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.

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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

$$N=C\int k(W)dW, \tag{1}$$

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 form[2] Smakula's equation is

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

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. Chako[3] 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.

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[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).

Recent theoretical papers by Dexter[4] and Lax[5,6] have served to make clearer the nature of the approximations involved in the equations of Smakula and Chako. Lax[5] adopts a local field approach from the onset. His starting point is the quantum-mechanical expression for the absorption cross section in the dipole approximation. In his first paper Lax discusses critically the various types of approximation which have been used to make the problem more tractable. Since the transition electric dipole moments are nearly independent of nuclear coordinates, one may write[6]

$$Nf=\left(\frac{mc}{\pi e^2h}\right)n\left(\frac{E}{E_e}\right)^2\int k(W)dW, \tag{3}$$

where N, f, n, k, and W have the same meaning as in Eq. (2). E is the average electric field in the dielectric. E_e is the effective field at the center. The effective mass of the center electron has been set equal to the electronic mass in obtaining (3). Equation (3) becomes identical with Chako's equation[3] if one inserts the expression for the Lorentz local field (6). It is thus equivalent to Smakula's equation[2] with the further assumption of a Lorentzian line shape.

Dexter[4] begins his treatment by taking a very general approach to the problem of impurity absorption that avoids any local field assumptions. He then restricts his treatment when forced to by mathematical difficulties. His final result also agrees with Chako's and Smakula's to lowest order.

An experimental check on Smakula's equation, or a measurement of C in Eq. (1), requires that the optical absorption spectrum be measured and compared with an independent measurement of N. The latter measurement involves some difficulty and until quite recently had seldom been carried out. The first experimental check of Smakula's equation was made by Kleinschrod,[7] who measured N chemically by observing the color change of a calibrated indicator solution when a colored sample was dissolved in it. Since a modification of Kleinschrod's method is employed here, it will be discussed in detail under "Chemical Measurements."

For many years Kleinschrod's early measurements gave the only direct evidence on the strength of the F absorption band. Recently, several new independent methods have been used to measure the F-center concentration N. Silsbee[8] has used electron spin resonance to assay the concentration of F centers. Rauch and Heer[9] have used the temperature dependence of the F-center paramagnetic susceptibility near absolute zero to determine N. Most recently Scott and Hill[10] have used a chemical method based upon the direct measurement of the amount of hydrogen gas evolved upon dissolution of colored samples in pure water. The results obtained in all these previous experiments will be discussed and compared with the present work. For the present we simply note that all previous measurements have been reported in the form of oscillator strengths computed using Smakula's equation.

In this work a somewhat different viewpoint will be taken. It is not obvious that one should assume that the local field at the F center is given by the Lorentz expression, indeed there is a certain degree of arbitrariness in this choice. Because other plausible choices of local field are available we wish to turn the problem around and make an assumption that seems slightly less arbitrary. We shall assume that the oscillator strengths given by Eq. (3) obey the usual sum rule

$$\textstyle\sum_b f_{ab}=1. \tag{4}$$

We may then use Eq. (3) to calculate the local field from the experimental data. Of course the integral appearing in (3) must now be extended over the entire F band in order to include all transitions. In the discussion the experimental values of local field will be compared with various theoretical values that have been suggested.

OPTICAL MEASUREMENTS

The optical absorption spectra were measured with a Beckman D.U. spectrophotometer. Optically homogeneous samples were cleaved from larger colored crystals and were polished on a damp surface. Uncolored reference crystals were similarly prepared. It was possible to keep the optical density zero correction small by polishing the sample and reference crystals so that the apparent optical density was nearly zero at 1000 mμ. A subtraction was made to allow for residual difference in reflection from sample and reference crystals by arbitrarily setting the minimum optical density measured equal to zero. The absorption coefficient in cm^{-1} was plotted *versus* photon energy in ev and the resulting curves were integrated both planimetrically and by weighing. The accuracy of the optical measurements becomes quite poor for heavily colored samples because of the difficulty in preparing and measuring very thin samples. For this reason very dark crystals were not used. An estimate of the over-all precision of the optical measurement based upon the obvious sources of error, physical and optical homogeneity, thickness measurements, photometric accuracy, graphical integration, etc., may be made. In the present work it is probable that an average precision of no better than 5% can be claimed for the optical measurements. While no direct use will be made of this estimate, it will allow a rough check on the precision of the chemical measurements.

