

second doublet in BaS is observed to be the same as that of the first within experimental accuracy. It is tempting to correlate the higher energy absorption peak at about 2085 Å in BaO with the second doublet in BaS; indeed the width and shape of the 2085 Å peak in BaO suggests that it might consist of more than one absorption line.

The results of the photoemission measurements coupled with the assumption that the bottom of the conduction band is at or below the vacuum level indicates that some of these transitions, if of the exciton type, are to states above the bottom of the conduction band.<sup>25</sup> Alternatively these higher energy

peaks may be associated with band-to-band transitions although it seems unlikely that such sharp structure would occur in this case. No prominent features may readily be associated with the band-to-band transitions although part of the general rise in absorption toward higher energies may arise from this cause.

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<sup>25</sup> This situation appears to exist also in some of the alkali iodides if recent experimental results are correctly interpreted. H. R. Philipp and E. A. Taft, *J. Phys. Chem. Solids* **1**, 159 (1956);

E. A. Taft and H. R. Philipp, *J. Phys. Chem. Solids* **3**, 1 (1957); W. Martienssen, *J. Phys. Chem. Solids* **2**, 257 (1957); K. Teegarden, *Phys. Rev.* **108**, 660 (1957).

## Refractive Index and Faraday Effect in Solid Solutions\*

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The change in the index of refraction and the magnitude of the Faraday effect are computed for non-metallic crystals (or solutions) containing impurities or color centers. Both effects are found to be easily measurable. A brief comparison with previous experimental and theoretical work is presented, and a suggestion is made for further experiments.

A GREAT deal of experimental and theoretical work has been done on the optical properties associated with impurities and other imperfections in nonmetallic solids.<sup>1</sup> Almost all of this work has dealt with absorption, emission, and excitation spectra; for powdered samples the reflection spectrum has also been investigated.<sup>2</sup>

Recently a few papers have appeared in the Japanese and Soviet literature on the effects of imperfections on the index of refraction of the crystal. Such effects are usually small, but some powerful experimental optical techniques are available for their investigation, e.g., the Faraday effect and interferometry. Since no theory has yet appeared in the literature, adequate to interpret the existing experiments or to predict new results, it seems worthwhile to describe the following extremely simple calculation, which should be approximately

valid under many experimental conditions.<sup>3</sup> Although the discussion will be in terms of crystals, the arguments, equations, and conclusions are equally valid for liquid solutions.

We consider a host crystal with atomic density  $\mathfrak{N}$ , and real index of refraction  $n_0(E)$ , where  $E$  is the energy. It is explicitly assumed that the host crystal is transparent at the wavelengths of interest, i.e., near the absorption bands introduced by the impurities. Upon introduction of  $N_j$  impurity atoms of type  $j$  (e.g.,  $F$  centers), the system will be characterized by the complex bulk polarizability  $\alpha_B = [(n - ik)^2 - 1]/4\pi$ . Here  $k(E)$  is the extinction coefficient which is nonzero in the vicinity of the absorption band or bands associated with the  $j$ th impurity. It is assumed that the impurities are randomly dispersed, and that  $N_j \ll \mathfrak{N}$ , so that we expect the index change  $n - n_0$  and  $k$  both to be small quantities in comparison with unity.

The complex polarizability of an oscillator at energy  $E$  is given by

$$\alpha_j(E) = \frac{e^2 \hbar^2}{m} \left( \frac{f_j}{E_j^2 - E^2 + i\gamma_j E} \right), \quad (1)$$

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<sup>1</sup> See, for example, F. Seitz, *Revs. Modern Phys.* **26**, 7 (1954); M. Lax, *Proceedings of the Conference on Photoconductivity, Atlantic City, November 4-6, 1954* (John Wiley and Sons, Inc., New York, 1956), p. 111; C. C. Klick and J. H. Schulman, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5, p. 97; D. L. Dexter, in *Solid State Physics* edited by F. Seitz and D. Turnbull [Academic Press, Inc., New York (to be published)], Vol. 6.

<sup>2</sup> P. D. Johnson, *J. Opt. Soc. Am.* **42**, 978 (1952).

