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Color Centers in TlCl*

R. W. Christy and J. D. Dimock
Dartmouth College, Hanover, New Hampshire

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Although TlCl is thought to contain an equilibrium number of anion vacancies which is comparable with the alkali halides, no *F* centers can be produced in pure TlCl, either by x-ray irradiation at 100 or 300°K, or by addition of excess Tl metal. Addition of chalcogen impurities, however, produces an absorption peak in crystals quenched from high temperature. This peak lies at 409 mμ in $\mathrm{TlCl{:}Tl_2S}$ and at 420 mμ in $\mathrm{TlCl{:}Tl_2Se}$, with oscillator strengths of 0.22 and 0.27, respectively; the peak narrows and the position shifts when the absorption is measured at lower temperature. The direction of the temperature shift is unusual, in that it moves toward longer wavelength at low temperature. As the quenched crystal approaches equilibrium at room temperature, the peak transforms into another band whose peak is hidden by the fundamental absorption. This band is identical for the sulfur- and selenium-doped crystals, and it is independent of the temperature of measurement. At intermediate temperatures, the equilibrium absorption is a mixture of the two bands, which have an isosbestic point at 455 mμ. At room temperature the transformation occurs in the dark, although its rate is accelerated by illumination with white light. In both cases the rate is faster for the sulfur-doped crystals than for the selenium-doped ones. Similar bands are observed in $\mathrm{TlBr{:}Tl_2S}$ and $\mathrm{TlBr{:}Tl_2Se}$, although in this case all the peaks are hidden by the fundamental absorption. The room-temperature absorption, which is independent of the impurity and of temperature, is interpreted as due to colloidal Tl metal. The high-temperature peak, which is capable of reversible transformation into the colloid band, is interpreted as due to *F* centers associated with $\mathrm{S^-}$ or $\mathrm{Se^-}$ impurity ions. The transformation to the colloid absorption results from coagulation of the *F* centers. With this explanation, some comparisons are drawn with *F* centers in the cesium halides on one hand, and with the impurity absorption bands in chalcogen-doped silver halides on the other hand.

I. INTRODUCTION

OPTICAL absorption due to defect centers in crystals has been most extensively investigated in the monovalent alkali halides[1] and silver halides.[2,3] While these two systems exhibit some general similarities in their photochemical behavior, their differences, characterized by atomic and molecular centers in the alkali halides (*F*- and *V*-type centers) and colloid absorption in the silver halides (the photographic latent image), apparently reflect significant differences in the atomic constitution of the two crystal types. In the alkali halides, transformation of the atomic centers to metallic colloid centers is well known; but in the silver halides, absorption due to atomic precursors of the colloidal metal aggregates is still an interesting question in the pure crystal. One might suppose that the difference is associated with the known preponderance of Schottky defects in the alkali halides and Frenkel defects in the silver halides, in thermal equilibrium. The stability of anion vacancies is consonant with the observation of the *F* center (an electron trapped at an anion vacancy) in the alkali halides, but the cation interstitial in the silver halides is less well established as an electron trap. (The cuprous halides are probably similar to the silver halides.[4])

Long ago it was conjectured that the thallium halides might provide an intermediate case between the alkali and silver halides.[5] Hilsch and Pohl observed an absorption band in TlCl, produced by ultraviolet irradiation. This photochemically produced absorption displayed the phenomenon of selective bleaching ("Farbanpassung"), and they therefore identified it with a colloid absorption like that of AgCl, concluding that TlCl and AgCl show essentially identical behavior. More recently, however, it has been established[6,7] that Schottky defects predominate in TlCl rather than Frenkel defects. This fact therefore suggests a search for *F* centers in the thallium halides. It furthermore reinforces the supposition, abandoned by Hilsch and Pohl, that the thallium halides might combine some of the properties of the alkali and silver halides. Thallium chloride, although containing predominantly Schottky defects like the alkali halides, closely resembles silver chloride in its mechanical and optical properties. It is ductile, with a low melting temperature, and the tail of the fundamental absorption (or the exciton absorption) extends nearly into the visible spectrum. Unlike silver chloride, it crystallizes with the cesium chloride structure; and unlike the alkali halides, the anion vacancy is much more mobile than the cation vacancy.

In most of the alkali halides, *F* centers can be produced either photochemically or by the addition of excess alkali metal atoms (equivalent to addition of anion vacancies and electrons). Photochemical genera-

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[2] J. W. Mitchell, Rep. Progr. Phys. **20**, 433 (1957).

[3] O. Stasiw, *Elektronen- und Ionenprozesse in Ionenkristallen* (Springer, Berlin-Göttingen-Heidelberg, 1959).

[4] Y. W. Hsueh and R. W. Christy, J. Chem. Phys. **39**, 3519 (1963).

[5] R. Hilsch and R. W. Pohl, Z. Physik **64**, 606 (1930).

[6] K. Hauffe and A.-L. Griessbach-Vierk, Z. Elektrochemie **57**, 248 (1953).

