PHYSICAL REVIEW VOLUME 146, NUMBER 2 10 JUNE 1966

Variation of Refractive Index of MgO with Pressure to 7 kbar*

K. Vedam and E. D. D. Schmidt
Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania

(Received 2 September 1965; revised manuscript received 6 December 1965)

All the photoelastic investigations to date on single crystals have been limited to a maximum pressure of only 10–500 bar, since in all these studies uniaxial stress systems have been employed with consequent development of plastic deformation at higher stress levels. However, by adopting the hydrostatic pressure system the upper limit can be raised by one to two orders of magnitude. The variation of refractive index of MgO with pressure to 7 kbar has been determined, in the visible region of the spectrum, from the shift of the localized interference fringes across the crystal kept in the fluid pressure medium. Due allowance for the change in the thickness of the crystal was made with the help of Murnaghan's finite-strain theory and the third-order elastic constants. The refractive index decreases linearly with pressure in the range investigated with a slope of 1.58×10^{-4}/kbar for $\lambda5893$. The strain-optical constants p_{11} and p_{12} have been evaluated from these data and have the values -0.25_9 and -0.01_1, respectively. Mueller's strain-polarizability constant Λ_0 increases from a value of 1.23 at atmospheric pressure to 1.27 at 7 kbar. The decrease in the electronic polarizability of the oxygen ions with decrease in the interatomic distance is so large that one observes a net negative value of $dn/d\rho$ in spite of the positive contribution from the increase in density ρ. From the theory of Yamashita and Kurosawa it is found that the interaction energy due to overlap in all crystals crystallizing in the NaCl structure is very nearly the same *fraction* of their total energy even though the magnitude of the energy itself may vary considerably from crystal to crystal.

1. INTRODUCTION

THE photoelastic properties of crystalline magnesium oxide have been reported by Burstein and Smith[1] as well as Giardini and Poindexter.[2] Even though these authors agree in the fact that MgO is unique among substances crystallizing in the NaCl lattice in possessing a negative pressure coefficient of refractive index, their numerical values are at considerable variance. The reason for such a discrepancy is that these authors have used the conventional photoelastic techniques[3–6] employing uniaxial stresses with consequent limitation on the upper limit of stresses that can be employed and thus resulting in poor accuracy. By using a hydrostatic pressure system one can increase the pressure range as well as the accuracy considerably, as has been shown by Cardona, Paul, and Brooks[7] in their measurements on Ge and Si. A somewhat similar system has been developed and the results obtained in the variation of refractive index of MgO with pressure to 7 kbar are presented in this paper.

Since the linear laws of elasticity are no longer valid at these large stresses, the nonlinear theory of elasticity developed by Murnaghan,[8] Birch[9] and others[10] has been used to evaluate the necessary correction terms.

2. EXPERIMENTAL PROCEDURE

In principle the experimental method involves the adaptation of Ramachandran's[5] interferometric method to an optical high-pressure bomb. A schematic drawing of the experimental arrangement is shown in Fig. 1. Very good quality single crystals of MgO, obtained from Semi-Elements, Inc., were cleaved, ground and polished to be nearly optically parallel, so that one can easily observe localized interference fringes of the Newtonian type produced by interference of light reflected from the two surfaces of the crystal plate. The final dimensions of the specimens were about 0.8×0.8×0.3 cm,

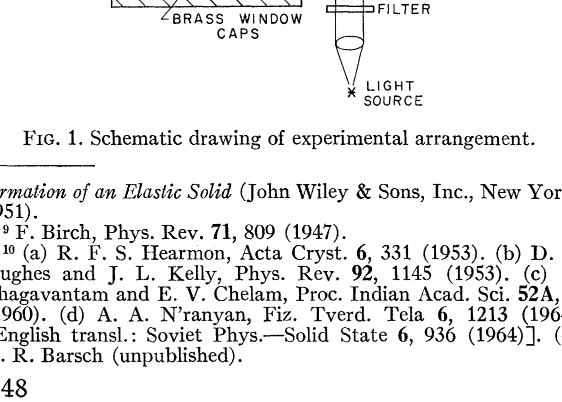

FIG. 1. Schematic drawing of experimental arrangement.

---

* This research has been supported by a grant from the National Science Foundation.

[1] E. Burstein and Smith, Phys. Rev. **74**, 229 (1948).

[2] A. A. Giardini and E. Poindexter, J. Opt. Soc. Am. **48**, 556 (1958).

[3] K. Vedam and S. Ramaseshan, in *Progress in Crystal Physics*, edited by R. S. Krishnan, (Interscience Publishers, Inc., New York, 1958), Vol. I.

[4] H. Leibssle, Z. Krist. **114**, 457 (1960).

[5] G. N. Ramachandran, Proc. Indian Acad. Sci. **25A**, 208 (1947).