<sup>3</sup> F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. 17, contains the necessary background for the present work.

where  $f_j$  is the oscillator strength,  $E_j$  is the resonant energy of the oscillator, and  $\gamma_j$  is the natural line width. An absorption band in a solid really results from a large number of oscillators with slightly different resonant frequencies, because of interaction with lattice vibrations. Thus Eq. (1) must be modified to read

$$\alpha_j(E) = \frac{e^2 \hbar^2 f_j}{m} \int_0^\infty \frac{G_j(E') dE'}{E'^2 - E^2 + i\gamma_j E}, \quad (2)$$

where  $G(E')$  describes the normalized distribution in resonance energy of the oscillators making up the total oscillator strength  $f_j$ . If the impurity of type  $j$  contributes more than one band, the polarizability consists of a sum of terms like (2):

$$\alpha_j(E) = \frac{e^2 \hbar^2}{m} \sum_l f_j^l \int_0^\infty \frac{G_j^l(E') dE'}{E'^2 - E^2 + i\gamma_j^l E}, \quad (3)$$

and if several impurities are present, each in concentration  $N_j$ , the total contribution to the polarizability by the impurities is given by

$$\alpha(E) = \sum_j N_j \alpha_j(E). \quad (4)$$

We may proceed under either of two conditions. Where the tight-binding model is valid, the crystal is cubic, and the center is well localized, it can be shown<sup>4</sup> that the influence of the crystal on the oscillator is approximately equivalent to the Lorentz local field, so that the Lorentz-Lorenz law and the principle of additivity of molar refractivities are applicable.<sup>3</sup> Under these conditions we obtain

$$\frac{(n - ik)^2 - 1}{(n - ik)^2 + 2} = (1 - \epsilon) \frac{n_0^2 - 1}{n_0^2 + 2} + \frac{4\pi}{3} \sum_j N_j \alpha_j. \quad (5)$$

If the center is diffuse so that it experiences the average field in the crystal, the Lorentz local field concept is not applicable, and each denominator in Eq. (5) should be replaced by 3. Further, for the diffuse center an effective mass should be used in Eq. (3).<sup>5</sup> In Eq. (5),  $\epsilon$  is a small dimensionless parameter to account for the possible reduction in the polarizability of the medium by the removal of some of the atoms of the pure crystal. Thus, for example, in the case of an interstitial impurity atom,  $\epsilon$  would be zero except insofar as the presence of the impurity changes the atomic density of the host crystal. For a substitutional impurity, such as  $\text{Tl}^+$  replacing  $\text{K}^+$  in a KCl crystal,  $\epsilon$  would be equal to the fractional concentration of  $\text{K}^+$  replaced, multiplied by the fractional contribution of  $\text{K}^+$  to the bulk refractivity of KCl. If several impurities or color centers are simultaneously present,  $\epsilon$  is the sum of the fractional concentrations of each, weighted by the relative contribution to the refractivity in Eq. (5), or to the

polarizability, in the case of the diffuse center, of the constituent replaced.

Equation (5) may be simplified considerably by making use of the circumstance that  $k(E)$  and  $\Delta n \equiv n(E) - n_0(E)$  are proportional to  $N_j/\mathfrak{R}$  and are thus small in comparison to unity. Expanding the left-hand side in Eq. (5) in terms of  $\Delta n$  and  $k$ , we find from the first-order terms

$$k(E) = \frac{2\pi e^2 \hbar^2 (n_0^2 + 2)^2}{9mn_0} \sum_i N_j \sum_l f_j^l \int_0^\infty G_j^l(E') dE' \times \left[ \frac{E\gamma_j^l}{(E'^2 - E^2)^2 + (\gamma_j^l E)^2} \right], \quad (6)$$

$$\Delta n(E) = \frac{-\epsilon(n_0^2 - 1)(n_0^2 + 2)}{6n_0} + \frac{2\pi e^2 \hbar^2 (n_0^2 + 2)^2}{9mn_0} \sum_i N_j \sum_l f_j^l \int_0^\infty G_j^l(E') dE' \times \left[ \frac{E'^2 - E^2}{(E'^2 - E^2)^2 + (\gamma_j^l E)^2} \right]. \quad (7)$$

For the diffuse center the parameter  $(n_0^2 + 2)$  should be replaced by 3 in each place where it appears, and again an effective mass should be used.

