

Absorption of Light by Colloids in Alkali Halide Crystals

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The thermal transformation of F centers into colloid has been observed in NaCl. The transformation occurs with constant integrated absorption cross section. The shape of the band depends upon the temperature at which the colloid is formed. A theory of the colloid band based upon the free electron model of the alkali metal and Mie's theory of the absorption of light by conducting spheres is presented. The theory makes assertions concerning the integrated absorption, maximum absorption, band width, and band position which are compared with experiment.

INTRODUCTION

ALKALI halide crystals colored by an excess of alkali metal may exhibit a great variety of optical absorption spectra, depending upon the manner of preparation and subsequent treatment of the sample. The absorption bands are in turn attributed to various color centers in the crystal arising from the presence of the excess metal. Two classes may be distinguished. In the first class are all the familiar electron centers which have been dignified by names: F , R , M , etc. These centers have the common feature that each consists of an electron which has become detached from its parent alkali metal atom and has been trapped at a lattice defect. It is the nature of the trap which determines the optical properties of the resultant center. The alkali metal ion assumes a normal lattice position at a vacant lattice site. In the present work only F centers are of any importance. All other members of this class are present in such small numbers as to play no role whatever in the phenomena to be discussed. Another class of color centers exists. This class consists of electrons trapped on alkali ions to form neutral metal. An enormous variety of possible centers of this type exists, ranging from single atoms of alkali metal lodged at irregularities in the lattice, up to actual macroscopic pieces of included metal. There are no known individual members of this class, first, because such a great variety of centers of this type may be present in any given sample, and second, because all members of this class seem to have similar and overlapping absorption bands. Because of the anonymity of the individuals, the entire class is grouped together and referred to as a colloid. No exact particle size is implied. It is a remarkable fact that the colloidal centers as a whole do possess a well-defined and regular absorption band. The present paper is devoted to a study of this band.

The early literature concerning colloids in alkali halides has been reviewed by Seitz¹ and by Przibram.² Only the most pertinent points need be discussed here. It has long been known that F centers and colloidal

particles can coexist in the same sample, and that the F centers can be transformed into colloidal particles by heat. Siedentopf,³ in one of the earliest observations on additively colored crystals, observed the thermal transformation from the yellow color characteristic of the F centers in NaCl, into the blue coloration associated with the colloid. With sufficiently long annealing times the particles of metal became visible under the ultramicroscope. Savostianova⁴ applied the Mie theory⁵ of absorption and scattering of light by metal spheres to the colloidal particles in additively colored NaCl. The good agreement she obtained between the theoretical and experimental values of the wavelength for maximum absorption supports this application of the Mie theory, as well as the identification of the colloidal particles as sodium. Scott⁶ has shown that the equilibrium between F centers and colloid may be likened to that which exists between a solution and its vapor. Here the F centers play the part of the vapor. The colloidal particles are large enough to be treated as a separate phase. From the insensitivity of the F center concentration to total concentration of excess alkali metal Scott set a minimum size of 10 atoms for the colloid particles. Moreover, since the electron microscope showed no trace of metal, Scott concluded that the particles must contain less than 1000 atoms. We shall mention later an interesting corroboration of Scott's estimate. Since the particles are very small, Scott used the limiting form of Mie's theory for particles of small diameter to predict the wavelength of maximum absorption. Using modern values of the optical constants of sodium and potassium Scott obtained agreement with experiment within the uncertainties in the optical constants employed. Scott and Smith⁷ compared the strength of the colloid band absorption with that of the F band using Smakula's equation.⁸ They found that the colloid band absorption was "very much greater" than that of the original F band. This is in disagreement with

³ H. Siedentopf, *Physik. Z.* **6**, 855 (1905).

⁴ M. Savostianova, *Z. Physik* **64**, 262 (1930).

⁵ G. Mie, *Ann. Physik* **25**, 377 (1908).

⁶ Scott, Smith, and Thompson, *J. Phys. Chem.* **57**, 757 (1953).

⁷ A. B. Scott and W. A. Smith, *Phys. Rev.* **83**, 982 (1951).