[6] (a) W. Primak and D. Post, J. Appl. Phys. **30**, 779 (1959). (b) R. Srinivasan, Z. Krist. **155**, 281 (1959).

[7] M. Cardona, W. Paul, and H. Brooks, J. Phys. Chem. Solids **8**, 204 (1959).

[8] F. D. Murnaghan, Am. J. Math. **49**, 235 (1937); *Finite Deformation of an Elastic Solid* (John Wiley & Sons, Inc., New York, 1951).

[9] F. Birch, Phys. Rev. **71**, 809 (1947).

[10] (a) R. F. S. Hearmon, Acta Cryst. **6**, 331 (1953). (b) D. S. Hughes and J. L. Kelly, Phys. Rev. **92**, 1145 (1953). (c) S. Bhagavantam and E. V. Chelam, Proc. Indian Acad. Sci. **52A**, 1 (1960). (d) A. A. N'ranyan, Fiz. Tverd. Tela **6**, 1213 (1964) [English transl.: Soviet Phys.—Solid State **6**, 936 (1964)]. (e) G. R. Barsch (unpublished).

with edges parallel to the principal crystallographic direction, even though such a specific crystallographic orientation is not necessary for these measurements. The surfaces of the crystal were silvered by aluminum evaporation process so as to increase the reflectivity and hence render the fringes sharp.

The optical pressure bomb is of conventional design with an alumina window whose optically flat polished surface presses against a matched optically flat steel plug as shown in Fig. 1. Seals at other closures have been effected using Daniels' armored O rings.[11] The pressure-generating system employed for these measurements is a fairly conventional screw pump in conjunction with a Harwood intensifier. Sovasol, an optically transparent and colorless fluid marketed by Mobil Oil Company, was used as the fluid pressure medium. The pressure was read on a 16-in.-diam 100 000-psi Heise gauge capable of reading to 100 psi, which itself was calibrated by the dead-weight piston gauge with an estimated accuracy of 3 parts in 100 000.

The crystal, supported suitably in the bomb, was illuminated with parallel light from a sodium lamp or a low-pressure mercury arc with appropriate filters. The localized fringes could be observed in the telemicroscope for measurements with λ5893 and λ5461. For measurements with λ4358 and λ4047 photographic methods were used.

As the crystal is subjected to hydrostatic pressure both the thickness and the refractive index of the crystal change, with consequent shift of the fringes across a fiducial mark on the crystal. The change in the refractive index Δn can be evaluated from the well-known interference formula

$$\Delta n = (p\lambda - 2n\Delta t)/2t_0, \tag{1}$$

where p is the number of fringes shifted, t_0 the thickness of the crystal, Δt the change in thickness of the crystal due to the applied pressure and λ the wavelength of light employed. In actual practice the values of Δn and Δt at each pressure (corresponding to some known fringe shift) were evaluated from a programmed calculation on an IBM 1620 and the value of n was corrected by this Δn before it was used for the computation of $\Delta n'$ for the additional pressure producing the next fringe shift. It should be noted that since the fiducial mark is on the sample surface, the change in the refractive index of the pressure medium and the distortion of the alumina windows do not affect the measurement of the fringe shifts.

3. RESULTS

Table I lists the values of the change in refractive index of MgO for λ5893 at various pressures up to about 7 kbar, along with the values of pressures at which successive fringe shifts were observed and the strain $\Delta t/t_0$. Since the pressures employed were fairly large, the one dimensional strain $\Delta t/t_0$ was evaluated with the help of the nonlinear theory of elasticity developed by Murnaghan, Birch and others. According to this theory, the Lagrangian strain ($\eta = \Delta t/t_0$) at a

TABLE I. MgO: Variation of refractive index with pressure: λ5893 Å, $n = 1.7379$, $t_0 = 0.217$ cm, $T = 22$°C.

