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Effect of Pressure on *F*-Center Absorption in Alkali Halides*

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Measurements are reported for the effect of hydrostatic pressure to 5000 atmospheres on the *F*-center absorption of seven alkali halides. An interpretation is made of the shift of the absorption band maximum with pressure, and of the difference between the shift with pressure and that with temperature. The shift with pressure depends almost entirely on the local interionic distance at the *F* center. The shift with temperature is largely governed by this same factor, but it must be supplemented by a contribution from the interaction of the *F*-center electron with the optical vibrations of the lattice. Effects of the pressure-induced structure transformation in RbCl are described for both photochemically and additively colored crystals.

I. INTRODUCTION

THE problems and phenomena associated with the externally induced colored absorption bands in alkali halide crystals have commanded considerable attention for many years. Both experimental and theoretical investigations of recent years in this field seem to confirm the defect model of the centers responsible for the absorption. This model assumes the presence of electrons in quasi-atomic or molecular states trapped in the vicinity of lattice imperfections in ionic crystals, and attributes the bands to electronic transitions between these states. Excellent reviews of this subject may be found in the work of Pohl,[1] of Mott and Gurney,[2] and of Seitz.[3]

Among these colored bands, the so-called *F* bands of the alkali halides play a very fundamental role. Their absorption spectra, in or near the visible range, are bell-shaped. The peak wave number and width may be made to vary with temperature and pressure. Over the range of alkali halide crystals with the NaCl lattice structure, Mollwo[4] has indicated that, at a given temperature, the peak wavelength of the *F* band is approximately proportional to the square of the interionic distance. More recently, Ivey[5] has made a better representation in this form using the exponent 1.84 instead of 2. This relation is an empirical one. Its successful prediction from theory is bound up with the problem of calculating the wave functions and energy levels of electrons trapped at lattice defects.

Most of the theoretical calculations for *F* centers have treated the crystal as a homogeneous dielectric continuum, with the electron moving in the central field of the halogen ion vacancy which serves as the trapping site. Among the contributors to this approach are Tibbs,[6] Kubo,[7] Simpson,[8] Inui and Uemura,[9] Pincherle,[10] and Krumhansl and Schwartz.[11] An alternative approach employs a molecular orbital model of the *F* center, wherein the wave function of the electron is taken as a linear combination of atomic orbitals, each representing the extra electron in an atomic state on one of the atoms adjacent to the halogen ion vacancy. The first calculations of this type are due to Muto[12] and to Inui and Uemura.[9] The molecular orbital model has received significant support from the electron spin resonance absorption experiment on colored KCl, performed by Hutchison and Noble.[13] Kahn and Kittel[14] have made an interpretation of this work, and additional experiments of this type have been done by Kip, Kittel, Levy, and Portis.[15] At the present time, the work of Inui and Uemura, confined to the lithium salts, is the only quantitative calculation of energy levels with this model.

In recent years considerable attention has been directed toward the explanation of the shift of the absorption peak toward longer wavelengths, and of the increase in the absorption band width, with increasing temperature. In the work of Muto,[12] Huang and Rhys,[16] Lax,[17] and O'Rourke,[18] both the shift and the broadening have been accounted for by considering the interaction of the electron with optical vibrations of the lattice. On the other hand, the temperature shift has been ascribed mainly to the thermal expansion of the lattice by Inui and Uemura,[9] and Nagamiya.[19]

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[1] R. W. Pohl, Proc. Phys. Soc. (London) **49**, 3 (1937).

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

[3] F. Seitz, Revs. Modern Phys. **18**, 384 (1946).

[4] E. Mollwo, Z. Physik **85**, 56 (1933).

[5] H. F. Ivey, Phys. Rev. **72**, 341 (1947).

[6] S. R. Tibbs, Trans. Faraday Soc. **35**, 1471 (1939).

[7] R. Kubo, J. Phys. Soc. Japan **3**, 254 (1948); **4**, 322, 326 (1949).

[8] J. H. Simpson, Proc. Roy. Soc. (London) **A197**, 269 (1949).