⁸ A. Smakula, *Z. Physik* **59**, 603 (1930).

¹ F. Seitz, *Revs. Modern Phys.* **26**, 7 (1954).

² K. Przibram, *Irradiation Colors and Luminescence* (Pergamon Press, London, 1956), p. 85.

the findings of Miescher⁹ who used the same criterion and found that for small colloids in NaCl the two bands were of equal strength. This question will be examined here experimentally and theoretically.

EXPERIMENT

The transition from F centers to colloid has been observed in NaCl. This material was chosen because the well-known difficulty of preparing colored samples of NaCl without the formation of a colloid band makes it ideal for the present study. Samples of additively colored NaCl were prepared by electrolysis. Rather pure F bands were obtained by rapid quenching in carbon tetrachloride. Optically homogeneous samples were cleaved from the interior portions of the colored crystals. These were polished on a damp surface and mounted permanently in a special holder designed for use with the Beckman D.U. spectrophotometer. The F -band absorption spectra were measured. The samples were then annealed at constant temperature without being removed from the holders. The absorption spectrum was remeasured from time to time. Figure 1 shows a typical transformation. The concentration of excess alkali metal in this sample was approximately 10^{17} atoms per cc. Concentrations were determined chemically using a modification of Kleinschrod's method.¹⁰ The details of the chemical method may be

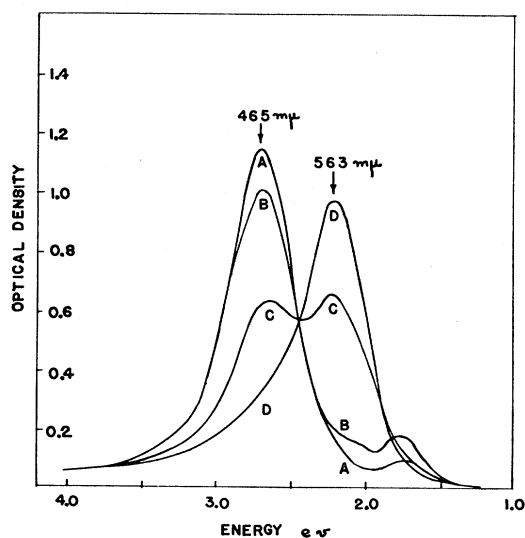


FIG. 1. Optical absorption spectra of additively colored NaCl at various stages of the transformation of F centers into colloid. Curve A shows the pure F band. Curve B , C , and D show the increase in the colloid band after the sample had been exposed to a temperature of about 175°C . for total times of 5, 20, and 120 minutes, respectively. Twelve hours further exposure at the same temperature produced no further change in curve D .

⁹ E. Miescher, Nachr. Akad. Wiss. Göttingen Math.-phys. Kl. No. 47, 329 (1933).

¹⁰ F. G. Kleinschrod, Ann. Physik 27, 97 (1936).

found elsewhere.¹¹ The sequence of events depicted in Fig. 1 is as follows: Curve A shows the initial F band. The sample was then annealed at the rather low temperature of 175°C . After total annealing times of 5, 20, and 120 minutes curves B , C , and D were obtained. After twelve hours of further annealing the spectrum was remeasured and the results were identical with curve D , indicating that coagulation is essentially complete. This statement will require qualification later, after the effect of the annealing temperature is discussed. The important feature of Fig. 1 is the area under the curve. The area under the curve is proportional to the integrated absorption cross section and it is found to be constant throughout the transformation. This was determined both planimetrically and by weighing. We must conclude that the excess electrons make the same contribution to the integrated absorption cross section regardless of whether they are atomically dispersed in the form of F centers or associated with colloidal specks of reduced metal. Considering the great difference in the nature of the absorbing centers the result seems, at first, rather surprising. However, the result admits of a simple explanation.

The occurrence of an isosbestic point near $500\text{ m}\mu$ is interesting. Such a point of constant extinction is the well-recognized criterion for the presence of a two-component system. The colloidal particles must either possess a fair degree of homogeneity or the optical properties of the particles are relatively independent of size. Probably both, as will appear below.