If we make use of the fact that the natural line widths  $\gamma_j^l$  are usually many orders of magnitude smaller than the widths of absorption bands in solids, we may replace the function in square brackets in Eq. (6) by  $(\pi/2E)$  times a Dirac delta function,  $\delta(E' - E)$ , perform the integration, and obtain

$$k(E) = \frac{e^2 \pi^2 \hbar^2 (n_0^2 + 2)^2}{9mn_0 E} \sum_i N_j \sum_l f_j^l G_j^l(E). \quad (8)$$

In terms of the absorption coefficient  $\mu(E) = 2kE/\hbar c$ , we may express this result in the more familiar form

$$\mu(E) = \frac{2\pi^2 e^2 \hbar (n_0^2 + 2)^2}{9mn_0 c} \sum_i N_j \sum_l f_j^l G_j^l(E). \quad (9)$$

Similarly in Eq. (7) we may ignore the natural line breadths  $\gamma_j^l$ , and the quantity in square brackets becomes  $(E'^2 - E^2)^{-1}$ . Thus we obtain the general result

$$\Delta n = \frac{-\epsilon(n_0^2 - 1)(n_0^2 + 2)}{6n_0} + \frac{2\pi e^2 \hbar^2 (n_0^2 + 2)^2}{9mn_0} \times \sum_i N_j \sum_l f_j^l \int_0^\infty \frac{G_j^l(E') dE'}{E'^2 - E^2} \equiv \Delta n_d + \Delta n_I. \quad (10)$$

The first term in this equation,  $\Delta n_d$ , represents the diminution of the refractive index as a result of the

<sup>4</sup> D. L. Dexter, Phys. Rev. **101**, 48 (1956).

<sup>5</sup> M. Lax, reference 1.

removal of part of the atoms of the host lattice, and this is usually a small effect. It can, however, be readily computed from the measured index of the pure crystal. The rest of the right-hand side of Eq. (10) is the effect of the impurities, and in the neighborhood of the absorption bands this term is about a factor of thirty greater than the first term and varies much more rapidly. From comparison of Eqs. (9) and (10), it is apparent that  $\Delta n_I$  may be written

$$\Delta n_I(E) = \frac{[n_0(E)^2 + 2]^2 \hbar c}{\pi n_0(E)} \int_0^\infty \frac{\mu(E') dE'}{E'^2 - E^2} \times \frac{n_0(E')}{[n_0^2(E') + 2]^2}, \quad (11)$$

and thus the change in index may be readily predicted from a measurement of the absorption coefficient and knowledge of the index of the pure crystal. In many cases the quantity  $[n_0^2(E) + 2]^2/n_0(E)$  varies only a little over the range of interest, and it is seen that in such a case the index  $n_0$  no longer appears in the expression for  $\Delta n_I$ , i.e.,

$$\Delta n_I = \frac{\hbar c}{\pi} \int_0^\infty \frac{\mu(E') dE'}{E'^2 - E^2}. \quad (12)$$

This is a well-known dispersion relation, whose connection with the principle of causality has been recently discussed by Toll.<sup>6</sup>

It has been shown by several workers that for many centers, for which the luminescent Stokes' shift is sizable, an absorption band is to a first approximation a Gaussian in shape.<sup>5</sup> For such a center we may obtain an explicit expression for  $\Delta n_I(E)$ , in terms of the oscillator strength for the transition and the width of the absorption band.

Let us consider the case of a single Gaussian absorption band of the (normalized) shape

$$W^{-1} \pi^{-\frac{1}{2}} \exp[-(E - E_0)^2/W^2],$$

where  $2(\ln 2)^{\frac{1}{2}}W$  is the full width at half maximum of the absorption band. Then from Eq. (10) we may write

$$\begin{aligned} \Delta n_I &= \frac{2\pi^{\frac{1}{2}} e^2 \hbar^2 (n_0^2 + 2)^2 f}{9mn_0W} \int_0^\infty \frac{\exp[-(E' - E_0)^2/W^2]}{(E' - E)(E' + E)} dE' \\ &= \frac{-2\pi e^2 \hbar^2 (n_0^2 + 2)^2 f}{9mn_0WE} \left[ \exp\left(-\frac{(E - E_0)^2}{W^2}\right) \right. \\ &\quad \times \int_0^{(E - E_0)/W} \exp(t^2) dt + \frac{W}{4E} \\ &\quad \left. + \frac{W(E - E_0)}{8E^2} + \dots \right]. \quad (13) \end{aligned}$$

The integral is a well-known and tabulated function, so that when an absorption band is close to a Gaussian in shape, Eq. (13) is the simplest way of predicting the index change. In other cases Eqs. (10), (11), or (12) should be used with a numerical integration.