[9] T. Inui and Y. Uemura, Progr. Theoret. Phys. **5**, 252, 395 (1950).

[10] L. Pincherle, Proc. Phys. Soc. (London) **A64**, 648 (1951).

[11] J. A. Krumhansl and N. Schwartz, Phys. Rev. **89**, 1154 (1953).

[12] T. Muto, Progr. Theoret. Phys. **4**, 181, 243 (1949).

[13] C. A. Hutchison, Jr., and G. A. Noble, Phys. Rev. **87**, 1125 (1952).

[14] A. H. Kahn and C. Kittel, Phys. Rev. **89**, 315 (1953).

[15] Kip, Kittel, Levy, and Portis, Phys. Rev. **91**, 1066 (1953).

[16] K. Huang and A. Rhys, Proc. Roy. Soc. (London) **A204**, 406 (1950).

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

[18] R. C. O'Rourke, Phys. Rev. **91**, 265 (1953).

[19] T. Nagamiya, J. Phys. Soc. Japan **7**, 354 (1952).

The last two investigators and Burstein and Oberly[20] have employed an adiabatic approximation to determine the effect of neighboring ion position on the F-center energy, and accordingly the effect of thermal agitation on the width.

Muto has pointed out that, in reality, we have to consider simultaneously not only effects arising from thermal expansion but also those connected with the excitation of lattice vibrations in order to obtain a full knowledge of the phenomena concerned. In an attempt to separate and clarify these effects, an investigation was undertaken to study the dependence on hydrostatic pressure of the F-band parameters. One limited experiment of this type has been reported briefly by Burstein, Oberly, and Davisson.[21] Measurements are reported below on the F-absorption band of seven alkali halides at room temperature up to pressures of 5000 atmospheres. The compounds studied were NaCl, NaBr, KCl, KBr, KI, RbCl, and CsCl. Other compounds were not studied owing to difficulties in procurement or preparation of suitable samples, experimental difficulties in the optical transmission of the pressure chamber, or the instability of their F band at room temperature.

The results of the experiments on the shift of the band peak with pressure are compared with the existing data in the literature on the shift with temperature, in an effort to interpret how the effects mentioned above have to be taken into account to form a consistent picture. For most of the compounds studied, the shift of the peak with pressure is less than that with temperature, when each is considered with respect to the corresponding change in lattice dimensions. In the analysis of the data for these compounds, it is shown that a small part (up to 5 percent) of the pressure shift is due to the interaction of the electron with the optical lattice vibrations. The remainder of the pressure shift is due to the explicit dependence of the F-center energy on local interatomic distance. The additional increment for the temperature shift above the pressure shift is attributed to a further interaction with optical lattice vibrations. An expression is obtained for the band width which combines the two existing theories and is consistent with the analysis of the shift of the band peak with pressure and temperature. The negligible effect of pressure on the band width is in agreement with these considerations.

A subordinate purpose of the present investigation is a study of the effects on the F band of the structure transformation in the rubidium halides. Excepting the fluoride, these salts show a polymorphic transition at room temperature and about 5000 atmospheres pressure, which was first observed by Slater[22] and was measured by Bridgman.[23] Jacobs[24] has shown that the crystal structure changes from the NaCl structure to the CsCl structure in the high-pressure form. Although various difficulties prevented the detection of a new F band in the transformed state, a number of interesting observations are described and discussed.

II. EXPERIMENTAL METHOD

A. Apparatus

A high-pressure system to allow for spectrophotometric measurements was constructed for this investigation. It was used in conjunction with a Beckman Model DU Quartz Spectrophotometer, employing the usual tungsten lamp and phototubes for the visible range. The system is capable of subjecting the sample to 8000 atmospheres pressure, although problems with failure of the windows restricted most of the work to a range of 5000 atmospheres.

The need for compactness and portability gave rise to several special features in this apparatus. The whole system is self-contained, with the pump for generating pressures made in the form of a plug which screws into the high-pressure bomb. To minimize the optical path through the bomb, a search was made for a more compact method of sealing the synthetic sapphire windows[25] than the Poulter[26] packing usually employed. Our experiments have shown that it is feasible to use ordinary synthetic rubber O-rings to seal pressures to at least 8000 atmospheres. With this technique only one O-ring is used to seal both the window and its supporting plug.