[7] R. J. Friauf, J. Phys. Chem. Solids **18**, 203 (1961); Suppl., J. Appl. Phys. **33**, 494 (1962); and private communication.

tion of F centers occurs as a result of x-ray irradiation; it can occur as a result of uv irradiation only to the extent that impurities are present. In silver halide crystals, excess silver metal is insoluble.[8] In fact, pure perfect crystals are also very insensitive to irradiation, and the photochemical behavior is probably due primarily to the presence of impurities or dislocations. Excess metal *is* soluble in several *molten* halides,[9] including silver and thallium, but it tends to precipitate out upon solidification of the salt. Furthermore, similar experiments with molten alkali halides[10] suggest that this phenomenon has nothing to do with F centers. The purpose of the present paper is to investigate the possibility of producing color center absorption bands in thallium chloride crystals, both photochemically and additively.

The role played by impurities is significant in the alkali halides and perhaps crucial in the silver halides. Four different roles can be distinguished. Most obviously, the impurity atoms themselves may absorb light, giving rise to impurity absorption bands. Secondly, the impurities may introduce a proportionate number of intrinsic defects, which give their own characteristic absorption band. Thirdly, it may be possible to produce intrinsic defects by photochemical action on the impurities. Finally, the impurities could *catalyze* the production of intrinsic defects in greater numbers. All of these effects are observed in the alkali or silver halides, and some will be seen to occur in TlCl. Of interest in our work are the chalcogen impurities O, S, Se, Te. In the silver halides these impurities produce absorption bands in the visible region; these bands and their photochemistry have been extensively studied by Stasiw and coworkers.[3] In KCl the addition of K_2O produces bands in the far uv near the fundamental absorption edge.[11]

In the following are described attempts to generate color centers in pure TlCl, and the absorption resulting from the introduction of chalogen impurities. To anticipate the results, no color centers are produced in pure TlCl by the absorption of x-rays at liquid-nitrogen or room temperatures, nor is it possible to produce color centers by introducing a nonstoichiometric excess of Tl metal into pure TlCl. Doping with chalocogens, however, produces absorptions whose equilibrium state, temperature dependence, and oscillator strength will be described. The absorption will be interpreted in terms of F centers associated with chalconide ions. We shall conclude that TlCl indeed forms a link between the alkali and silver halides. More importantly, it may exhibit some phenomena which have been conjectured to play a role in the silver halides, but uncomplicated by the presence of cation interstitials.

II. EXPERIMENTAL

Pure crystalline TlCl was prepared from TlCl powder (obtained from A. D. Mackay, Inc., New York). The powder was fused and then zone-refined. All high-temperature operations were carried out in a dry nitrogen atmosphere, in order to avoid oxidation of the TlCl. After 10 to 20 sweeps of the zone refiner, a transparent colorless ingot resulted. Spectrographic analysis of one such ingot[12] revealed less than 1 ppm of Mg, Al, Si, Ca, Fe, and Cu, with no other metallic impurities detectable. In some cases a special effort was made to remove any hydroxide which might be present. The removal was accomplished by bubbling through the molten TlCl a stream of anhydrous HCl gas, which had been dried by bubbling through sulfuric acid. (Sometimes halogen gas is used to remove hydroxide from alkali halides, but treatment of thallium chloride with chlorine gas results in the formation of thallium sesquichloride, Tl_4Cl_6, which is deep yellow.) Not all of the pure starting material was treated in this way, however, since no difference in properties was observed as a result of the treatment. Material to which hydroxide was intentionally added was also tested. This addition resulted from the reverse reaction, effected by bubbling steam through the molten TlCl.

The attempts to produce additive coloration of TlCl with excess Tl metal were carried out by melting the TlCl together with pure Tl metal (obtained from Mackay). In this process, special precautions are necessary to avoid oxidation of the metal. A small piece of metal was cut from the inside of a larger piece. This small piece, on which a thin oxide coating quickly formed, was melted together with a larger amount of TlCl in a nitrogen atmosphere. The oxide coating on the metal then dissolved in the TlCl, which, upon solidification, was cut away, leaving only the pure Tl metal, protected from further oxidation by a thin layer of TlCl. This piece of unoxidized Tl could then be added to pure TlCl to test for its solubility.

The thallium chalconide dopants were prepared by reacting thallium metal with sulfur, selenium, or tellurium. Stoichiometric proportions of the elements were melted together, and they reacted immediately to form the chalconide. (Thallium oxide was scraped off thallium metal oxidized in air.) The chalconide was then melted with TlCl to form a doped sample. In order to achieve a final concentration of the order of 10^{-5}, it was not practicable to add the impurity in one step. Instead an intermediate concentration of about 10^{-3} was prepared. Because it is doubtful whether so large an impurity concentration is soluble below the melting point, special precautions were taken to prevent segregation of the impurity upon solidification. One drop of the material was separated from the rest while still molten, and this entire solidified drop was then added to pure TlCl to get the final concentration.