In the course of the experiments it was noticed that the appearance of the thoroughly coagulated colloid depended upon the temperature at which the coagulation was carried out. Slow coagulation at low temperature, such as that shown in Fig. 1, produced a coloring which was of lower saturation, and which tended to be slightly bluish. Higher coagulation temperatures produced a more reddish crystal of greater saturation. The difference in appearance was readily apparent to the eye. This phenomenon is not to be confused with the shift of the absorption maximum to longer wavelengths which is predicted by the Mie theory for very large particles. This would be accompanied by observable scattering of light. No Tyndall cone was observed in any of these specimens. The absorption curves shown in Fig. 2 show in detail the spectral changes responsible for the subtle changes in appearance. Curve A shows the absorption spectrum of a colloid coagulated at 175°C . The spectrum was stable in that no further changes were noted with continued exposure to a temperature of 175°C . Curve B shows the same sample after exposure for a few minutes to a much higher temperature. Although the shape of the band changed, no change in integrated absorption was observed. The new shape of the colloid band was also stable at 175°C . The behavior is typical. Colloids prepared at very low temperatures

¹¹ W. T. Doyle, Phys. Rev. 111, 1072 (1958), this issue.

consistently had low, broad absorption bands, while those prepared at higher temperatures had much sharper, higher peaks. In both cases, however, the integrated absorption was found to be the same as that of the original F band to within an estimated experimental error of 5%.

The results presented here are in disagreement with the observation of Scott, quoted above, that the colloid absorption is very much greater than that of the original F band. The discrepancy could conceivably arise because Scott used Smakula's equation to estimate the strength of the band, while the integrated absorption is used here. However, Miescher also used Smakula's equation and concluded that the absorption was unchanged. The difficulty may lie in differences in the shape of the colloid bands obtained by Scott and by Miescher.

It is well known that the use of Smakula's equation in its usual form is not correct, even for the F band.¹² The use of Smakula's equation for the colloid band is even more questionable and requires justification. This is because Smakula's equation rests upon the assumption of a Lorentzian line shape and a Lorentz local field. Both assumptions are invalid for the F center; neither should be made for the colloid band without further investigation. For this reason the integrated absorption is used here as a measure of intensity.

THEORY

In attempting to understand the equality of integrated absorption of the F and colloid bands, as well as other remarkable properties of colloid absorption, simplified models of both types of center will be adopted. The primary aim will be qualitative understanding of the similarities and differences between the two types of center. If one treats the F center as a damped oscillator in a spherical cavity in a dielectric medium, a straightforward classical analysis¹³ yields for the integrated absorption of the F center

$$\int k(\nu) d\nu = \frac{\pi e^2}{mc} \frac{1}{n_0} \left(\frac{3n_0^2}{2n_0^2 + 1} \right)^2 N, \quad (1)$$

where ν is the frequency, k is the extinction coefficient in cm^{-1} , n_0 is the index of refraction of the host medium at the center of the absorption band, e and m are the charge and mass of the electron, and N is the number of F centers per unit volume. The local field of Onsager appears in (1) instead of the classical expression of Lorentz. This choice of local field, suggested by Silsbee,¹³ gives agreement with experiment.¹¹

The colloidal particles consist of many atoms and so are amenable to a completely classical treatment. Like Savostianova⁴ and Scott⁶ we begin by using the theory

¹² M. Lax, *Proceedings of the Conference on Photoconductivity, Atlantic City, November 4-6, 1954*, edited by R. G. Breckenridge et al. (John Wiley and Sons, Inc., New York, 1956), p. 111.