Fringe shift	Pressure (kbar)	Strain $(\Delta t/t_0)\times10^2$		$\Delta n\times10^2$			
		Bogardus	Bridgman	Bogardus	Bridgman	Λ_0^{LL}	Λ_0^{D}
−0.55	0.152	−0.003	−0.003	−0.002	−0.002	1.23	1.38
−1.55	0.427	−0.009	−0.009	−0.006	−0.007	1.23	1.38
−2.55	0.703	−0.014	−0.014	−0.010	−0.011	1.23	1.38
−3.55	0.986	−0.020	−0.019	−0.013	−0.015	1.22	1.37
−4.55	1.248	−0.026	−0.024	−0.017	−0.019	1.23	1.39
−5.55	1.503	−0.031	−0.029	−0.022	−0.024	1.24	1.41
−6.55	1.737	−0.036	−0.034	−0.027	−0.030	1.26	1.44
−7.55	2.000	−0.041	−0.039	−0.031	−0.034	1.26	1.44
−8.55	2.289	−0.048	−0.045	−0.035	−0.038	1.25	1.43
−9.55	2.558	−0.052	−0.050	−0.039	−0.043	1.25	1.43
−10.55	2.827	−0.058	−0.055	−0.043	−0.047	1.25	1.43
−11.55	3.089	−0.063	−0.060	−0.047	−0.052	1.26	1.43
−12.55	3.351	−0.068	−0.065	−0.051	−0.057	1.26	1.43
−13.55	3.606	−0.074	−0.070	−0.056	−0.062	1.26	1.44
−14.55	3.861	−0.079	−0.075	−0.061	−0.067	1.26	1.44
−15.55	4.116	−0.084	−0.080	−0.065	−0.072	1.27	1.45
−16.55	4.371	−0.089	−0.085	−0.070	−0.077	1.27	1.45
−17.55	4.633	−0.094	−0.090	−0.074	−0.082	1.27	1.45
−18.55	4.895	−0.097	−0.095	−0.078	−0.086	1.27	1.45
−19.55	5.150	−0.105	−0.100	−0.083	−0.091	1.27	1.45
−20.55	5.426	−0.110	−0.105	−0.087	−0.096	1.27	1.45
−21.55	5.695	−0.116	−0.110	−0.091	−0.100	1.27	1.45
−22.55	5.964	−0.121	−0.116	−0.095	−0.105	1.27	1.45
−23.55	6.232	−0.127	−0.121	−0.099	−0.110	1.27	1.45
−24.55	6.502	−0.132	−0.126	−0.103	−0.114	1.27	1.45

---

[11] W. B. Daniels and A. A. Hruschka, Rev. Sci. Instr. **32**, 885 (1961).

pressure P is given by

$$P=-(c_{11}+2c_{12})\eta + (c_{11}+2c_{12}-\tfrac{1}{2}c_{111}-3c_{112}-c_{123})\eta^2, \quad (2)$$

where c_{ij} and c_{ijk} are the second- and third-order elastic constants. The second- and third-order elastic constants of MgO have recently been determined by Bogardus[12] in this laboratory, and the values obtained by him are given in Table II. Using these values of the elastic constants the strain $\Delta t/t_0$ at the various pressures were evaluated with the help of Eq. (2) and are entered in column 3 of Table I.

The third-order elastic constants are available for only very few crystals. On the other hand, Bridgman has carried out extensive measurements on compressibility and its variation with pressure for a large number of crystals. Since the strain $\Delta t/t_0$ for cubic crystals can easily be evaluated from Bridgman's data, it will be useful to compare these values of strain with those calculated using the third-order elastic constants. Bridgman has fitted his data with a quadratic equation

$$\Delta V/V_0=-aP+bP^2, \quad (3)$$

where V_0 is the initial volume; ΔV the incremental volume change induced by hydrostatic pressure P, and a and b are temperature-dependent constants. In the case of MgO, according to Bridgman[13] a and b have the values 5.95×10^{-7} bar and 1.0×10^{-12} (bar)^2, respectively. Using these values $\Delta V/V_0$ $(=3\Delta t/t_0)$ and hence the corresponding change in refractive index were evaluated and have also been entered in Table I.

Similar sets of measurements were carried out for three other wavelengths in the visible region of the spectrum and the results are shown in Fig. 2. The origin of each curve for the different wavelengths is displaced in order to fit all the curves on the same graph. The values of Δn given in Fig. 2 correspond to those evaluated by using the third-order elastic-constants data of Bogardus.

4. STRAIN-OPTICAL CONSTANTS

From the data given above it is seen that the change in refractive index varies linearly with both stress and strain in the range of pressure investigated. This is not surprising when one considers the fact that the elastic constants of MgO are fairly large and consequently the maximum strain involved $\Delta t/t_0$ is only about 0.13%. For such small strain one would expect Pockels's linear laws to hold.

TABLE II. Elastic constants[a] used in Eq. (2).[b]

$c_{11}=29.708$	$c_{111}=-489.5$
$c_{12}=9.536$	$c_{112}=-9.5$
$c_{44}=15.613$	$c_{123}=-6.9$

[a] See Ref. 12.
[b] All constants are in units of 10^{11} dyn/cm^2.