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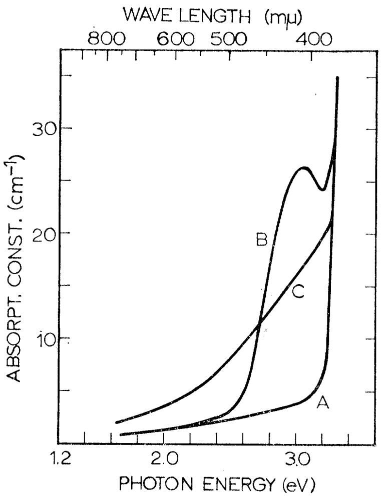

FIG. 1. Optical absorption of pure and sulfur-doped TlCl crystals, measured at room temperature. Curve A: pure TlCl. Curve B: TlCl:Tl_2S, quenched from high temperature. Curve C: TlCl:Tl_2S, in equilibrium at room temperature.

Optical samples of pure or doped material were prepared by pressing thin crystals between Pyrex plates at about 300°C. Improvement of the optical quality of the surface was sometimes obtained by polishing on a wet paper towel. The optical samples were usually about 1 mm thick. The optical absorption was measured with a Unicam SP-700 recording spectrophotometer.

X-ray irradiation was done with a tungsten target x-ray tube, operated at 50 kV and 40 mA. The crystal was normally placed on a 1-mm thick microscope slide in contact with the x-ray tube window.

III. RESULTS

A. Pure TlCl

Attempts to produce coloration in pure TlCl crystals by dissolving excess Tl metal were not successful. The metal did dissolve in the molten TlCl at high temperature, transforming the normally clear orange liquid TlCl into an opaque black solution, as observed previously.[9] As the temperature was lowered, however, the metal came out of solution, and on reaching the freezing point the clear yellow color of the normal liquid was apparently restored. At room temperature the solidified TlCl showed no trace of color.

Pure TlCl was also found to be very insensitive to x-ray irradiation. One sample was irradiated for 64 h at room temperature in a nitrogen atmosphere, without producing any unmistakable coloration. A KCl crystal irradiated under similar conditions would produce 10^{17} *F* centers/cm^3 in about 15 min. A crystal was also irradiated near liquid-nitrogen temperature for 3 h with similar results. Thus if color centers are formed by the irradiation, they are apparently unstable even near 100°K.

B. Addition of Chalcogen Impurities

1. Absorption Spectrum

A number of different chalconide impurities have been added to TlCl, but the specimens doped with Tl_2S have been studied in greatest detail. The absorption spectrum in the visible region is shown in Fig. 1 for a TlCl crystal containing a mole fraction of 1.2×10^{-5} Tl_2S. The absorption edge of a pure TlCl crystal is also shown for comparison. All the absorption measurements were made at room temperature. When the doped crystal is quenched from high temperature, a resolved absorption peak appears on the low-energy side of the absorption edge, giving the crystal a yellow color. As it remains at room temperature, however, this peak transforms into an absorption tail, which produces a brown color. A similar yellow color, which transforms with time into brown, has been observed in TlCl doped with the following chalconides: Tl_2O, Tl_2S, Tl_2Se, K_2O, K_2S, Na_2S, Ag_2S. Beside Tl_2S, the only dopant whose effects have been studied quantitatively is Tl_2Se. The solubility of oxide is small, and the transformation from yellow to brown progresses very quickly; additions of Tl_2Te produced only a brown color. Nevertheless, all these additives appear to have qualitatively similar effects.

When the absorption of pure TlCl is subtracted from that of the sulfur-doped crystal, curves like those of Fig. 2 are obtained. This figure shows the peak which gives the yellow color, at 409 mμ (3.03 eV), and the absorption tail which gives the brown color. In addition it shows two intermediate states of the crystal. The isosbestic point at 455 mμ (2.73 eV) is worth noting, since it indicates that the centers which give rise to the peak actually transform into those which produce the tail. The equilibrium between these two kinds of centers as a function of temperature, and the rate of approach to equilibrium at room temperature, will be discussed in more detail in Sec. 3.

The height of the peak is found to be proportional to the amount of Tl_2S which is added. From the proportionality constant and the measured half-width, one obtains by means of Smakula's formula as modified by Dexter[1] an oscillator strength of 0.22 for this peak. In making the calculation it is necessary to extrapolate the refractive index of TlCl from the value measured at

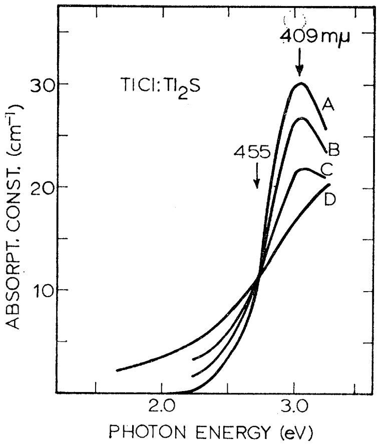

FIG. 2. Absorption produced by addition of 16 ppm of Tl_2S to TlCl, measured at room temperature. Curve A: quenched from high temperature. Curve D: in equilibrium at room temperature. Curves B and C: intermediate states.

589 mμ, but the quoted oscillator strength is probably accurate to within about 10%.

Additions of Tl_2Se to TlCl give results which are similar to those described for additions of Tl_2S. In fact, the absorption tail which produces the brown color is exactly identical to the one which results from the same concentration of sulfide. Thus the absorption tail is not associated with the chalconide itself; it will be argued in Part IVB that it is due to small colloidal particles of thallium metal. The peak which produces the yellow color is similar to the one in sulfur doped samples, but it is at slightly longer wavelength, 420 mμ (2.95 eV), and is slightly wider. The calculated oscillator strength is 0.27. In addition, in the selenium-doped crystals the transformation from the peak to the tail occurs much more slowly at room temperature, as will be shown in Sec. 3.