¹³ R. H. Silsbee, *Phys. Rev.* **103**, 1675 (1956).

of Mie for absorption of light by small spheres. Since no Tyndall cone was observed in any of the samples we may neglect scattering and use Mie's expression for the absorption in the limit of very small particles. According to Mie,⁵ the extinction coefficient for absorption is given by

$$k = -\frac{N'V6\pi}{\lambda'} \text{Im} \left(\frac{\mathbf{n}^2 - n_0^2}{\mathbf{n}^2 + 2n_0^2} \right), \quad (2)$$

where k is the extinction in cm^{-1} , N' is the number of colloidal particles per unit volume, V is the volume of a colloidal particle, λ' is the wavelength of the light in the host medium, \mathbf{n} , is the complex index of refraction of the metal [$\mathbf{n} = n(1 - i\kappa)$], and n_0 is the real index of refraction of the host medium at midband. Here n_0 is treated as a constant. Inserting the expression for the complex index of refraction of the metal into (2) one finds

$$k = \frac{36\pi N'V}{\lambda} \frac{(n^2\kappa/n_0)}{[(n/n_0)^2 + (\kappa/n_0)^2]^2 + 4[(n/n_0)^2 - (\kappa/n_0)^2 + 1]}, \quad (3)$$

where λ is the wavelength of the light in free space. The other symbols are defined under Eq. (2). Equation (3) has been used by Scott to compute the absorption

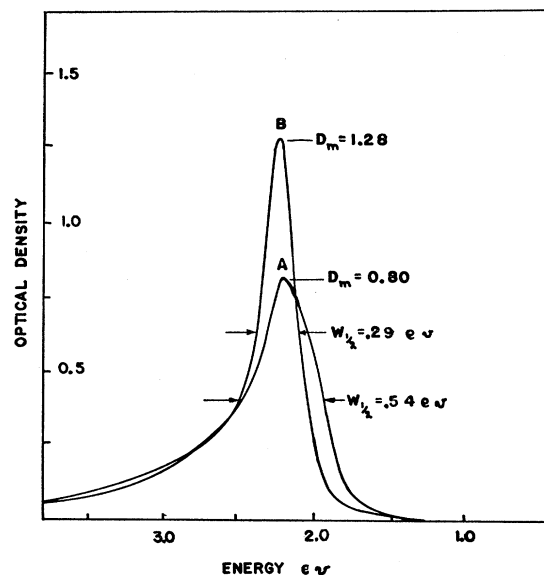


Fig. 2. Colloid band absorption spectra. Curve A shows the absorption spectrum of a low-temperature colloid formed by prolonged exposure to a temperature of about 175°C . Curve B shows the absorption of the same sample after a few minutes exposure to a much higher temperature. D_m is the maximum optical density and $W_{1/2}$ is the full width at half-maximum. Although the shapes differ, the integrated absorption is the same for the two curves.

TABLE I. Position of the colloid band: comparison of observed and calculated values of λ_0 (in Å). The observed values are those of Scott.^a The second column contains values calculated by Scott using Eq. (3). The entries in the third column were obtained using calculated values of the critical wavelength λ_c . The final column was obtained using the experimental values of the critical wavelength.

	Observed	Scott	Eqs. (7) and (9)	Eq. (9)
KCl	7750	7300	6800	7300
KBr	8500	7600	7070	7620
KI	8850	8000	7430	8000
NaCl	5650	5180	5010	5040

^a See reference 6.

spectrum of colloids in several crystals using empirical values of the optical constants of sodium and potassium. The agreement with experiment is rather good as can be seen in Table I. The first column contains the experimental values of λ_0 , the wavelength for maximum absorption by the colloidal particles. The second column shows the values predicted on the basis of Eq. (3). The theory is considered to agree with experiment within the uncertainties in the "bulk" optical constants.

While Eq. (3) is very convenient for working directly from the experimental optical constants, it does not indicate in a simple way the properties of the particles which determine the spectrum. For example, Savostianova⁴ calculated a value of 550 μ for NaCl using older values of the optical constants. Clearly λ_0 is sensitive to small changes in n and $n\kappa$. One would like to know which properties of the system determine λ_0 .