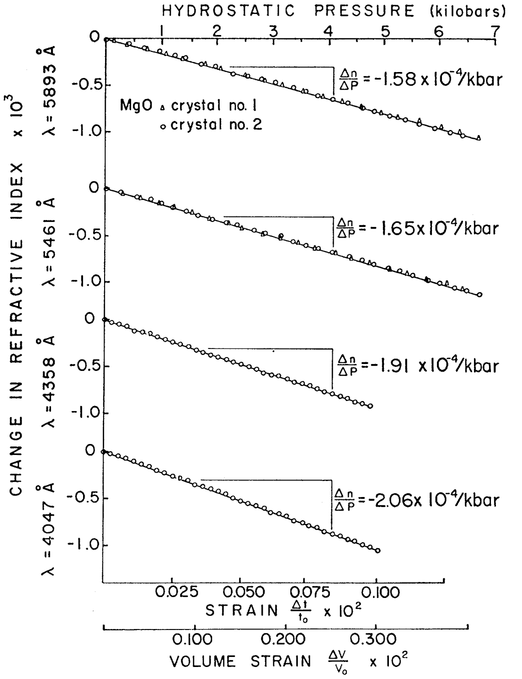

FIG. 2. Variation of refractive index of MgO with pressure and strain.

The proportional change in refractive index with density $\rho(dn/d\rho)$ can be obtained from the slope of the curve Δn versus the volume strain, since

$$\rho(dn/d\rho)=-\Delta n/(\Delta V/V_0). \quad (4)$$

From the theory of photoelasticity of cubic crystals of NaCl type it can be shown[3] that

$$\rho(dn/d\rho)=\tfrac{1}{6}n^3(p_{11}+2p_{12}), \quad (5)$$

where p_{ij} are Pockels's elasto-optic constants. Hence, from the observed slope of the curve Δn versus the strain, the value of $(p_{11}+2p_{12})$ can be evaluated. The individual values of p_{11} and p_{12} can be obtained from this value of $(p_{11}+2p_{12})$ and the values of $(p_{11}-p_{12})$ obtained by the standard procedure of subjecting the crystals to uniaxial pressure along [100] and measuring the birefringence induced along [010] or [001]. The values of p_{ij} so obtained are tabulated in Table III along with the values of earlier workers.[2,7,14]

It must be pointed out here that since the birefringence can be measured very accurately by the various well known techniques (such as using the Babinet compensator), the values of $(p_{11}-p_{12})$ and p_{44} which depend only on the birefringence, can be determined accurately, as is seen from the very good agreement

---

[12] E. H. Bogardus, Ph.D. thesis, The Pennsylvania State University, 1964 (unpublished); J. Appl. Phys. 36, 2504 (1965).

[13] P. W. Bridgman, Geol. Soc. Am. Spec. Paper No. 36 (1942)

[14] C. D. West and A. B. Makas, J. Chem. Phys. 16, 427 (1948).

between the values obtained by the different workers. An average of these values for $(p_{11}-p_{12})$ was used in the present study and it is indicated in parenthesis in Table III. On the other hand, the individual values of p_{11} and p_{12}, if determined by the conventional methods used previously, are susceptible to large errors for the following reasons.

It has been the usual practice to subject the crystal to pressure along [100] and measure the change in refractive index for the light polarized parallel and perpendicular to the direction of stress, either by interferometric methods or by the minimum-deviation technique using prisms. As mentioned earlier, since the maximum uniaxial pressure these crystals can withstand before they begin to deform plastically is very small, the number of fringe shifts observed is also very small (about 0.1 to 1), as against the large number of fringe shifts (about 24 in the case of MgO) that can be observed with the hydrostatic pressure system. Furthermore, the observed shift of the interference fringes arises from the changes in the refractive index as well as the thickness of the sample. The latter depends on the elastic modulus s_{12} for uniaxial stresses and $(s_{11}+2s_{12})$ for hydrostatic stresses. s_{12} is usually determined with very poor accuracy as compared to $(s_{11}+2s_{12})$.

Mueller's ultrasonic method[15,16] of determining the ratio of p_{11}/p_{12} is also one of the techniques previously employed to evaluate the individual values of p_{11} and p_{12}. Even this method is subject to serious errors in view of the fact that one has to employ very low-amplitude ultrasonic waves with correspondingly small changes in the state of polarization of the diffracted light.

Hence, it is not surprising to find that the values of p_{11} and p_{12} determined by various workers are at considerable variance with each other. In fact, in the case of MgO even the sign of p_{12} is different in the two reported measurements as can be seen in Table III.

5. DISCUSSION

It is seen from Table I that the difference between the values of the strain evaluated from the third-order elastic constants of Bogardus and those evaluated from the compressibility data of Bridgman, becomes significant at pressures above a few kilobars. A difference of 5% in the values of the strain observed at the highest pressure investigated, introduces a difference of 10% in the values of Δn. As Murnaghan has shown from finite-strain theory, for the computation of the strain one should use, instead of Eq. (3), a more elaborate equation of the type

$$P=\tfrac{3}{2}K_0[(V_0/V)^{7/3}-(V_0/V)^{5/3}]\times\{1-\xi[(V_0/V)^{2/3}-1]\}, \quad (6)$$

where K_0^{-1} is the initial compressibility and ξ is a theoretical parameter of the order unity. In view of this, in the following discussion as well as in Fig. 2, the values computed from the third-order elastic constants data of Bogardus have been used.