Far from the absorption band, i.e., when  $|E - E_0| \gg W$ , the asymptotic value of Eq. (13) is given by

$$\Delta n_I(E) = \frac{2\pi e^2 \hbar^2 f N}{mn_0} \left( \frac{n_0^2 + 2}{3} \right)^2 \frac{1}{E_0^2 - E^2}. \quad (14)$$

That is, the index change behaves just as if the absorption were all concentrated at  $E_0$ .

For many centers the width of the absorption band is much less than the energy of the midpoint. In such cases little error is made in replacing the factor  $(E' + E)$  in the denominator of Eq. (13) by  $(E_0 + E)$ , and we obtain the simple result

$$\begin{aligned} \Delta n_I(E) &= \frac{-4\pi e^2 \hbar^2 (n_0^2 + 2)^2}{mn_0W} \frac{f}{(E_0 + E)} \\ &\quad \times \left[ \exp\left(-\frac{(E - E_0)^2}{W^2}\right) \int_0^{(E - E_0)/W} \exp(t^2) dt \right]. \quad (15) \end{aligned}$$

The function in square brackets, referred to below as  $K(E - E_0)$ , represents the principal energy dependence of the index, and varies inversely with its argument for large values of  $|(E - E_0)|/W$ .

As a specific example, let us consider a case representative of the  $F$  center in KCl, where we may approximate the absorption band by a Gaussian centered at 2.30 eV, with a width at half maximum of 0.20 eV at liquid nitrogen temperature, i.e.,  $W = 0.120$  eV. Since  $W/E_0$  is indeed much less than unity, we may use Eq. (15) and obtain

$$\Delta n_I(E) = -1.274 \times 10^{-21} N f \frac{(n_0^2 + 2)^2 K(E - E_0)}{n_0 (E + E_0)}, \quad (16)$$

where  $N$  is in units of  $\text{cm}^{-3}$ , and  $E$  and  $E_0$  are in electron volts. The quantity  $\epsilon$  in Eq. (10) is equal to  $(N/\mathcal{N})$  times  $9.00/(9.00 + 2.23) = 0.802$ , where 9.00 and 2.23 are the refractivities of the  $\text{Cl}^-$  and the  $\text{K}^+$  ions, respectively.<sup>3</sup> (This value for  $\epsilon$  of course results from the circumstance that each  $F$  center replaces one  $\text{Cl}^-$  ion.) If we arbitrarily assign the value 0.6 to the oscillator strength,<sup>7</sup> and set  $N$  equal to  $10^{18} \text{ cm}^{-3}$ , we may evaluate Eqs. (16) for  $\Delta n_I$  and (10) for  $\Delta n_d$ , sum the two contributions, and obtain the curve marked  $a$  in Fig. 1. (The contribution from  $\Delta n_d$  varies from  $-0.028 \times 10^{-3}$  to  $-0.031 \times 10^{-3}$  in the region 1.1 to 3.5 eV, and thus represents only a small fraction of the total index change.) Curve  $a$  in Fig. 2 shows the same

<sup>7</sup> Values close to this have been obtained by several workers, e.g., 0.58 by R. H. Silsbee, Phys. Rev. **103**, 1675 (1956); 0.50 by C. J. Rauch and C. V. Heer, Phys. Rev. **105**, 914 (1957); and 0.81 in the older work of F. G. Kleinschrod, Ann. Physik **27**, 97 (1936).

<sup>6</sup> J. S. Toll, Phys. Rev. **104**, 1760 (1956).

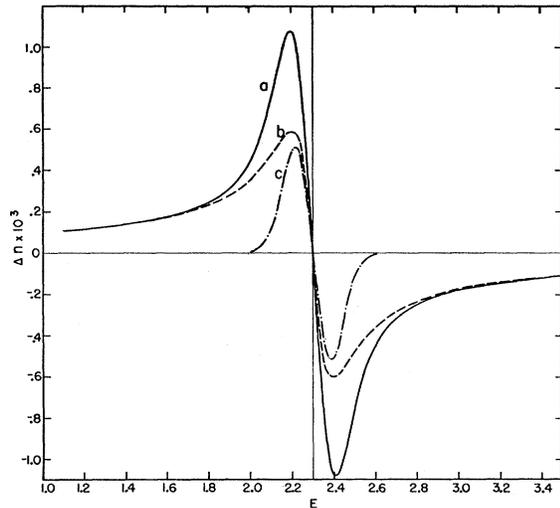


FIG. 1. The predicted change in the index of refraction versus energy (in eV) resulting from the introduction of  $10^{18}$   $F$  centers per  $\text{cm}^3$  in KCl at liquid nitrogen temperatures. Curve  $a$  is the result of the present treatment, curve  $b$  results from the assumption of a Lorentzian band shape, and curve  $c$  (in arbitrary units) represents the Davydov theory.<sup>14</sup>