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[4] D. L. Dexter, Phys. Rev. **101**, 48 (1956).

[5] M. Lax, J. Chem. Phys. **20**, 1752 (1952).

[6] M. Lax, *Photoconductivity Conference* (John Wiley and Sons, Inc., New York, 1956), p. 111.

[7] F. G. Kleinschrod, Ann. Physik **27**, 97 (1936).

[8] R. H. Silsbee, Phys. Rev. **103**, 1675 (1956).

[9] C. J. Rauch and J. C. V. Heer, Phys. Rev. **105**, 914 (1957).

[10] A. B. Scott and M. E. Hill, J. Chem. Phys. **28**, 24 (1958).

CHEMICAL MEASUREMENTS

The procedure adopted here is a modification of Kleinschrod's[7] method for determining the concentration of color centers in additively colored crystals. It rests upon the assumption that each excess alkali atom gives rise to one F center. The number of F centers may thus be determined by measuring the stoichiometric excess of alkali metal. Because of the extremely small amounts of excess alkali metal involved, Kleinschrod devised a sensitive colorimetric analysis. The colored crystal was dissolved in a methyl-red indicator solution and the change in absorbance of the indicator at 530 mμ was measured in an absorption spectrophotometer. The stock indicator solution was then calibrated by observing the change in absorbance due to the addition of small measured amounts of dilute potassium hydroxide. From the calibration curve the concentration of excess alkali metal could readily be determined.

Kleinschrod's method has been criticized by Scott[11] on the grounds that an absorbance change could result from the change in ionic strength of the solution due to the presence of the dissolved host crystal. Errors could occur if the activities of the indicator ions were sensitive to changes in ionic strength in the range encountered in Kleinschrod's work. According to Scott this salt effect might well cause an absorbance change as large as that due to the shift in pH. The difficulties Scott has pointed out were avoided by using the following modification of Kleinschrod's method.

A stock of methyl-red indicator was prepared by dissolving 5 grams of Eastman Kodak methyl red in one liter of ethanol. For each run a 200-ml portion of stock solution was prepared by adding 2 ml of indicator to 198 ml of distilled water. The indicator solution was filtered and acidified to a pH of 5. Two Beckman cuvettes were filled with equal amounts (3 ml) of indicator solution. After checking to make certain that each solution had the same initial optical density, a sample crystal was dissolved in one cuvette and an identical uncolored reference crystal was dissolved in the other. The difference in the final optical densities was observed. A calibration curve was then taken for the indicator solution at the same ionic strength as resulted from the dissolution of the sample and reference crystals. Here the salinity of the solution was turned to advantage for it allowed a convenient calibration of the indicator solution. This was done by electrolyzing a 100-ml portion of indicator solution of appropriate ionic strength using a platinum cathode and silver anode. A constant-current source produced known amounts of hydroxide at the cathode. The calibration curve of total charge *versus* optical density so obtained permitted ready calculation of the F-center concentration. Since only the difference between the final absorbance of the sample and reference crystals enters into the calculations, errors due to impurities in the raw crystal material are also eliminated. The reference material was always cleaved from the same block as the sample before coloration. This proved desirable as the uncolored Harshaw crystals consistently gave a higher alkaline indication than did Baker's analytical reagent.

SAMPLE PREPARATION

Additively colored crystals were prepared by electrolysis at high temperatures using platinum electrodes. The crystals were quenched rapidly in carbon tetrachloride. Homogeneous interior portions were cleaved out and polished on a damp surface. The typical sample size of 50–70 mg was limited by optical homogeneity requirements. Sample thickness was always chosen to give a maximum optical density well within the range of the Beckman spectrophotometer. The F-center concentrations obtained by electrolysis are rather low, a desideratum for optical measurements. However the chemical measurements demanded higher concentrations, so only the most heavily colored uniform samples obtainable were employed.