Before discussing the implication of the results obtained it will be useful to briefly recapitulate the essential features of Mayburg's[17] data on the pressure dependence of the low-frequency dielectric constant of ionic crystals. It was found that the dielectric constant of MgO decreases linearly with pressure with a slope $(\delta \ln\epsilon/\delta p)_T$ of -0.32×10^{-5} bar^{-1} up to 8 kbar, the range of pressure investigated by him. The dielectric constants of the alkali halides were also found to decrease in a similar fashion though with different initial slopes.

No such similarity between MgO and the alkali halides is observed in the pressure dependence of the optical dielectric constant. For, Burstein and Smith[1] as well as Leibssle[4] found that the refractive index of alkali halides increase on compression, that of MgO decreases on compression. Our results on MgO, though not in agreement with those of Burstein and Smith in the numerical values, do not contradict the previous statement. The reason for this difference in the behavior of the dielectric constants at different frequencies becomes clear when one considers the fact that at optical frequencies the dielectric constant arises wholly from the electronic polarizabilities of the ions whereas at frequencies lower than the characteristic frequencies of the lattice there is also a polarization caused by the displacement of the lattice of positive ions with respect to the lattice of negative ions. Since the variation of the lattice polarization is much larger than that of the electronic polarization, the former swamps the latter effect and one finds a decrease of the dielectric constant with pressure both in MgO and the alkali halides.

Mayburg discussed his data in terms of the constant of the inner field γ, introduced by Mott and Littleton.[18] It is defined by an equation of the type

$$F=E+\gamma(4\pi/3)P \quad (7)$$

for the effective field, where the terms F, E, and P have the usual significance. The quantity γ has the value unity when the inner field can be described by the Lorentz field, which is the case in NaCl-type structure

TABLE III. Strain-optical constants of MgO (λ5893 Å).

	$(p_{11}-p_{12})$	p_{44}	p_{11}	p_{12}
Burstein & Smith[a]	−0.24		∼−0.3	∼−0.08
West & Makas[b]	−0.253	−0.096		
Giardini & Poindexter[c]	−0.25	−0.10	−0.21	0.04
Present authors	(-0.24_8)		-0.25_9	-0.01_1

[a] See Ref. 7. [b] See Ref. 14. [c] See Ref. 2.

---

[15] H. Mueller, Z. Krist. **99A**, 122 (1938).

[16] K. Vedam and G. N. Ramachandran, Proc. Indian Acad. Sci. **34A**, 240 (1951).

[17] S. Mayburg, Phys. Rev. **79**, 375 (1950).

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

if there is no overlap between adjacent ions. Mott and Littleton find that the value of γ is nearly zero in the case of alkali halides and thus these authors conclude that the relation between the high-frequency dielectric constant and polarizability should be of the Drude type and not the Lorentz-Lorenz type. Further, they attribute this decrease of γ from the Lorentz value of one to nearly zero values to the interpenetration of nearest neighbor ions. Since the effect of high pressures on these crystals would be to reduce the interionic distance and thus to increase the overlap, γ should decrease further with increasing pressure. Even though Mayburg finds such a decrease in γ with pressure from an analysis of his data, Rao[19] finds that while KCl and KBr behave as expected, the values of γ were found to increase in the case of LiF and NaCl. Rao arrived at these anomalous results from an analysis of the same data of Mayburg with the help of the well-known Born and Madelung relations. Neither Mayburg nor Rao was able to carry out such an analysis of the data on MgO since γ was found to have an imaginary value for MgO and this was attributed to the noncentral forces in MgO or to the neglect of next-nearest-neighbor interactions.

Mueller,[20] on the other hand, assumed that the Lorentz-Lorenz equation is still valid in the crystalline state except that the polarizability of the ions in the crystalline state is different from that of the free ions. This latter condition is in accordance with the earlier observations of Fajans and Joos[21] that the refraction of ions in crystals are smaller than that in solutions, and also with the recent conclusions of Tesseman, Kahn and Shockley.[22] With this assumption Mueller developed the theory of the photoelastic effect in cubic crystals, the full significance of which has been discussed in detail by Burstein and Smith.[23] According to Mueller, when a crystal is stressed, in general its symmetry is altered and hence the calculation of the photoelastic constants is based on the evaluation of the changes in (1) the Coulomb field, (2) the Lorentz-Lorenz field and (3) the intrinsic polarizability of the ions. If, however, the crystal is subjected to hydrostatic pressure, the symmetry is not altered; then the Coulomb as well as the anisotropic Lorentz-Lorenz field contributions will be zero. Hence one need only take into account the change in Lorentz-Lorenz contributions due to the increase in the density of the crystals and the changes in the polarizability of the ions with decreasing inter-ionic distance. To evaluate the latter term, Mueller introduced a phenomenological parameter called the strain-polarizability constant Λ_0 defined by the following equation:

$$R=R_0(1+\Lambda_0 dV/V_0)=R_0(1-\Lambda_0 d\rho/\rho_0)\,, \qquad (8)$$

where R_0 and R are the molar polarizability of the undeformed and deformed crystal, respectively. This implies that a decrease of the volume by 1% decreases the molar polarizability by Λ%. The observed change in refractive index with density can then be written as

$$\begin{aligned}(dn/d\rho)_{\text{obs}}&=(\delta n/\delta\rho)_R(1-\Lambda_0)\\ &=[(n^2+2)(n^2-1)/6n\rho](1-\Lambda_0)\,. \qquad (9)\end{aligned}$$

Thus the values of Λ_0 can be evaluated from the observed values of $dn/d\rho$ and these values are entered in column 7 of Table I.

It is seen that the value of Λ_0 increases from a value of 1.23 at atmospheric pressure to 1.27 at 7 kbar. As Burstein and Smith have shown, Λ_0 can be considered as a measure of the ionic overlap and homopolar bonding and hence it is not surprising to find the value of Λ_0 increasing with pressure.

The last column of Table I gives the values of Λ_0 calculated from an equation similar to Eq. (9), but derived from the Drude-type equation. It is seen that while the actual value of Λ_0 is dependent on the type of dispersion equation used, the magnitude and sign of Λ_0 calculated from the two equations show the same trend.

Recently, Yamashita[24] has derived a general theory of the dielectric constant of simple ionic crystals from quantum theory and this has also been extended by Yamashita and Kurosawa[25] to evaluate the pressure effect on the high-frequency dielectric constant. In this theory, the polarizability of the positive ion was neglected and the perturbed wave function of $2p$ electrons of the negative ion was assumed to be

$$\phi(\mathbf{r})=\phi_0(\mathbf{r})(1+\lambda r\cos\theta)\,, \qquad (10)$$

where ϕ_0 is the unperturbed wave function, λ the variational constant and θ is measured from the field direction. Then the energy change per ion pair under the influence of electric field F at optical frequencies, is given by

$$\Delta E=-4\langle r^2\rangle_{\text{av}}\lambda F-\frac{1}{2}\,\frac{4\pi}{3}\,\frac{(4\langle r^2\rangle_{\text{av}}\lambda)^2}{2r_0^3}+A_0\lambda^2+A\lambda^2\,, \qquad (11)$$

where $\langle r^2\rangle_{\text{av}}$ is defined by

$$\langle r^2\rangle_{\text{av}}=\int r^2\phi_0(\mathbf{r})d\tau\,, \qquad (12)$$

r_0 the interionic distance, $A_0\lambda^2$ is the change of the intra-energy of a negative ion, and $A\lambda^2$ arises due to the mutual interaction of the deformed parts of the wave function $\lambda\phi_0(\mathbf{r})r\cos\theta$. The polarizability α_n can

---

[19] D. A. A. S. Narayana Rao, Phys. Rev. **82**, 118 (1951).

[20] H. Mueller, Phys. Rev. **47**, 947 (1935).

[21] K. Fajans and G. Joos, Z. Physik **23**, 1 (1924).

[22] J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953); W. Shockley, *ibid.* **73**, 1273 (1948).

[23] E. Burstein and P. L. Smith, Proc. Indian Acad. Sci. **28A**, 377 (1948).

[24] J. Yamashita, Progr. Theoret. Phys. (Kyoto) **8**, 280 (1952).

[25] J. Yamashita and T. Kurosawa, J. Phys. Soc. Japan **10**, 610 (1955).

then be shown to be given by

$$\alpha_n=1/2a=(4\langle r^2\rangle_{\mathrm{av}})^2/2(A_0+A). \tag{13}$$

From Eq. (13) it is seen that the polarizability α_n is dependent not only on the nature of the corresponding atom, but also on the nature of the crystal through the interionic interaction A.

When the crystal is subjected to hydrostatic pressure the lattice constant will decrease and $A\lambda^2$ will increase rapidly since it is a sensitive function of the interionic distance. Assuming a simple functional form for A of the type

$$A(r)=U\exp(-pr) \tag{14}$$

Yamashita and Kurosawa derived the following expression for the proportional variation of refractive index with density:

$$\rho\frac{dn}{d\rho}=\frac{(n^2-1)(n^2+2)}{6n}-\frac{A(r_0)p}{6nr_0^2(4\langle r^2\rangle_{\mathrm{av}})^2(2a-2\pi/3r_0^3)^2}. \tag{15}$$

From Eqs. (4) and (13) it is seen that all the quantities in Eq. (15) except $A(r_0)/(4\langle r^2\rangle_{\mathrm{av}})^2$ and p are observed values.