Experiments have also been carried out on TlBr with additions of Tl_2S and Tl_2Se, with results which are similar to those in TlCl. In this case, however, all the peaks are hidden by the fundamental absorption. Although the impurity bands probably lie at longer wavelengths in the bromide as compared with the chloride, the fundamental absorption is displaced even more toward long wavelength, so that only the tail of the impurity absorption can be seen. The transformation from the high-temperature absorption to the room-temperature equilibrium is faster in the bromide, the rate for $TlBr{:}Tl_2Se$ being three times that for $TlCl{:}Tl_2Se$. The isosbestic point is observable, lying at 500 mμ (2.48 eV) in $TlBr{:}Tl_2Se$.

2. *Temperature Dependence*

When the temperature of a sulfur-doped TlCl crystal is lowered from room temperature to the vicinity of liquid-nitrogen temperature, the absorption tail which gives the brown color at room temperature remains exactly the same. This temperature-independent absorption is the behavior which is expected of colloidal metal particles. On the other hand, the high-temperature peak which gives the yellow color narrows and the peak wave-length position shifts when the temperature is lowered. (See Fig. 3.) This temperature dependence of the position and shape of the absorption band is characteristic of an atomic center. In Part IVB we shall present reasons for identifying the high temperature peak with an *F* band. The *direction* of the shift, however, toward lower energy with a decrease of temperature is very unusual.

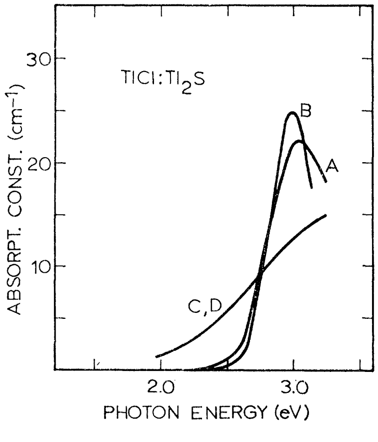

FIG. 3. Temperature dependence of the absorption produced by 12 ppm Tl_2S. Curves A and B are for quenched samples, curves C and D for room temperature equilibrium samples. Curves A and C are measured at 300°K, curves B and D at 115°K.

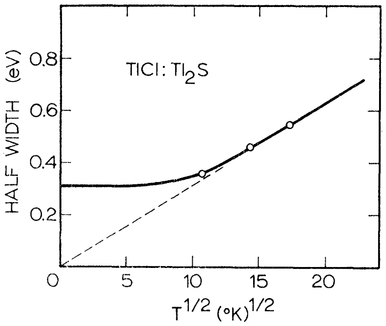

FIG. 4. Full width at half-maximum as a function of temperature for sulfur-doped TlCl.

It is of interest to plot the measured half-width *W* versus the square root of absolute temperature *T*, since the relation

$$W=A[\coth(h\nu/2kT)]^{1/2}$$

is expected to hold for an *F* band,[1] giving *W* proportional to $T^{1/2}$ at high temperatures. In Fig. 4 the measured half-width for a sample containing 1.2×10^{-5} Tl_2S has been fit to this expression, with

$$A=0.31 \text{ eV},\ \nu=4\times10^{12} \text{ sec}^{-1}.$$

Although the fit is satisfactory, very little accuracy can be claimed for the values of the parameters, since the low-temperature range was inaccessible with our equipment. The values can be regarded as upper limits. (Measurements could not be made appreciably above room temperature either, because the peak and the absorption edge move toward each other and the peak is unresolved.) Nevertheless, the approximate values of the parameters are reasonable, being about the same as for the *F* band in NaCl.

The properties of the absorption peak in TlCl doped with Tl_2S and Tl_2Se are summarized in Table I. This table gives the peak position and full width at half-maximum *W* at room temperature; the change in position and width when the temperature is lowered to

TABLE I. Properties of the absorption peak in doped TlCl. λ and $h\nu$ are the wavelength and energy at the peak; *W*, the room-temperature full width at half-maximum; ΔW and $\Delta h\nu$, the changes in *W* and $h\nu$ when the temperature is lower to ≈110°K; *f*, the oscillator strength.

Impurity	λ	$h\nu$	W	$\Delta h\nu$	ΔW	f
Tl_2S	409 mμ	3.03 eV	0.58 eV	0.06 eV	0.26 eV	0.22
Tl_2Se	420	2.95	0.67	0.03	0.14	0.27

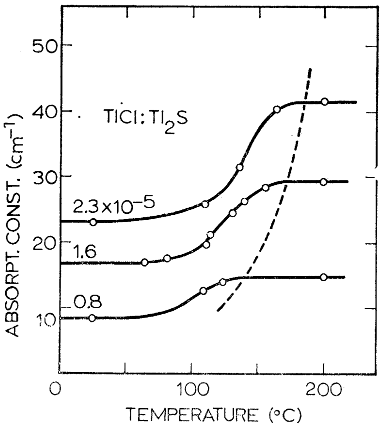

FIG. 5. Equilibrium absorption at 409 mμ, as a function of temperature, for different sulfur concentrations. Absorption measured at room temperature immediately after quenching from the equilibrium temperature.

about 110°K; and the oscillator strength f calculated from the peak height and width. The peak wavelength λ is accurate to about ± 2 mμ; W and f are accurate to within 10%; $\Delta h\nu$ and ΔW are accurate to about 20%.