EXPERIMENTAL RESULTS AND DISCUSSION

It has been the custom to estimate the integrated absorption by taking the product of k_m and $W_{\frac{1}{2}}$, as in Smakula's equation. This practice is so convenient it will probably be continued. Whatever the actual shape of the spectrum, we may write

$$\int k(W)dW=Sk_mW_{\frac{1}{2}}, \tag{5}$$

provided each center makes an identical contribution to the integrated cross section. In Table I the shape factor S is tabulated for Lorentzian and Gaussian line shapes, together with several observed values. The observed values of S were obtained by graphical integration of the room-temperature absorption spectra over the entire absorption spectrum from 290 mμ to 1000 mμ. The empirical values of S are in all cases averages for several specimens. For KCl both additively colored and x-rayed specimens were used. For KBr only additively colored specimen were used. For NaCl only x-rayed specimens were used.

At first glance the results tabulated in Table I would seem to be in poor agreement with both the Gaussian and the Lorentzian line shapes. However, in interpreting Table I one must bear in mind that the experimental values of S include a contribution from the short-wavelength tail of the F band, which at low temperatures often exhibits a resolved peak, the K band. It was long thought that the K band arose from transitions to the higher excited state of the F center.[12] Recently, however, it has been shown that this K band is due

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[11] A. B. Scott, Nuovo cimento **1**, 104 (1955).

[12] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), p. 114.

TABLE I. Theoretical and experimental values of the ratio of the integrated absorption constant to the product of peak height and half-width.

F band	$S=\int k(W)dW/k_mW_{\frac{1}{2}}$
Lorentzian	$\frac{1}{2}\pi=1.57$
Gaussian	$\frac{1}{2}(\pi/\ln 2)^{\frac{1}{2}}=1.07$
KCl	1.19 ± 0.05
KBr	1.31 ± 0.05
NaCl	1.19 ± 0.05

TABLE II. Experimental values of the integrated absorption constant per center.

$N\times10^{-17}$ (cm^{-3})	$\int k(W)dW/N$ cm$^2\times$ev	$N\times10^{-17}$ (cm^{-3})	$\int k(W)dW/N$ cm$^2\times$ev
KCl		KBr	
2.74	1.09	1.09	1.17
1.46	0.92	2.22	1.05
2.10	0.79	1.29	1.14
1.18	0.91	1.80	1.23
3.79	1.00	2.95	1.02
2.90	1.05	2.28	0.92
1.93	0.92		
1.16	0.96	Average $(1.08\pm0.09)\times10^{-16}$	
4.38	1.10		
2.63	0.90		
4.13	0.78	NaCl	
2.21	0.96	1.15	1.00
3.56	0.88	0.89	0.96
1.96	0.99	1.08	0.88
5.22	1.22		
11.20	1.06	Average $(0.95\pm0.05)\times10^{-16}$	
1.53	1.10		
1.96	0.98		
0.98	1.27		
Average $(0.99\pm0.12)\times10^{-16}$			

to an independent electron center.[13,14] Thus the experimental values of S may be too large. If we may take the results of Geiger for the K- to F-band ratio as typical, it would be necessary to reduce the experimental values of S by as much as 16%. This would indicate that the Gaussian line shape is more nearly correct, in agreement with theoretical predictions.[6,15] This result is not necessarily in conflict with the results of Hesketh and Schneider[16] since S is a measure of the area under the curve and so is not sensitive to detailed shape. It is evident that none of the crystals examined agree well with a Lorentzian shape. Clearly this introduces an appreciable error into Smakula's equation. It will be seen that Smakula's choice of local field tends to compensate for this error.

In Table II the experimental values of the integrated absorption per excess electron are presented in a form which avoids any specific assumption regarding the nature of the absorbing centers. The quantity tabulated is just the constant of proportionality C from Eq. (1). The standard deviations are not as small as one would estimate from the apparent precision of the various measurements. This is attributed to the difficulties in preparing large uniform samples using electrolysis. The chemical measurements, while they require care, are not believed to be the limiting factor. If the above estimate of precision of the optical measurements is realistic, it would mean that the optical and chemical measurements were of comparable precision here. Thus, if one had available larger, more highly colored, uniform samples, the optical errors would determine the precision.