A repulsive potential of the type $C\exp(-r/\rho)$ is usually employed for analyzing the cohesive energy of crystals. The results of such analysis show that the value of r_0/ρ lies between 7 and 10 in many cases. Hence, we can suppose that (pr_0) in Eq. (14) will also lie between 7 and 10. With this assumption, the values of $[A/(4\langle r^2\rangle_{\mathrm{av}})^2]$ for MgO were evaluated from Eq. (15) and it was found that the interaction A amounts to about 19 to 27% of the total energy change $(4\langle r^2\rangle_{\mathrm{av}})^2a$ using values of p as 10 and 7, respectively. This value is nearly identical to those calculated for LiF and NaCl by Yamashita and Kurosawa. Thus it appears that the interaction energy due to overlap in all crystals crystallizing in the NaCl structure is very nearly the same *fraction* of their total energy, even though the magnitude of the energy itself may vary considerably from crystal to crystal. It must be mentioned, however, that this conclusion is based on Yamashita's calculations using the earlier $dn/d\rho$ data on NaCl and LiF, which may have to be modified.

As is well known, in MgO as well as in α-quartz and vitreous silica it is the oxygen which is mainly responsible for their optical properties in the visible region of the spectrum. However, if one compares the values of $(dn/d\rho)$ of these materials one notices that while $(dn/d\rho)$ for MgO is negative it is positive for α quartz[26] and vitreous silica.[27,28] In glasses,[29] where again it is the oxygen which is the dominant contributor to the molar polarizability, the sign of $dn/d\rho$ is positive. In other words MgO is clearly anomalous in this respect. However, a closer examination will reveal that such a comparison is not appropriate for the following reasons: α-quartz is a rhombohedral crystal and anisotropic in both its elastic and optical properties and hence it is quite probable that the averaging procedure adopted to evaluate $dn/d\rho$ for hydrostatic pressure may not be valid. In the case of glasses as well as vitreous silica it is well known from the work of Bridgman[30] that their compressibility *increases* with pressure, indicating that the SiO_4 tetrahedra rearrange themselves under pressure in such a way the void spaces in the glassy matrix gradually get filled by the movement of some of the oxygens surrounding the void spaces. Analogous to the behavior of Ge,[31] it is much easier to change the O-Si-O angle than to reduce the Si-O bond distance. In other words the system would favor slight rotational movements of SiO_4 tetrahedra, especially those near the voids, in such a way as to "push in" the oxygens in the voids. Permanent densification by such a procedure would naturally have to overcome an energy barrier and hence would be time and temperature-dependent. The kinetics of this problem as well as the influence of shear stresses on the permanent densification of glasses have been studied extensively by Cohen and Roy.[32] Under such circumstances it is natural to expect the deformability or the polarizability of the oxygen ions in the vitreous silica and glasses, to decrease with pressure in a much less pronounced fashion than in MgO.

Since the Lorentz-Lorenz contribution due to the increase in density is always positive, the net observed change in refractive index can be positive or negative depending on the relative magnitudes of this term and the change in ionic polarizability. In the case of MgO the decrease in polarizability with pressure is so large that one observes a net negative value of $dn/d\rho$ in spite of the positive contribution from the increase in density, whereas in vitreous silica and glasses the latter term dominates with the result that positive values of $dn/d\rho$ are observed.

Finally, it should be mentioned that the appropriateness of the usual assumption of the existence of O^{--} ions in the crystalline state has not been well established theoretically, even though most of the experimental facts can be explained at least qualitatively by this assumption. It is a well-known fact that the doubly charged negative oxygen ions have not been observed in the gaseous phase.[33] Further, as Yamashita[34] has shown from quantum-mechanical calculations, the energy of the $(2p)^6$ configuration of O^{--} ion is higher

---

[26] F. Pockels, Ann. Phys. Chem. (Leipzig) **37**, 269 (1889).

[27] (a) E. S. Jog, J. Indian Inst. Sci. **39**, 93, 101 (1957). (b) W. Primak and D. Post, J. Appl. Phys. **30**, 779 (1959).

[28] K. Vedam and E. D. D. Schmidt, Bull. Am. Ceram. Soc. **44**, 638 (1965); K. Vedam, E. D. D. Schmidt, and R. Roy, J. Am. Ceram. Soc. (to be published).

[29] C. Schaffer and H. Nassenstein, Z. Naturforsch. **8a**, 90 (1953).

[30] P. W. Bridgman, Am. J. Sci. **10**, 359 (1925).

[31] A. Segmüller, Phys. Letters **4**, 277 (1963).

[32] H. M. Cohen and R. Roy, J. Am. Ceram. Soc. **44**, 523 (1961).

[33] H. S. W. Massey, *Negative Ions* (Cambridge University Press, Cambridge, England, 1950).