To go beyond Eq. (3) one is forced to assume a model for the colloid particle. We apply the free electron model to the metal particles. The model should be a fairly good one for alkali metals. In the free electron approximation the complex index of refraction of the metal is¹⁴

$$\mathbf{n} = \left[1 + 4\pi \left(i \frac{\omega}{\sigma_0} - \frac{\omega^2 m}{N_0 e^2} \right)^{-1} \right]^{\frac{1}{2}}. \quad (4)$$

Inserting this value of \mathbf{n} into Mie's formula (2), one obtains

$$k = \frac{9N'Vn_0^3\omega_0^4}{4\pi c\sigma_0} \left[\frac{\omega^2}{(\omega_0^2 - \omega^2)^2 + (\Delta\omega_{\frac{1}{2}})^2\omega^2} \right], \quad (5)$$

with

$$\omega_0^2 = \omega_c^2 / (1 + 2n_0^2), \quad (6)$$

$$\omega_c^2 = 4\pi N_0 e^2 / m, \quad (7)$$

$$\Delta\omega_{\frac{1}{2}} = N_0 e^2 / m\sigma_0, \quad (8)$$

where k is the extinction coefficient for absorption, N' is the number of colloid particles per unit volume, n_0

is the index of refraction of the host crystal, ω_0 is the angular frequency for maximum absorption, ω is the frequency of the light, c is the velocity of light, σ_0 is the conductivity of the metal at zero frequency, $\Delta\omega_{\frac{1}{2}}$ is the full width of the colloid band at half-maximum, ω_c is the critical frequency for ultraviolet transparency of the metal (Zener frequency), N_0 is the number of valence electrons per unit volume of the metal, and e and m are the charge and mass of the electron.

According to the simple model used here, the colloid band has a Lorentz shape. The maximum absorption occurs at a wavelength λ_0 given by

$$\lambda_0 = (1 + 2n_0^2)^{\frac{1}{2}} \lambda_c, \quad (9)$$

where λ_c is the critical wavelength for the onset of ultraviolet transparency of the alkali metal. In general λ_0 is a property of both the host crystal and the metal. The ratio N_0/m is the particular metallic property which determines the position of the colloid band. The predicted position of the colloid band using Eq. (9) with calculated values of λ_c is shown in Table I. The values obtained compare favorably with those based upon the experimental optical constants. If one uses the observed instead of the calculated values of λ_c in Eq. (9) the results are almost identical with those given by the empirical Eq. (3).

The maximum value of the extinction coefficient, k_m , is obtained by setting $\omega = \omega_0$ in (5); thus,

$$k_m = N'V \frac{1}{n_0} \left(\frac{3n_0^2}{2n_0^2 + 1} \right)^2 \frac{4\pi}{c} \sigma_0. \quad (10)$$

The peak absorption is proportional to the zero-frequency conductivity of the metal. Since only the total concentration of alkali metal ($N'V$) appears in (10), one can readily compare the predicted value with the peak value of curve D in Fig. 1. The predicted value is too high by a factor of 10. The reason for this discrepancy will become apparent when the factors determining the peak width have been discussed.

The integrated absorption of the colloid band is readily found. Since the line shape is Lorentzian, the area under the band is $\frac{1}{2}\pi k_m \Delta\nu_{\frac{1}{2}}$. Thus

$$\int k(\nu) d\nu = \frac{\pi e^2}{mc n_0} \frac{1}{(2n_0^2 + 1)^2} N' N_0 V. \quad (11)$$

Now the product $(N'N_0V)$ is just the number of excess alkali atoms per unit volume of the crystal. Hence Eq. (11) is of exactly the same form as Eq. (1) which expresses the integrated absorption of an equivalent number of F centers. That is, the free electron theory is in agreement with the observation that the integrated absorption is the same whether the excess metal is atomically dispersed in the form of F centers or coagulated in the form of colloidal particles. This conclusion depends, of course, upon insensitivity

¹⁴ N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford University Press, Oxford, 1936), p. 111.

in the functional dependence on n_0 . As it happens, the factor $n_0^3/(2n_0^2+1)^2$ is very nearly a constant over the region of interest.

In deriving Eqs. (1) and (11) the effective mass of the electrons in both F centers and colloidal particles has been set equal to the free electron mass m . This procedure leads to agreement with experiment for F centers in KCl, KBr, and NaCl.¹⁵ Thus the present experiment indicates that the effective mass of the electrons in sodium is very nearly equal to the mass of the free electron, a finding which is in agreement with theoretical calculations¹⁵ as well as with the optical measurements of Ives and Briggs¹⁶ on bulk metal.