result on an expanded energy scale, and the curve labeled  $\mu$  is the Gaussian absorption band postulated (in arbitrary units). The other curves will be discussed below.

These results may be used to treat the Faraday effect in crystals containing absorption bands associated with imperfections. It will be recalled that the Faraday effect is the rotation of the plane of polarization of a light beam, propagating in a medium in the direction of a magnetic field, because of a difference in the index of refraction of the medium for the two components comprising a plane-polarized beam. That is, if we consider a plane-polarized beam to consist of two circularly polarized components, for which the energy of transitions in the medium is split by the Zeeman effect, we may write the angular rotation of the plane of polarization in the form

$$\theta = \frac{2\pi r \delta n}{\lambda_0} = \frac{2\pi r}{\lambda_0} \frac{dn}{dE} |Z^+ - Z^-|, \quad (17)$$

where  $r$  is the path length in the medium,  $\lambda_0$  is the wavelength of the light *in vacuo*, and where  $\delta n$  is the difference of the index, and  $Z^+ - Z^-$  the difference in Zeeman splitting for the two components of circular polarization. The "weak-field" magnetic energy of an electron with the magnetic quantum number  $m$  is given by<sup>8</sup>

$$Z = \frac{e\hbar}{2m_e c} H g m, \quad (18)$$

<sup>8</sup> L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 283.

where  $H$  is the magnetic field strength,  $g$  is the Landé  $g$  factor, and  $m_e$  is the effective electronic mass. The constant of proportionality between the angular rotation  $\theta$  and the product  $Hr$  is called the Verdet constant.

$$\mathcal{V} = \frac{2\pi}{\lambda_0} \frac{dn}{dE} \frac{e\hbar}{2m_e c} |m^+ - m^-|, \quad (19)$$

which is usually expressed in minutes of arc per gauss cm. For the  $F$  center in KCl, the  $g$  factor<sup>9</sup> is very close to 2, and  $|m^+ - m^-|$  is equal to 2. Thus, setting  $m_e$  equal to the electronic mass, we obtain for the Verdet constant the result

$$\mathcal{V} = 4.04 E \frac{dn}{dE} \text{ min (gauss cm)}^{-1}. \quad (20)$$

The approximation of replacing  $\delta n$  by  $|Z^+ - Z^-| dn/dE$  is extremely good for our purposes, since even with  $H$  as large as  $10^4$  gauss, the splitting is only  $4.7 \times 10^{-4}$  eV, which is very small compared with the energy in which  $n$  changes appreciably. Since the Zeeman splitting is very small indeed compared with the band width of most impurity bands (for the KCl  $F$  center the ratio is  $2 \times 10^{-3}$ ), one would not expect to be able to observe the Zeeman effect on color centers, but the Faraday effect may still be sizable because of the possible high concentration of centers. In some of the semiconductors where absorption lines associated with impurities are much narrower, the Zeeman effect should be measurable at liquid helium temperature, thus allowing the determination of the effective-mass tensor in Eq. (18).

The Faraday effect in nominally pure crystals of KCl has been investigated, and a Verdet constant of 0.0286 min/gauss cm has been reported at 5893 Å at

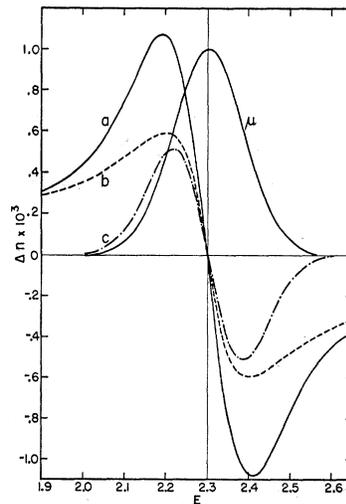


FIG. 2. The same as Fig. 1 in an expanded energy scale. Curve  $\mu$  is the absorption band postulated (in arbitrary units).