The results presented in Table II are not in a form which offers ready comparison with other published work. This is because other workers, with the exception of Silsbee, have attempted to apply Smakula's equation. Silsbee,[8] however, does present his results in the form of an integrated absorption cross section. He finds 0.85×10^{-16} and 0.91×10^{-16} cm$^2\times$ev for the integrated absorption cross sections of the F band in KCl and NaCl, respectively. The corresponding values in Table II are somewhat higher as might be expected since Silsbee made an arbitrary subtraction of the K-band absorption, whereas here every effort was made to include the entire absorption band. Although the difference between the two sets of values might be significant it could not be considered trustworthy as a quantitative measure of K-band absorption, especially since little is known about paramagnetic resonance in the K center.

The K-band contribution has not been subtracted in computing Table II. There are several reasons for this. First, there are probably few K centers present. The largest K to F ratio reported is that of Geiger[14] (16%), who mentions the difficulty of obtaining an appreciable K band in additively colored crystals. However, even if a concentration as large as Geiger's were present, it would lead to only a small error, since the chemical measurement would also be increased by nearly the same factor. In fact, if the integrated absorption of K centers is the same as that of F centers, no error would be incurred at all. In this connection it should be noted that the integrated absorption per excess electron is very nearly equal for a number of electron centers. For example, Pick[17] found that the integrated absorption is unchanged in the transformation of F centers into F' centers. Moreover, the transformation of F centers into R, M, and N centers occurs with constant integrated absorption.[18] Even the transformation from F centers to colloid has been found to proceed with no change in integrated absorption.[19] Thus, it is appropriate to include the K-band contribution to the absorption spectrum and to tolerate the small residual error that could arise from a difference in integrated absorp-

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[13] H. W. Etzel and F. E. Geiger, Jr., Phys. Rev. **96**, 225 (1954).

[14] F. E. Geiger, Phys. Rev. **97**, 560 (1955).

[15] D. L. Dexter, Phys. Rev. **96**, 615 (1954).

[16] R. V. Hesketh and E. E. Schneider, Phys. Rev. **95**, 837 (1954).

[17] H. Pick, Ann. Physik **31**, 365 (1938).

[18] S. Petroff, Z. Physik **127**, 443 (1950).

[19] W. T. Doyle, Phys. Rev. **111**, 1067 (1958), this issue.

TABLE III. Theoretical and experimental values of the local field correction.

	n	$(E_e/E)^2$, exp.	$(E_e/E)^2$, Onsager[a]	$(E_e/E)^2$, Lorentz
KCl	1.49	1.34±0.18	1.46	1.96
KBr	1.56	1.54±0.13	1.56	2.18
NaCl	1.56	1.35±0.07	1.56	2.18

[a] This is the square of the second factor in (7). The first factor does not appear in the integrated absorption.

tion in the two kinds of centers. This is fortunate, since it would not be possible to make a quantative correction for K-center contributions either to the chemical measurements, or to the unresolved room-temperature spectrum.

The stability of the integrated absorption under transformation from one type of center to another seems to be a general characteristic of electron centers in additively colored crystals. This suggests the operation of a general sum rule. In the local-field approximation the constancy of integrated absorption implies that the quantity

$$\sum_b f_{ab}(E_e/E)^2/nm$$

is the same for all of these centers. Although it is quite conceivable that the quantities which appear in this expression could vary from center to center in such a way as to leave the expression unchanged, the great variety of centers involved makes this seem unlikely. It seems preferable to invoke the sum rule and to set the mass m equal to the electron mass. This choice is supported by the fact that small colloids are among the centers concerned. Moreover, both of these assumptions would apply under sufficiently restrictive conditions. Thus the assumption about the mass of the center electron would be most appropriate for a compact center, while the sum rule should hold for an electron trapped in a rigid ion core potential (the usual proof requires that the wave function and its derivatives vanish at infinity). Actually, Dexter[20] has computed the oscillator strength for the $1s-2p$ transition in the F center and finds $f=1.4$. He attributes the apparent violation of the sum rule to the use of an observed, rather than a calculated, energy difference between the two states. Of course departures from the sum rule can arise when appreciable interaction with the core electrons occurs. However, this aspect of the problem is handled, to an uncertain extent, by the local field approach. It seems preferable to make the entire correction via the local field. Indeed, this is what the Smakula equation purports to do.

