

creasing the accidental rate. Other improvements should be noted, such as a higher beam energy (although multiple π -production might hinder this); an improved β -gate; and generally refined electronics. It can be seen, using reasonable factors for these improvements, that while the μ -pair/ π^+ ratio could be improved, the electromagnetic pair production yield would be far from reached.

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The Optical Absorption and Photoconductivity of Rutile*

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RUTILE (TiO_2) single crystals¹ have been investigated by optical and electrical methods. The optical density of a 1-mm plate, cut perpendicular to the optic axis, is shown in Fig. 1. The absorption edge at 0.4μ is steep even at room temperature, and becomes very sharp at low temperatures ($<30^\circ\text{K}$). The 0.4μ absorption has been identified as the fundamental lattice absorption of rutile at 3.06 ev. This absorption has been correlated with the high temperature ($350^\circ\text{--}850^\circ\text{C}$) conductivity measurements which give a value $E_G = 3.05$ ev.

The 1-mm thick crystal shows photoconductivity (ac method) peaking on the rise of the fundamental absorption at 0.41μ and having a long wavelength response extending into the infrared beyond 1μ , with a corresponding tail of the optical absorption.

Upon slightly reducing the crystal in a hydrogen atmosphere at 600°C (or heating in vacuum), a blue color which accompanies the oxygen loss from the crystal is noted. The weight loss during reduction has been studied; the reduction-oxidation cycle proves reversible for small oxygen loss as far as weight changes are concerned. This reversibility shows that the formation of oxygen ion vacancies in the crystal does not lead to a loss of titanium under these conditions. The blue coloring arises from the visible tail of an optical absorption band with its maximum at approximately 1.8μ , as shown by the dotted lines in Fig. 1.

A simple atomic model² has been used for a calculation of the

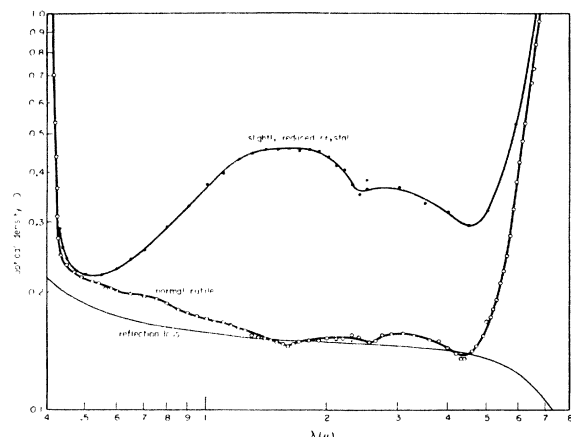


FIG. 1. Optical density vs wavelength for normal and slightly reduced rutile.

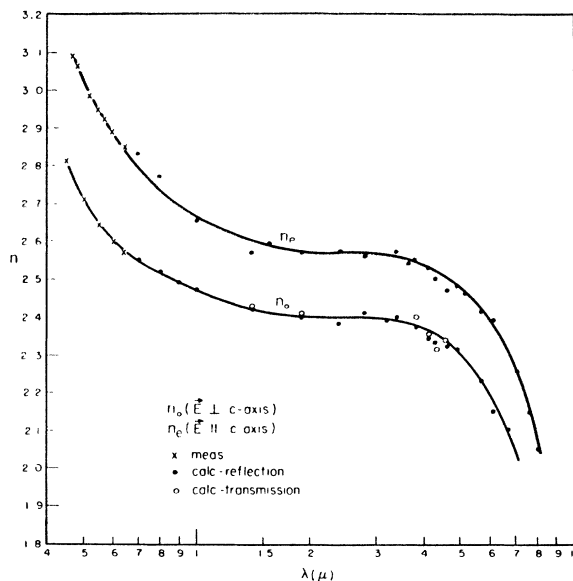


FIG. 2. Index of refraction vs wavelength of ordinary and extraordinary ray.