<sup>9</sup> C. A. Hutchison, Jr., and G. A. Noble, *Phys. Rev.* **87**, 1125 (1952), have found the value  $g = 1.995 \pm 0.001$ .

16°C.<sup>10</sup> The removal of a small fraction of the Cl<sup>-</sup> ions by the introduction of *F* centers may therefore be ignored, since, as we shall see, each *F* center has a much larger influence near the *F* band than has the Cl<sup>-</sup> ion it replaces. This argument is further strengthened by the approximate constancy of the quantity  $\Delta n_d$  in Eq. (10), so that in comparing the difference in the Faraday effect in pure and in colored crystals, it is a good approximation to consider only the variation with energy of  $\Delta n_l$ . Thus, making use of Eqs. (16) and (20), we may obtain the quantity, *V*, defined as the difference between the Verdet constant in the hypothetical system of 10<sup>18</sup> *F* centers/cm<sup>3</sup> in a KCl crystal at liquid nitrogen temperature and in an uncolored crystal. This quantity is plotted against energy in Fig. 3, and is labeled curve *a*. Its magnitude at the center of the absorption curve is seen to be about -0.153 minute per gauss cm. It will be recalled that in the pure crystal the value was 0.0286 in the same units, so that this is a large effect. Indeed, at the center of the *F* band each *F* center has an effect about 10<sup>5</sup> greater than that of the Cl<sup>-</sup> ion it replaces.

Experimental results qualitatively similar to the above have been obtained in recent years. Gorban' and Shishlovskii<sup>11</sup> have compared, with a Rayleigh mirror interferometer, the index of refraction of two parts of a NaCl crystal, one part of which was colored by x-irradiation. Uchida and Fukuda<sup>12</sup> have investigated the Faraday effect in electrolytically-colored NaCl, and

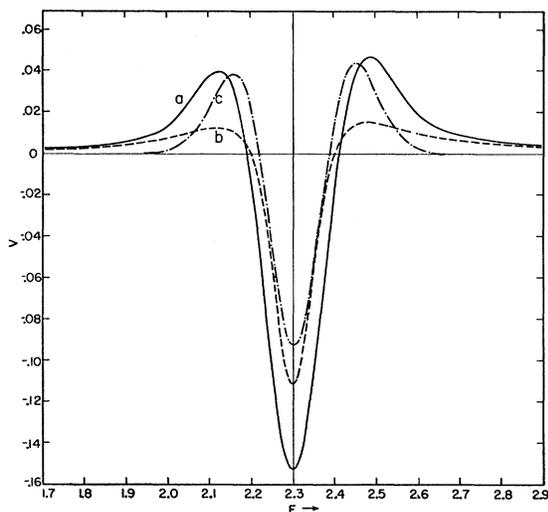


FIG. 3. The change in the Verdet constant associated with the index change of Figs. 1 and 2. Curves *a*, *b*, and *c* result, respectively, from the present treatment, the assumption of a Lorentzian line shape, and from Davydov's theory.<sup>14</sup>

<sup>10</sup> *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, 1946), thirtieth edition, p. 2303.

<sup>11</sup> I. S. Gorban' and A. A. Shishlovskii, *Doklady Akad. Nauk S.S.S.R.* **108**, 53 (1956).

<sup>12</sup> Y. Uchida and K. Fukuda, *Mem. Coll. Sci., Univ. Kyoto Ser. A*, **26**, 63 (1950).

Matumura *et al.*<sup>13</sup> have made similar measurements, as well as on the temperature dependence, on KCl crystals colored with cathode rays. In all of these experiments there presumably were other color centers produced by the method of coloration used, and insufficient experimental detail is given to allow quantitative comparison.

Gorban' and Shishlovskii suggested an interpretation of their results on the basis of a theory of Davydov<sup>14</sup> on the dispersion and absorption associated with centers which interact strongly with their environment, e.g., with the host crystal. For absorption this theory predicts the usual Gaussian curve, and the index of refraction is computed to be of the form

$$n = 1 + C(E_0 - E) \exp[-(E_0 - E)^2/W^2], \quad (21)$$

where *C* is proportional to the oscillator strength and to the concentration of centers. The index change and Verdet constant predicted by Eq. (21) are shown plotted in arbitrary units in Figs. 1-3 on the curves labeled *c*. Although the two treatments are formally dissimilar, it is surprising that they should give such different results, when the absorption bands are of the same shape. The source of the disagreement has been traced to the approximate evaluation of Eq. (39) of reference 14. Evidently Davydov's treatment for the Gaussian band shape would give a result essentially equivalent to Eq. (15), except for the "local field" factor  $(n_0^2 + 2)^2/9$ , if one were to evaluate his Eq. (39) correctly. His computed index change is proportional to a function [see Eqs. (37) and (39) of reference 14]

$$F(E - E_0, W) = \frac{-1}{W\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{E' \exp[-(E_0 - E - E')^2/W^2]}{\gamma^2 + E'^2} dE'. \quad (22)$$