In Table III the experimental values of the square of the ratio of the local field to the mean field in the crystal $(E_e/E)^2$ are tabulated. In calculating these values Eq. (3) was used. The experimental values of $(E_e/E)^2$ in Table III may be compared with the Lorentz local field correction

$$(E_e/E)^2=(n^2+2)^2/9, \tag{6}$$

which is also tabulated for the three materials studied. The agreement is seen to be quite poor.

The use of the Lorentz local field has often been questioned in the past. In fact, the proper choice of local field is a central difficulty in the classical theory of electric polarization.[21] An alternative to the Lorentz local-field approach is due to Onsager.[22] This model treats the polarizable entity as a point dipole in a spherical cavity in a dielectric medium. The local field at the dipole consists of two parts, the field at the center of an empty cavity due to the action of the applied field alone, and an additional reaction field due to inhomogeneous polarization of the surrounding dielectric by the induced dipole inside the cavity. The Onsager local-field correction for polarizable atoms with no permanent electric moment is

$$\frac{E_e}{E}=\left(\frac{1}{1-\varphi\alpha}\right)\left(\frac{3n^2}{2n_0^2+1}\right), \tag{7}$$

where

$$\varphi=\left(\frac{2n^2-2}{2n^2+1}\right)\frac{1}{a^3}, \tag{8}$$

and a is the radius of the cavity, α is the polarizability of the enclosed dipole, and n is the refractive index of the dielectric medium. The first factor inside the brackets expresses the feedback effect of the reaction field. The second factor in the brackets is the local field in an empty cavity. The feedback effect is frequency dependent since it is determined by the complex polarizability α. The chief effect of feedback is to shift the frequency of maximum absorption of the dipole, treated as a classical damped oscillator. For narrow lines φ, and thus the ill-defined cavity radius a, does not appear in the expression for integrated absorption. This fact allows a certain leeway in the choice of a, and supports the conjecture of Silsbee[8] that a thorough quantum-mechanical treatment of the center, treating the trapped electron and several nearest neighbor ions as the polarizable entity, subject to the Onsager local field, might be useful. The Onsager local-field corrections are tabulated in Table III. The agreement with experiment is considerably better than for the Lorentz field. For KCl and KBr the deviation of the Onsager field from the experimental value lies within experimental error. Only NaCl lies somewhat outside the misleading standard deviation.

The correction required to bring the experimental results into agreement with the Lorentz local fields may be compared with the theoretical correction to the Lorentz field derived by Herring.[23] Herring's approach

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[20] D. L. Dexter, Phys. Rev. **83**, 435 (1951).

[21] C. J. F. Böttcher, *Theory of Electric Polarization* (Elsevier Publishing Company, Amsterdam, 1952).

[22] L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).

[23] C. Herring, *Photoconductivity Conference* (John Wiley and Sons, Inc., New York, 1956), p. 81.

is similar to Onsager's in that it takes account of the difference in polarizability between the center and the host lattice ion. It differs from Onsager's in treating the host medium as a collection of polarizable point dipoles. Herring finds

$$(E_e/E)^2=\tfrac{1}{9}(n^2+2)^2(1-\zeta\alpha_H), \tag{9}$$

where ζ is the contribution to the local field arising from the polarization of the surrounding ions due to a unit dipole at the center lattice point, and α_H is the polarizability of the missing halogen ion. From Table III we see that the values of $(\zeta\alpha_H)$ required are 0.83, 0.62, and 0.64 for NaCl, KCl, and KBr, respectively. These corrections are much larger than Herring's estimate of a few percent, based upon known dipole lattice sums and polarizabilities. This discrepancy is puzzling since one would expect Herring's method to give at least as good an approximation as the Onsager model. Apparently the Onsager treatment of the surrounding medium as a dielectric continuum compensates for errors introduced by the many approximations which are made in reaching Eq. (3). At any rate the Onsager approach gives results which are remarkably consistent with the simple model of the *F* center, and with the sum rule.