3. Thermal Equilibrium

When a sulfur-doped TlCl crystal is quenched in air from a temperature near the melting point to room temperature, the observed absorption is the resolved peak which produces the yellow color. In equilibrium at room temperature, however, the absorption is the tail which produces the brown color. At intermediate temperatures, the equilibrium absorption is a mixture of these two bands. This equilibrium is shown as a function of temperature in Fig. 5. Here the absorption constant at 409 mμ is plotted as a function of the equilibrium temperature from which the crystal was quenched, for three different concentrations of sulfur. All the absorption measurements were made at room temperature immediately after quenching. At high temperatures the curves saturate at a peak height proportional to the impurity concentration; and at low temperatures they saturate at a point on the tail attributed to colloidal metal, whose height is also proportional to impurity concentration. At intermediate equilibrium temperatures the absorption is due to the sum of the two bands in equilibrium with each other. It may be noted that the high-temperature saturation is attained at higher temperatures the greater is the impurity concentration. This is the type of behavior which would be expected if the equilibrium were between colloidal metal particles and a "vapor" of isolated F centers.

The rate of approach to equilibrium is shown in Fig. 6, for Tl_2Se as well as Tl_2S doped crystals. For crystals quenched from near the melting point, the absorption at 409 mμ is plotted versus time at room temperature, as an excess over the final equilibrium value of absorption. These curves show that the rate of approach to equilibrium is much slower for selenium doping than for sulfur doping. They also show that in both cases the rate is accelerated by shining light (from a 100-W bulb 20 cm distant) on the crystal. Nevertheless, the transformation from the peak to the absorption tail is not a purely photochemical effect, since it also occurs in the dark, although at a slower rate. This is also the kind of behavior which is observed in alkali halides when F centers coagulate to form colloidal metal.

When the colored crystals are annealed in air for a long time at high temperature—say several days at 300°C—the color disappears completely. This effect does not occur, however, when the annealing takes place in a nitrogen atmosphere. An explanation will be given below, in terms of diffusion of oxygen into the crystal.

IV. DISCUSSION

A. Pure TlCl

It has been found that no color centers can be observed in pure TlCl, either as a result of x-irradiation or addition of excess Tl metal. Assuming that Schottky defects predominate in TlCl as in the alkali halides, one may ask why not. The question can be discussed separately with respect to photochemical and additive coloration, since, for example, LiCl is known to form F centers under irradiation but attempts to color it additively have been unsuccessful. The problem of additive coloration is primarily a thermodynamical one, concerning the solubility of excess metal in the form of F centers. The photochemical problem, on the other hand, is a kinetic one, depending on the mechanism of F-center formation, which is not yet completely understood. Since the thermodynamical problem is the simpler one, we shall discuss it first.

The F center concentration x_F in a crystal in equilibrium with a vapor containing n_v metal atoms per unit volume has been calculated by Gurney and Mott.[13]

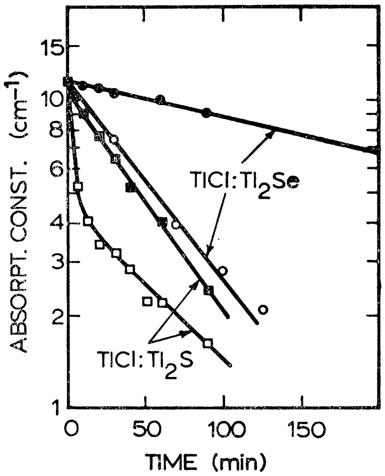

FIG. 6. Approach to equilibrium at room temperature for sulfur- and selenium-doped TlCl quenched from high temperature, as a function of time after quenching. In each case the upper curve is for a sample held in the dark and the lower curve is for a sample illuminated with white light.

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[13] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, Oxford, England, 1948), 2nd ed., pp. 144–7.

The result is

$$x_F = n_v(2\pi mkT/h^2)^{-3/2}e^{-W_F/kT},$$

where W_F is the energy required to add an excess metal atom to the crystal, forming an F center. The quantity W_F contains the difference between the ionization energy of the metal atom and the binding energy of the salt; in addition it contains the difference between the energy needed to remove a negative ion from the crystal and the energy needed to remove an electron from an anion vacancy. The formula successfully accounts for the additive coloration of alkali halides by holding them at high temperature in an atmosphere of alkali metal vapor. Although the method by which we attempted to color TlCl differed, the formula is still applicable if we consider the three-phase equilibrium between metal, salt containing F centers, and vapor. Then n_v is the equilibrium vapor density of the metal at temperature T.