Finally, it is worth noting that the expression in brackets in Eq. (11) is just the Onsager local field correction. Its appearance here occasions no surprise since Mie's theory applies to metal spheres imbedded in a dielectric medium. The ratio of the local field in an empty spherical cavity in a dielectric to the mean field in the surrounding medium is just $3n_0^2/(2n_0^2+1)$. The constancy of integrated absorption thus supports the use of the Onsager local field in Eq. (1) for F centers as well.

The width of the absorption band is given by Eq. (8). This formula offers a convenient check on the validity of the theory because only properties of the metal appear. The interesting feature is that the half-width is inversely proportional to the zero frequency conductivity of the metal. If one calculates the width to be expected using the values of N_0e^2/m and σ_0 tabulated by Kittel¹⁷ for sodium, one finds that the predicted half-width is 0.02 ev. The experimental values range from 0.15 to 0.60 ev. This very poor agreement with experiment helps to explain the equally poor agreement between the observed and calculated values of k_m . Since the product of k_m and $\Delta\omega_1$, i.e., integrated absorption, is in accord with experiment, σ_0 is the parameter responsible for the discrepancy. One must conclude that the zero-frequency bulk conductivity is completely inappropriate to the problem. However, a better choice may be made. The bulk conductivity is given by¹⁷

$$\sigma_0 = N_0e^2\Lambda/mu, \quad (12)$$

where Λ is the mean free path of an electron at the Fermi energy and u is the velocity corresponding to the Fermi energy. Since any large error in N_0/m has already been excluded by the excellent agreement of Eq. (11) with experiment, and since u is not likely to be much in error either, the difficulty must lie in the choice of Λ . The room-temperature mean free path in sodium is about 350 angstroms, corresponding to a predicted half-width of 0.02 ev. The observed half-widths are

from ten to thirty times larger, corresponding to mean free paths of from 36 to 12 angstroms, respectively. Such mean free paths indicate that the electron is colliding with the walls of the colloidal particles. The mean free path cannot be larger than the diameter of the colloidal particle. Since the particle diameter is much smaller than the mean free path in bulk material, we may assume that each free path begins and ends at the surface. If the electrons are reflected diffusely from the surface, the mean free path will be equal to the radius of the colloidal particle. Using the observed half-widths, together with the known metal lattice constants, the size of the colloidal particles may be calculated. For sodium a line width of 0.6 ev corresponds to a particle containing about 200 atoms, while a line width of 0.2 ev corresponds to a particle composed of about 4800 atoms. This is roughly the range of particle sizes observed in Fig. 2. The line width is inversely proportional to the cube root of the number of atoms in the particles.

In Scott's work^{6,7} line widths of roughly from 0.2 ev to 0.3 ev were encountered. This range of widths corresponds to colloidal particles containing from 1250 to 400 potassium atoms. This range of sizes agrees well with the limits set by Scott on other grounds, even allowing for an uncertainty in effective mass. Scott also observed that the shape of the colloid band was unaltered at the temperature of liquid nitrogen. The bulk conductivity changes by a factor of five in this temperature range so one would expect a like change in the width of the absorption band if the mean free path appropriate to bulk material were used. The constant band width follows immediately, however, when the mean free path is limited by particle size.

The difference in shape of the low- and high-temperature colloid bands (Fig. 2) may also be attributed to departures of the mean free path from bulk values. The low-temperature colloid band is due to a large number of very small colloidal particles. Hence the broad absorption band. Once formed, these small particles are stable at the low forming temperature, as shown by the fact that even prolonged annealing does not result in further change in band shape. Even the smallest particles seem firmly frozen into position. When the sample is exposed to higher temperatures the larger colloid particles grow at the expense of the smaller, due to the higher vapor pressure of the smaller particles. As the mean particle size increases, the band width decreases in accordance with Eq. (8).

It should be re-emphasized that all of the foregoing considerations apply only when the particle size is small enough so that only the electric dipole term need be included in Mie's expression for the absorption coefficient. In theoretical terms, the restriction means that the particle diameter must be very much smaller than the wavelength of the light. In experimental terms, there must be no scattered light.