various impurity and lattice-defect levels inserted in the electronic structure of the material. An impurity atom of valence $+3$ or $+5$ will act as an acceptor or donor, respectively, if it enters substitutionally at a titanium site (Ti^{4+}); for such an impurity, the ionization energy would be that of a hydrogen atom immersed in a polarizable medium of dielectric constant κ_e . In this case, the ionization energy is vastly reduced and amounts to the ionization energy divided by the square of the dielectric constant, that is, $13.6/\kappa_e^2$ ev. Similarly, a vacant oxygen site may be considered as a doubly-charged center resembling a helium atom and having the ability to trap two electrons with the reduced ionization energies of helium, $24.6/\kappa_e^2$ and $54.4/\kappa_e^2$ ev. The value $\kappa_{e0} = (2.40)^2$ has been determined from the flat portion of the index of refraction curve (Fig. 2) for the ordinary ray. For rutile, the index of refraction has been calculated from the reflecting power curves of Liebisch and Rubens.³ Transmission data support this calculation in the 1.5μ to 5μ region.

The three optical absorptions (corresponding to impurity-level ionization energies) predicted in this manner are given in Table I. Experimental values derived from maxima of optical absorption and of photoconductivity are indicated for comparison. If this same type of calculation is carried out using the static dielectric constant, ionization energies as small as 0.002 ev are found for the hydrogen-like impurity levels. The approximation of using the macroscopic index of refraction should have greater validity in the case of a material with high index of refraction, since the electronic charge cloud is spread out over a larger volume of the material. For the case of the alkali halides a similar calculation yields only qualitative agreement with experiment.

This work was done under the supervision of Professor A. von Hippel to whom we are indebted for his interest and encouragement. We are grateful to Professors L. Harris and R. C. Lord,

TABLE I. Impurity-level ionization energies for rutile.

Origin of added energy level	Electronic configuration	Ionization energy calculated		Ionization energy observed
Impurity atom, valence 3 or 5	Hydrogen	0.42 ev	$2.9 \lambda(\mu)$	$2.8\text{--}3.2^a \lambda(\mu)$
Vacant oxygen site	Helium	0.74	1.7	$1.5\text{--}1.9^b$
	He^+	1.64	0.76	0.73^c

^a From absorption measurements; the evidence is not conclusive.

^b Definite evidence from absorption and from photoconductivity for wavelengths between 1 and 3μ .

^c Some evidence from photoconductivity measurements.

Massachusetts Institute of Technology, for the absorption measurements in the 0.8μ to 7μ region.

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¹ Courtesy of the National Lead Company, Titanium Division, Research Laboratory, South Amboy, New Jersey.

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Absorption Spectrum of Thallium-Activated Potassium Chloride Phosphor at Low Temperatures

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AN important feature of recent quantitative theoretical work on solid-state luminescence is the effect of zero-point energy in maintaining broad absorption and emission spectra at low temperatures.¹ A comparison of experimental optical absorption of KCl:Tl in the band near 5 ev due to Tl⁺, reported here, with calculated absorption indicates the existence of zero-point energy² of the calculated order of magnitude.

A clear crystal of KCl:0.00021 Tl grown from the melt in a furnace of the type described by Strong³ is clamped in the copper sample holder of the cooling apparatus shown in cross section in Fig. 1. The only openings in the holder are two 3×5 -mm rectangles