From the formula, it appears that the failure to observe additive coloration in TlCl results from the large ionization energy of Tl, the small vapor pressure of Tl, and the low melting point of TlCl. The highest concentration of F centers which could be expected would be that quenched in from the melting point of the crystal. The value of n_v for Tl metal vapor near the melting point of TlCl is nearly a million times smaller than the value for K metal near the melting point of KCl. The F-center concentration in TlCl might be further depressed in comparison to KCl by a larger value of W_F: The binding energy of TlCl is about the same as that of KCl, but the ionization energy of Tl is appreciably larger than that of K, contributing an increase of 1.5 eV to W_F, and another factor of about 10^{-10} to x_F. Thus a negligible number of F centers in TlCl is perhaps not surprising.

The reason for the failure to observe F centers produced by x-ray irradiation is less clear. As in the alkali halides, the number of anion vacancies present in a pure crystal in thermal equilibrium at room temperature and below is so small that, even if every vacancy were to trap a photoelectron, the resulting number of F centers would be unobservably small. The production of F centers in large numbers in the alkali halides depends on a mechanism whereby new anion vacancies are created by the x-ray photons, together with complementary halogen molecule centers. It is possible that the difference in the case of TlCl depends on the higher mobility of the anion vacancy. Perhaps the mobility is sufficiently high, even at 100°K, that halogen vacancy-interstitial pairs produced by the x rays are able to recombine immediately. In this connection, it would therefore be interesting to see whether color centers could be produced by irradiating TlCl at 4°K.

B. Doped TlCl

Although we have been unable to observe F centers in pure TlCl, we believe that the absorption of chalcogen-doped crystals can be understood in terms of F centers and metallic colloids. The addition of Tl_2S, for example, would normally be expected to introduce S^{--} impurities on anion sites and an equal number of anion vacancies. It may be, however, that a lower energy state results from ionizing the S^{--} to S^- and trapping the extra electron at the anion vacancy to form an F center. The electron affinity of S^- is actually negative,[14] whereas the electron should be bound to the anion vacancy with a positive energy. The F centers may be associated with the S^- ions (i.e., located on adjacent anion sites), or they may be free. In the latter case they may be able to coagulate into aggregates of F centers, which develop into colloidal Tl particles when they are sufficiently large.

We attribute the isolated peak which produces the yellow color to F centers, and the absorption tail which produces the brown color to coagulated F centers or metal colloid. This identification is based on similarities to the behavior of F centers and colloids in the alkali halides.[15,16] There is an equilibrium between the two kinds of centers, with the F centers stable at high temperatures. For different impurity concentrations, the maximum numbers of the two kinds of centers are proportional; and the transformation between them is reversible. The existence of an isosbestic (equal-extinction) point can be taken as further evidence that the two absorptions result from the transformation of one center into the other. The F center widens and the peak wavelength shifts as the temperature is raised, as is expected for an atomic center; on the other hand, the colloid absorption shows the proper independence of temperature.

The brown color attributed to colloidal Tl shows the same absorption spectrum regardless of whether the impurity is Tl_2S, Tl_2Se, K_2S, etc. This is, this absorption could not be due to the precipitated doping compound itself, and so it must be due to Tl metal. The peak attributed to the F center, however, is at a slightly different wave length depending on whether it is introduced by S or Se. This effect could be due to association between the F center and the impurity. We assume that the F centers are nearly free of the S^- impurities, but are more tightly bound to the Se^-. A shift in peak position of approximately 0.1 eV is probably not an unreasonable perturbation from an impurity as next-nearest neighbor in the CsCl structure. As an empirical substantiation of this statement, we may point to the roughly comparable shift in the F-band position in alkali halide mixed crystals,[17] due to localized distortion in the vicinity of the F centers. The assumption of association between the Se^- and the F centers explains

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[16] W. T. Doyle, Phys. Rev. **111**, 1067 (1958).

[17] G. Miessner, Z. Physik **134**, 576 (1953).

the inhibition of *F*-center coagulation to form colloids in the Se-doped crystals, as compared with the S-doped ones.

Absorption by O^-, S^-, or Se^-, has tacitly been assumed to be unobservable, presumably because it lies in the uv and is obscured by the fundamental absorption. With this assumption, bleaching of the *F* centers by annealing in air can be understood. Neutral O atoms diffuse in to occupy the *F* centers, forming O^- and replacing the *F*-center absorption with the unobservable O^--absorption.

C. Color Centers in TlCl

If one accepts the identification of the observed absorptions in doped TlCl with *F* centers and metal colloid, as proposed in the last section, then these centers show some interesting features in TlCl. First, the *F*-band peak shifts toward *higher* energy (shorter wavelength) as the temperature increases. The direction of this temperature shift is opposite to that observed for the *F* band in the alkali halides[18] (although the magnitude of the shift is comparable), and indeed almost all other absorption bands shift toward lower energy with an increase in temperature. It is interesting, however, that the exciton peaks in TlCl also shift toward higher energy.[19,20] This anomaly is in contrast to the shift of the exciton peaks in the alkali halides,[21] and also the silver halides,[22] toward lower energy. The fundamental absorption edge in the thallous halides shifts towards lower energy.[20]