¹⁵ F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 354.

¹⁶ H. E. Ives and H. B. Briggs, *J. Opt. Soc. Am.* **26**, 238 (1936).

¹⁷ C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1953), first edition, p. 240.

CONCLUSIONS

It has been found experimentally that the thermal transformation of F centers into colloid in NaCl takes place without change in integrated optical absorption. The colloid band shape is dependent upon the temperature of formation. Low forming temperatures give rise to low, broad colloid bands. High forming temperatures result in high, narrow bands.

A theory of the colloid band has been presented which gives a qualitative understanding of the prominent features of the colloid band. The theory is based upon the free electron model of alkali metals and upon the Mie theory for the absorption of light by conducting

spheres. The theory predicts no change in integrated optical absorption when F centers are transformed into colloid provided that the Onsager local field is used for the F center and provided that the effective mass of the colloid electron is equal to the free electron mass. The half-width of the colloid band is not in agreement with the value predicted by the theory when the bulk conductivity of the alkali metal is used. This discrepancy arises because the bulk conductivity corresponds to a mean free path much larger than the colloidal particle. Assuming that the mean free path is equal to the mean particle radius, one can use the experimental colloid band width to compute the particle size.

Optical Absorption by F Centers in Alkali Halides

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The integrated optical absorption due to F centers in KCl, KBr, and NaCl has been measured using a modification of Kleinschrod's method which eliminates salt-effect errors. Assuming the validity of the f sum rule, the results are used to obtain experimental values for the local field correction. The Onsager local field gives better agreement with experiment than does the classical expression of Lorentz. To facilitate comparison with other work the results have also been used to compute oscillator strengths using Smakula's equation. The f values are 0.91 ± 0.12 , 0.85 ± 0.08 , and 0.86 ± 0.05 for KCl, KBr, and NaCl, respectively.

INTRODUCTION

WHEN alkali halide crystals containing excess alkali metal are quenched rapidly from a high temperature, a characteristic strong F absorption band appears. If each center makes a contribution of the same form to the observed absorption spectrum the area under the absorption curve will be proportional to the number of absorbing centers. Thus

$$N = C \int k(W) dW, \quad (1)$$

where N is the number of absorbing centers per unit volume, k is the absorption constant, and W is the energy of the incident photons. The constant C could depend upon temperature but, in fact, is found to be nearly temperature independent. Experiment also indicates that C is independent of N , showing that the centers are independent. The latter fact endows C with practical interest for it enables one to measure F -center concentrations using optical means. Moreover, this constant C is itself an important property of the F center. The determination and interpretation of this constant is the chief concern of the present paper.

The first theoretical attempt to evaluate C was made

by Smakula.¹ Smakula treats the F center as a classical damped oscillator imbedded in the dielectric medium of the host crystal and acted upon by the Lorentz local field. In its corrected form² Smakula's equation is

$$fN = \frac{mc}{2e^2h} \left(\frac{3}{n^2+2} \right)^2 n k_m W_{\frac{1}{2}}, \quad (2)$$

where N is the number of centers per unit volume in cm^{-3} , n is the index of refraction of the host crystal at the center of the absorption band, k_m is the maximum absorption constant in cm^{-1} , $W_{\frac{1}{2}}$ is the full width of the absorption band at half-maximum in eV, and f is the oscillator strength. Equation (2) is known to physicists as Smakula's equation and to chemists as Chako's equation. Chako³ actually derived a more general equation (discussed later) since he did not assume a Lorentz line shape. Like Smakula, however, Chako assumed a Lorentz local field. It is unfortunate that Chako's early paper escaped the notice of physicists for it contains one of the earliest correct versions of Smakula's equation and is of more general form.

¹ A. Smakula, *Z. Physik* **59**, 603 (1930).

² E. Mollwo and W. Roos, *Göttingen Nachr.* No. 8, 107 (1934).

³ N. Q. Chako, *J. Chem. Phys.* **2**, 644 (1934).