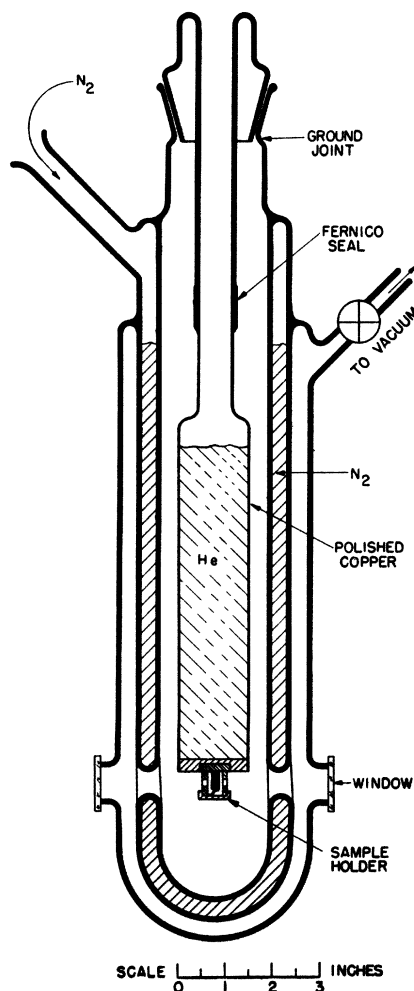


FIG. 1. Apparatus for optical absorption of crystals at liquid helium temperature.

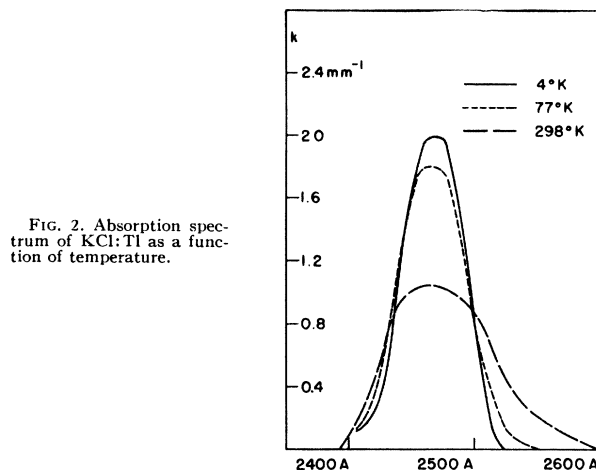


FIG. 2. Absorption spectrum of KCl:Tl as a function of temperature.

to allow passage of transmitted light. An advantage in the construction of this apparatus is that there are only two quartz windows in the optical path. These, being at room temperature, can be attached with vacuum sealing wax. Except for the inner container, the apparatus is of Pyrex, silvered on all surfaces exposed to the vacuum. The apparatus with crystal in position is placed between a low voltage hydrogen discharge lamp and the entrance slit of a recording grating spectroradiometer. Heating of the crystal by the hydrogen lamp is found to be negligible. Recordings of the light from the source transmitted by the crystal at room temperature, then with liquid N₂ in both coolant containers, and finally with liquid helium in the inner container are obtained. From these and a recording of the unattenuated output of the hydrogen lamp, the absorption as a function of wavelength at the various temperatures as given in Fig. 2 is determined. The error in estimation of half-widths of the absorption band is less than 10 percent. On continued irradiation by the hydrogen lamp at 77°K or 4°K a weak absorption band not shown in Fig. 2, possibly due to V-centers,⁴ developed in the crystal with peak at 2340 Å. The thallos ion absorption reported here has been obtained taking care to minimize development of V-centers, since the two absorption bands overlap to some extent.

Table I compares the experimental half-widths in electron volts with the calculated values. If zero-point energy is neglected, only the 4°K half-width is affected appreciably, being reduced to 0.031 ev. There is no doubt that the experimental values can be reconciled only with the values calculated using zero-point energy; and the zero-point energy used in the calculations must be of the correct order of magnitude. It should be pointed out also that the experimental variation with temperature in peak height of absorption shown in Fig. 2 agrees well with the calculated absorption.¹ The area under the absorption curve is substantially independent of temperature, the oscillator strength being 0.06 in all cases.

TABLE I. Absorption half-width.

Temp.	Experimental	Calculated
4°K	0.108 ev	0.122
77°K	0.127	0.132
298°K	0.204	0.193

We are indebted to Dr. M. D. Fiske of the cryogenic laboratory for assistance and advice in designing the double vacuum flask and in the use of liquid helium.

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