The fact that the temperature shift of the band we attribute to *F* centers is in the same direction as that of the exciton band in TlCl, as is also the case in the alkali halides (although the direction of both shifts in TlCl is opposite to those in the alkali halides), may perhaps be accepted as additional confirmation of our interpretation of the TlCl absorption as due to *F* centers. Hilsch and Pohl's charge transfer model of the exciton absorption[23,19] is similar to the simplest model of the *F*-center excitation.[24] Thus the explanation of the anomalous shifts in TlCl may be sought in some peculiarity of the TlCl crystal. It is presumably not due to the properties of the thallous ion itself, since the absorption of Tl^+ impurities in the alkali halides shows a normal red shift toward lower energy.[25] Neither is it due simply to the CsCl structure, since the cesium halides also show a normal shift toward lower energy, in both the *F* center[26] and exciton absorption.[21] The theory of the temperature shift of the *F* band[27] depends on the change of the normal-mode frequencies of the lattice vibrations when the electron is raised to an excited state. The vibrational frequencies would normally be expected to be lower in an excited electronic state, resulting in a smaller energy difference of the electronic transition and a red shift of the absorption band. It is not obvious, however, that the frequency of the dominant local modes in the vicinity of a defect must be lower. Thus the observed blue shifts in TlCl pose an interesting theoretical problem. Part of the observed shift with temperature could be attributed merely to the increase of lattice constant associated with thermal expansion, and the effect of a pure lattice constant change can be measured in high pressure experiments.[28] The *F* center in alkali halides shows a red shift,[28,29] as would be expected from the Mollwo relation. If the *F* center in TlCl were to show a similar red shift, then the contribution to the observed blue shift from the lattice vibrations would have to be even greater.

It is interesting to compare our presumed *F*-center absorption with the *F* band in the cesium halides, since TlCl has the cesium chloride structure. The *F*-band position in the alkali halides with the sodium chloride structure rather closely obeys the Mollwo relation, which asserts that the peak wavelength is proportional to the square of the nearest-neighbor distance. In the cesium halides, however, the *F*-band peaks lie at shorter wavelengths than those which would be obtained by inserting the nearest-neighbor distances into the Mollwo relation, and our peak in TlCl lies at an even shorter wavelength in comparison to the cesium halides. Another peculiar feature of the cesium halides is that the *F* band appears to be a triple peak, with the three peaks nearly resolved in CsCl at liquid-helium temperature.[30] If our peak in TlCl is indeed an *F*-center peak, then either it does not possess this triple structure, or else the three peaks are widely enough separated that two of them are obscured by the fundamental absorption. The latter explanation could perhaps account for the relatively small oscillator strength which was calculated from the peak height.

The theory of the colloid band has been treated by Doyle,[16] on the basis of the free-electron theory of the metal. The peak of the colloid band for very small metal particles occurs at a wavelength

$$\lambda_0=(1+2n_0^2)^{1/2}\lambda_c,$$

where n_0 is the index of refraction of the host crystal

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and λ_c is the wavelength of light corresponding to the plasma frequency of the conduction electrons in the metal. This frequency is

$$\omega_c^2 = 4\pi N e^2/m.$$

Assuming that in Tl metal there are three conduction electrons per atom, with an effective mass of 1.15 electron masses,[31] and extrapolating the index of refraction of TlCl to the presumed colloid peak position, we find $\lambda_0 \cong 400$ mμ. Since this wavelength lies near the absorption edge in TlCl, the calculated position is consistent with the observation only of the long wavelength tail of the colloid absorption. Doyle has also shown that the integrated absorption of the *F* band should be the same as that of the colloid band. Our single *F* band clearly contains less area than the colloid absorption band, again suggesting that perhaps our *F* peak is only one part of a triplet, the other two peaks of which lie beyond the absorption edge.

D. Comparison with Silver Halides

Like thallium chloride, the silver halides will not dissolve an excess of metal and the pure perfect crystal is insensitive to radiation. The introduction of chalconide impurities, however, produces absorptions[3] which have some similarities to those in TlCl. At room temperature the impurities extend the absorption further into the visible region, and at liquid-nitrogen temperature resolved peaks are observed.[32] The most prominent peak is at 2.62 eV (470 mμ) in AgCl containing Se. The peak position depends slightly on the impurity element, but comparison of AgCl and AgBr shows the validity of the Mollwo relation between peak wavelength and square of the nearest-neighbor distance in the host crystal. Irradiation into the impurity band produces other photochemical absorption bands. At low temperatures irradiation forms an unstable absorption peak,[33] at 2.35 eV (525 mμ) in AgCl(Se), which depends only slightly on the impurity and obeys the Mollwo relation. At room temperature, a colloid band is formed by irradiation. At intermediate temperatures, a stable peak is formed,[34,35] at 1.79 eV (690 mμ) in AgCl(Se), which does not obey the Mollwo relation.