Since  $\gamma$ , the natural, atomic line width, is negligibly small for all centers of interest here, we may drop it from the denominator and obtain, except for a multiplicative constant, the same function  $K(E - E_0)$  defined here in Eq. (15). Davydov, however, replaced his shape function  $F(E - E_0, W)$  by a function [see Eq. (42) of reference 14]  $(E - E_0) \exp[-(E - E_0)^2/W^2]$ , which is not even approximately of the same form as his Eq. (39) except very close to the center of the absorption band. Thus we conclude that Eq. (21) above and curves *c* of Figs. 1-3 are incorrect, not because of a basic fault in Davydov's theory, but rather as a result of a simple mathematical error.

Yamashita and Watanabe<sup>15</sup> have attempted to interpret the observations of Uchida and Fukuda on the Faraday effect in colored NaCl. Applying Rosen-

<sup>13</sup> Matumura, Inomata, and Okazaki, *Mem. Fac. Sci. Kyūsyū Univ. Ser. B*, **1**, 103 (1954).

<sup>14</sup> A. S. Davydov, *J. Exptl. Theoret. Phys. U.S.S.R.* **24**, 197 (1953).

<sup>15</sup> Z. Yamashita and M. Watanabe, *Rept. Inst. Sci. and Technol. Univ. Tokyo* **2**, 124 (1948).

feld's theory<sup>16</sup> of the Faraday effect in alkali atoms to the  $F$  center, they note that a negative Verdet constant, such as is observed in the  $F$  band, is not predicted unless a nonzero width is attributed to the  $F$  band. Upon approximating the absorption band by a classical Lorentzian band, they found that  $V$  should indeed be negative in the  $F$  band. According to the present treatment, the effect of a Lorentzian absorption line would be given by Eq. (7) with the distribution function  $G(E')$  replaced by a delta function  $\delta(E' - E_0)$  and with  $\gamma$  equal to the width of the line at half-maximum. The results for the index change and Verdet constants for the hypothetical system discussed here, with the sole change of a Lorentzian rather than a Gaussian line shape, are shown in Figs. 1-3 on the curves marked  $b$ . The absorption width at half-maximum is taken to agree with our previously postulated value 0.20 eV. Far from the absorption line the Gaussian and Lorentzian curves become very similar, as one would expect. It will be noticed that the Verdet constant becomes considerably less positive for the Lorentzian curves on the edges of the absorption band, consistent with the circumstance that the Lorentzian is a less rapidly varying function than the Gaussian in this region. Since the great breadth of absorption bands in solids does not arise from a source consistent with the Lorentz line shape but rather from interaction with lattice vibrations, the curves marked  $a$  are probably more nearly applicable in most systems.

<sup>16</sup> L. Rosenfeld, Z. Physik 57, 835 (1930).

Yamashita and Watanabe were particularly concerned with the experimental result that  $V$  remained negative in regions of lower energy than the  $F$  band. They suggest that transitions of the  $F$  center to excited states of higher energy than the first are responsible for this anomaly. It is not clear to the writer how higher energy transitions could cause a *negative* Verdet constant at lower energy than the  $F$  band, and in any case it seems more plausible that the negative value is associated with additional absorption bands, e.g., the  $M$ ,  $R_1$ , and  $R_2$  bands, introduced by the electrolysis. The absorption data are not shown, but additional centers are usually created by such treatment.

It appears to the writer that such experiments as have been mentioned here could profitably be performed on additively colored crystals, such as KCl, which have been quenched to liquid nitrogen temperatures to prevent the formation of colloid bands or  $M$  or  $R$  centers. Thin crystals containing concentrations of the order  $10^{17}$  cm<sup>-3</sup> should be convenient for investigation, and the absorption spectrum should be measured for purposes of comparison.

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