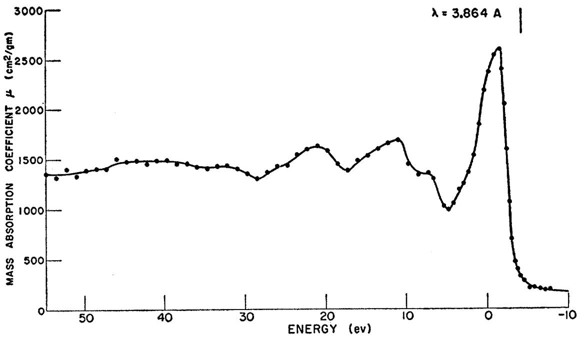

FIG. 3. Mass absorption coefficient of the solid argon to higher energies.

The experiments on the *K*-absorption edge structure of krypton at 0.86 A were performed with a tungsten target Machlett diffraction tube as x-ray source. For the gas absorption measurements the sample was contained in a cell closed with 0.001-in. thick aluminum windows. The solid krypton experiments were conducted in the same manner as those for argon.

Figure 2 shows the *K*-absorption edge structure of gaseous and solid argon. Values of the mass absorption coefficient were computed from the intensity data by assuming a suitable thickness of solid absorber to give agreement with the well-known values of the absorption coefficient at energies more than one hundred electron volts from the absorption discontinuity. Statistical uncertainty in the absorption coefficients is ±30 cm²/g and the absolute uncertainty in fitting to the known absorption coefficients[3] is also ±30 cm²/g.

The zero energy point has been chosen to agree with the series limit of the $1s \rightarrow np$ Kossel lines as proposed by Parratt.[4] The $1s \rightarrow 4p$ and $1s \rightarrow 5p$ lines are shown clearly resolved by the calcite crystals. The spectra of Fig. 2 have not been corrected for instrumental resolving power. When so corrected, the sharp absorption lines can be made to yield the true width of the inner *K* state.[5]

Figure 3 shows the absorption spectrum of solid argon

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[2] L. G. Parratt, Rev. Sci. Instr. **6**, 387 (1935).

[3] A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand Company, Inc., New York, 1935), second edition, p. 805.

[4] L. G. Parratt, Phys. Rev. **56**, 295 (1939).

[5] The present data indicated that the argon inner level width is less than 0.75 ev. Parratt has determined this width to be about 0.58 ev.

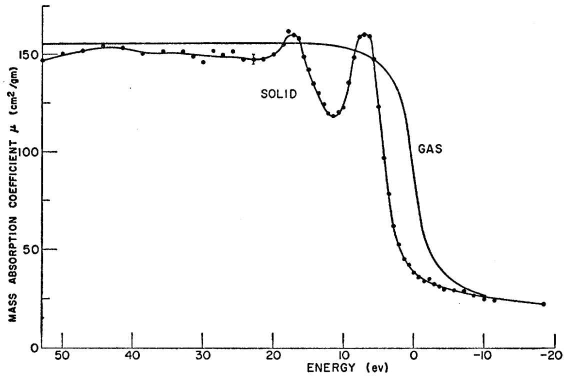

FIG. 4. Mass absorption coefficient of gaseous and solid krypton in the region of the *K*-absorption edge at 0.86 A.

to 40 ev from the absorption edge. Figure 4 shows the corresponding result for krypton. The Kossel lines in the gas absorption spectrum are unresolved, as observed previously.[6] However, as before, the zero of the energy scale has been assigned by analyzing the edge into component lines approaching a series limit.[6] Two principal maxima are seen in the solid krypton spectrum. The mass absorption coefficients were computed as for argon by fitting the observed data to the known absorption coefficients at energies far from the absorption discontinuity. The uncertainty in the plotted points is approximately ± 2 cm^2/g.

Richtmyer[7] has shown that x-ray transitions involving a continuum or band of energy levels having a sharply defined edge will result in an emission or absorption edge structure of arc tangent shape. Figure 2 shows such calculated arc tangent points fitted to the observed solid argon spectrum. The sharp initial rise at the absorption edge is clearly too high to be accounted for wholly by such transitions. It appears that x-ray-induced transitions into the *p*-symmetry states in the conduction band of solid argon exhibit strong resonances for energies 1 or 2 ev less than the ionization energy of the isolated argon atom. This result is in good agreement with present ideas concerning the formation of excitation states near the lower edge of the conduction band in x-ray excited solids.

The initial rise at the absorption edge of solid krypton, although displaced 4 ev to greater energies than the ionization potential of the isolated atom, also shows the steep slope to be expected on the basis of exciton theory.

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[6] C. H. Shaw, Phys. Rev. **57**, 877 (1940).

[7] Richtmyer, Barnes, and Ramberg, Phys. Rev. **46**, 843 (1934).

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Effective Ionic Charge in Alkali Halides

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An expression is derived for the effective charge in the Born-Szigeti equation for the dielectric constant of ionic crystals with the NaCl structure. The derivation is based on a coupled oscillator model in which the lattice vibrations are coupled to the electronic motions within the ions. The deviation of the ionic charge from its nominal value is found to be proportional to the difference in electronic polarizability between the positive and negative ions. Agreement between theory and experiment is satisfactory. Secondary effects on the index of refraction and the reststrahl frequency are calculated. The model is in semiquantitative agreement with the observed dipole moments of alkali halide molecules.

INTRODUCTION

THE dielectric constant of an ionic crystal at low frequencies exceeds its value at optical frequencies owing to the lattice distortion produced by the application of an electric field. The contribution of a lattice of rigid ions was first estimated by Born,[1] who derived for an NaCl type crystal the relation

$$\epsilon - n^2 = 3Le^2/\mu\Omega_t^2 v, \tag{1}$$

where ϵ is the static dielectric constant, n the index of refraction, v is the volume of a unit cell, e the ionic charge, L the Lorentz factor, μ is the reduced mass of a neutral ion pair, and Ω_t is the infrared, angular resonance frequency for transverse electric waves of infinite wavelength.

At optical frequencies, where the ionic displacement is negligibly small compared to the electronic displacement, we may write

$$n^2 - 1 = (\alpha_0/v)(Ln^2 - L + 4\pi), \tag{2}$$

where n is the index of refraction and α_0 is the polarizability of a unit cell in the lattice. It is customary to assume that polarizabilities are additive so that for a diatomic crystal such as NaCl

$$\alpha_0 = \alpha_0^+ + \alpha_0^-, \tag{3}$$

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[1] M. Born, Physik. Z. **19**, 539 (1918).