[34] J. Yamashita, J. Phys. Soc. Japan **7**, 261 (1952).

than the $(2p)^5$ of an O^- ion and that the O^{--} ion becomes stable in MgO crystal only because of the Madelung energy, exchange energy, and S energy. In other words if the O^{--} ion is stabilized in an oxide crystal by the effect of the crystalline field of the surrounding ions, the wave function of the O^{--} ion need not be the same in all oxide crystals but should have different values characteristic of each crystal. This explains the reason why Tessman, Kahn and Shockley[22] could not find a unique value of the optical polarizability of the O^{--} ion in their least-squares-fit determination, but concluded that the polarizability of the O^{--} ion could vary in the wide range of 0.5 to 3.2.

It is also natural to expect that the change of polarizability with interatomic distance will vary strongly from crystal to crystal, especially since the coordination of oxygen changes from 6 (in MgO) to 2 (in vitreous silica and glasses). It would be most interesting to study the photoelastic behavior of oxide crystals with cubic symmetry with an oxygen coordination of 4 as in ThO_2. Such experiments in ThO_2 and in spinel are in progress.

ACKNOWLEDGMENTS

We are grateful to Professor Rustum Roy for various experimental suggestions and for reading the manuscript. We are also indebted to Professor W. B. Daniels of Princeton University, Princeton for the loan of the optical bomb for the study.

PHYSICAL REVIEW VOLUME 146, NUMBER 2 10 JUNE 1966

Zero-Phonon Lines and Phonon Coupling of ZnSe:Mn and CdS:Mn

Dietrich W. Langer
Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio

and

Hans Jochen Richter*
University of Dayton, Dayton, Ohio

(Received 4 November 1965; revised manuscript received 17 January 1966)

Absorption and emission spectra of ZnSe:Mn and of CdS:Mn crystals were measured at 4.2°K. The structure on the absorption and emission bands was identified in terms of phonon emission coupled to one electronic transition in each band. Zero-phonon lines were found in ZnSe:Mn at 18 025, 19 598, and 21 110 cm^{-1} and in CdS:Mn at 18 620 cm^{-1}. They should correspond to the Mn transitions in a cubic crystalline field ${}^6A_1 \rightarrow {}^4T_1$, ${}^6A_1 \rightarrow {}^4T_2$, and ${}^6A_1 \rightarrow {}^4A_1$, ${}^4E$ in ZnSe. The ionic parameters $F_2 = 55\,454$ and $F_4 = 34\,520$ cm^{-1} and the value of the crystalline field, $Dq = 405$ cm^{-1}, are deduced for Mn in ZnSe. Principal phonons participating have values of about 70, 94, 160, 209, and 242 cm^{-1}, which is in agreement with the phonon energies of the ZnSe host lattice.

FINE structure in optical spectra of ZnS:Mn have been reported recently by McClure[1] and by Langer and Ibuki.[2] In agreement with earlier work the broad absorption and emission bands have been associated with electronic transitions between crystal-field split terms of the Mn^{2+} ion. The transition ${}^6A_1 \leftrightarrow {}^4T_1$ was associated with the emission band and the absorption band of lowest energy. The ${}^6A_1 \rightarrow {}^4T_2$ and the ${}^6A_1 \rightarrow {}^4E$, ${}^4A_1$ transitions were associated with the second and third lowest absorption bands, respectively. The fine structure in the ${}^6A_1 \rightarrow {}^4T_2$ and ${}^6A_1 \rightarrow {}^4E_1\,{}^4A_1$ absorption bands was interpreted by McClure in terms of transitions between exchange-coupled manganese ions. In contrast, Langer and Ibuki, while observing identical and additional structure, point out that an interpretation in terms of phonon-assisted transitions is possible, because the energy intervals between the lines are in good agreement with phonon energies of the ZnS host lattice.

In measuring the spectra of ZnSe:Mn we found strong support for the proposed phonon coupling mechanism as the origin of the line structure. Namely, the energy differences appearing in the structure of ZnSe:Mn are different from those in ZnS:Mn but it is important to note that they are nearly identical to the phonon energies of the ZnSe host lattice.

The ZnSe:Mn (0.1 mole %) samples were melt-grown and of predominantly cubic structure with stacking faults. The CdS:Mn crystals reported on below were grown from the vapor phase with Mn content less than 0.1 mole %. They were prism-shaped and of hexagonal structure.

RESULTS ON PHONON COUPLING

The center of the ${}^6A_1 \rightarrow {}^4A_1$, ${}^4E$ absorption band of Mn^{2+} in ZnSe coincides with large values of the intrinsic absorption. Structure on the low-energy side of this band, however, is observable in the tail region of the

---

* This work was performed at the Aerospace Research Laboratories.

[1] D. C. McClure, J. Chem. Phys. 39, 2850 (1963).

[2] D. Langer and S. Ibuki, Phys. Rev. 138, A809 (1965).