Stasiw has proposed models for these absorbing centers. The main impurity band is attributed to a doubly negative chalconide ion (S^{--} or Se^{--}), located at an anion site.[36] The unstable low-temperature photoproduct is attributed to an electron trapped at a complex consisting of a chalconide ion and halogen vacancy—i.e., an *F* center associated with a doubly charged chalconide ion.[33] The stable intermediate temperature photoproduct is produced by the association of an Ag^+ interstitial ion with the previous center.[35] Mitchell proposed an alternative model for the impurity center[14] (which he later abandoned,[2] at least as an explanation of sulfur-sensitization in emulsions), consisting of an *F* center associated with a *singly* charged chalconide ion. This is the same structure which we have adopted for the impurity absorption in TlCl. Although Mitchell assumed that Schottky defects predominated in the silver halides, an assumption which is no longer tenable,[37] his structure is generally consistent with Stasiw's scheme, if some of the chalconide impurities are associated with halogen vacancies. In particular, the unstable low-temperature photoproduct could also be ascribed to an *F′* center (two electrons trapped at a halogen vacancy) associated with a singly charged chalconide ion, a structure chemically equivalent to Stasiw's center.

A primary difference between the silver halides and the thallium halides (and also the alkali halides) is the preponderance of Frenkel defects in the former. This does not mean, however, that no halogen vacancies can exist in the silver halides. Indeed, measurements[38] of halogen diffusion in silver halides indicate that the concentration of Schottky defects at the melting point may be as large in silver halides as in alkali halides (of the order of 0.01%), although their effects are normally swamped by the extraordinarily large concentration of Frenkel defects, which are present in concentrations of the order of 1% at the melting point. At lower temperatures the concentration of halogen vacancies in thermal equilibrium would be severely depressed according to the mass-action law, by the large silver vacancy concentration. Stasiw's crystals are not in thermal equilibrium, however, but are quenched from temperatures near the melting point, and "lagering" at room temperature for long periods erases the effects which were decribed above. Thus it seems possible that the behavior exhibited by TlCl may have some relevance to phenomena which can occur in the silver halides. It should be emphasized, however, that Stasiw's calculated oscillator strengths are much smaller than those in TlCl, suggesting that only a small fraction of the added chalconide is producing the absorbing centers in the silver halides. The rest is presumably present as doubly charged anions (absorbing in the uv), with compensating Ag^+ interstitials. Thus the minority of the chalconide ions which produce the optical absorption in the silver halides may not be directly relevant to other effects such as ionic conductivity and the photographic process.

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V. CONCLUSIONS

Thallium chloride, although it contains Schottky defects in thermal equilibrium like the alkali halides, differs from the alkali halides in that *F* centers cannot be produced in pure crystals, either additively or by irradiation. The insolubility of excess Tl metal is probably connected with the large ionization energy of Tl metal and its low vapor pressure, and the low melting point of TlCl. The insensitivity to x-irradiation may be related to the high mobility of the Cl vacancy in TlCl.

Absorption bands are introduced by the addition of chalcogen impurities. The absorption band in equilibrium at room temperature shows the properties of a colloid absorption, in that it is independent of temperature and of the added impurity. Its position is consistent with that calculated for colloids of Tl metal, with three conduction electrons per atom. The band in equilibrium at elevated temperatures we have ascribed to *F* centers, since it transforms reversibly into a proportional amount of colloid absorption, as in the alkali halides. The comparatively small oscillator strength of the *F* band may indicate that it consists of three peaks as in the cesium halides, the other two peaks here being hidden by the fundamental absorption.

The reversible transformation between *F* centers and colloids in TlCl links it to the alkali halides, but there are also similarities to chalcogen-doped silver halides, although their behavior is generally more complex. These similarities might revive a suggestion of Mitchell's that the center responsible for impurity absorption in the silver halides is an *F* center associated with a singly charged chalconide ion.

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Errata

Theory of the Range of Hot Electrons in Real Metals, STEPHEN L. ADLER [Phys. Rev. **130**, 1654 (1963)]. Because of a decimal-point error in the matrix elements calculated in Appendix I, the conclusions stated in Sec. III of this paper are incorrect. In Appendix I, $A_{1s}(k_0)$ should be 0.0149 rather than 0.149, giving

$$\langle|M(\mathbf{q},\mathbf{K})|^2\rangle_{\mathrm{av}}\approx 4\times10^{-3},$$
$$\langle|M_s(\mathbf{q},\mathbf{K})|^2\rangle_{\mathrm{av}}\approx 0.8\times10^{-6}.$$

Thus, the conclusions of Sec. III should be: (i) In the one-OPW model, umklapp and umklapp-local-field effects give a correction of only a few percent to the Quinn formula; (ii) umklapp and umklapp-local-field effects have very little effect on the plasmon creation rate.

These corrected results agree with Eq. (12), which states that

$$\sum\nolimits_{\mathbf{K}\neq 0}|\langle\mathbf{p}-\mathbf{q}|\exp[-i(\mathbf{q}+\mathbf{K})\cdot\mathbf{x}]|\mathbf{p}\rangle|^2 \approx V_a^{-1}\int_0 d\mathbf{x}|u_p(\mathbf{x})|^4-1.$$

When the integral

$$I=V_a^{-1}\int_0 d\mathbf{x}|u_p(\mathbf{x})|^4$$

is evaluated using the one-OPW wave functions given in Appendix I, one finds that $I-1$ is of the order of a few hundredths. The qualitative statements which follow Eq. (13), suggesting that $I-1$ is of order unity, are incorrect.

I wish to thank Dr. B. B. Varga for pointing out the numerical error.