Two other instances where the Onsager local field leads to agreement with experiment may be mentioned. While neither instance involves a system closely resembling the *F* center both suggest that a strong physical basis underlies Onsager's model. Studies of the polarizability of nonpolar gases at high densities have demonstrated that the Lorentz local field is inadequate even for pure nonpolar gases. Böttcher[21] has shown that the data may be fitted surprisingly well by using the Onsager local field, treating α/a^3 as a single adjustable parameter. A similar test would not be available for color centers because one normally measures integrated absorption constants so the parameter α/a^3 does not appear. Moreover, the concentration of *F* centers, through variable, is too low. Finally, it is not possible to study the effect of the host medium independently; *F* centers would not even exist in the absence of the lattice. Measurements have been performed,[24,25] however, on the difference in the integrated optical absorption of organic molecules in the vapor state and in solution in inert solvents. No change in integrated absorption is observed in going from the vapor to solution, in disagreement with the equation of Chako. However, if Chako's equation is modified by substituting the Onsager local field the predicted change in integrated absorption becomes very small, in agreement with experiment.

OSCILLATOR STRENGTH

In order to facilitate a comparison with other work, oscillator strengths have been calculated by using Smakula's equation. Table IV shows the results of the present work, together with all previously published results. The disparity between the results of the various experiments gives an indication of the difficulties involved. Our results are higher than most of the others quoted with the exception of the recent measurements of Scott and Hill.[10] The discrepancy between the present results and those of Rauch and Heer is too great to ascribe to random error and may indicate either an inadequacy in the model of the *F* center, as has been suggested by Scott and Hill, or some systematic error. For the present the situation remains unexplained. Table IV also contains the weighted mean of all published *f* values, including the present ones. For lack of a better criterion all measurements were considered equally reliable and the published values were weighted according to the number of independent measurements presented. Our results are in satisfactory agreement with these weighted mean values.

TABLE IV. Oscillator strengths computed from Smakula's equation.

Source	KCl	KBr	NaCl	Method
Kleinschrod[a]	0.81			Chemical (*p*H)
Pick[b]	0.81	0.9+	0.7	Photochemical
Silsbee[c]	0.85		0.87	Magnetic resonance
Rauch and Heer[d]	0.66	0.71	0.7	Magnetic susceptibility
Scott and Hill[e]	1.17			Chemical (pressure)
Present work	0.91±0.12	0.85±0.08	0.86±0.05	Chemical (*p*H)
Weighted Mean	0.90	0.80	0.81	All published work

[a] See reference 7.
[b] See reference 17.
[c] See reference 8.
[d] See reference 9.
[e] See reference 10.

CONCLUSIONS

The integrated optical-absorption cross section has been measured for the *F* band of several alkali halides. Experimental values of the local field at the center obtained using the *f* sum rule as a guide are in better agreement with the Onsager local field than with the usual expression of Lorentz. The integrated *F*-band absorption is overestimated by a Lorentz line shape of the same half-width as the *F* band. Smakula's equation thus contains two errors which partially compensate. A better representation of the *F* center is given by Chako's equation if the Onsager local field is substituted for the Lorentz field.

It must be admitted that it is not clear why the Onsager local field approach should be so favored. The surprising thing is that such a simple model should work at all considering the many rough approximations inherent in it. Perhaps the most one can say is that it somehow contains essential physical elements which a more detailed treatment would reveal.

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[24] V. Henri and L. W. Pickett, J. Chem. Phys. **7**, 439 (1939).
[25] L. E. Jacobs and J. R. Platt, J. Chem. Phys. **16**, 1137 (1948).