The high-pressure apparatus consists of the pump, the bomb, a mounting carriage with wheels, and a baseboard arrangement for positioning the Beckman spectrophotometer. This baseboard provides a track on which the carriage can be rolled so that either the observation hole or the blank reference hole is in position in the light path. A black cloth is fastened over the bomb and photocell units to keep out stray light during measurements. The pump is capable of producing a pressure of 2000 atmospheres. The pump liquid is 20-centistoke DC-200 silicone fluid (Dow-Corning). Figure 1 shows a diagram of the high-pressure bomb. The bomb contains a piston intensifier to magnify the 2000-atmosphere pressure delivered by the pump to a maximum pressure of 8000 atmospheres at the sample. Pressure is determined by measurement of the change in resistance of a manganin resistance gauge which is immersed in the pressure fluid. The gauge calibration procedure has been described previously.[27] The hy-

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[20] E. Burstein and J. J. Oberly, National Bureau of Standards Circular No. 519 (U. S. Government Printing Office, Washington D. C., 1952), p. 285.

[21] Burstein, Oberly, and Davisson, Phys. Rev. **85**, 729 (1952).

[22] J. C. Slater, Phys. Rev. **23**, 488 (1924).

[23] P. W. Bridgman, Z. Krist. **67**, 363 (1928).

[24] R. B. Jacobs, Phys. Rev. **54**, 468 (1938).

[25] Purchased from The Linde Air Products Company, Synthetic Gem Division, Chicago, Illinois.

[26] T. C. Poulter, Phys. Rev. **35**, 297 (1930); see also P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, Ltd., London, 1949), p. 58.

[27] D. Lazarus, Phys. Rev. **76**, 545 (1949).

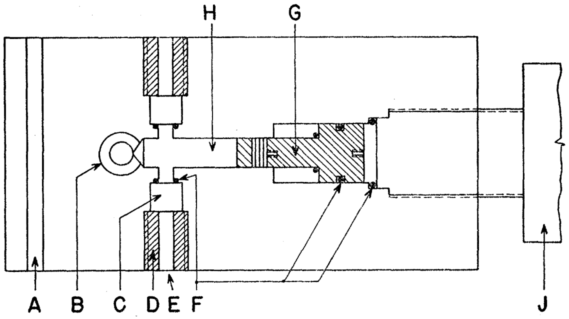

FIG. 1. Diagram of the high-pressure bomb. *A*, reference hole; *B*, gauge plug hole; *C*, synthetic sapphire window; *D*, window plug; *E*, sample observation hole; *F*, O-rings; *G*, piston intensifier; *H*, sample region; *J*, portion of pump.

draulic medium around the sample is 3-centistoke DC-200 silicone fluid, which is sufficiently transparent over the visible range. The sample holder is a split cylinder, with a $\frac{1}{4}$-inch hole transverse to the cylinder axis to permit passage of light. One of the cylinder halves has a recess $\frac{3}{8}$ in.$\times\frac{5}{16}$ in.$\times\frac{1}{16}$ in. for the crystal samples which are cleaved to that size. A coil spring around the cylinder keeps the halves together and provides the necessary friction with the walls to maintain the holder in a fixed position in the bomb.

The Beckman spectrophotometer needs no modification for use with the high-pressure system except for the separation of the photocell housing from the main unit by about 4 inches to accommodate the bomb.

B. Preparation of Samples

The specimens of NaCl, KCl, and KBr used in this work were cleaved from single-crystal blocks obtained from the Harshaw Chemical Company. No analysis of these samples was made, but the work of Duerig and Markham[28] includes a representative analysis of this type of commercial sample. Single-crystal specimens of the other four compounds were grown in the laboratory. The NaBr salt was Mallinckrodt, Analytical Reagent, and the KI salt was Baker and Adamson, Reagent. The CsCl salt used was 99+ percent, 0.5 percent K, 0.02 percent Pb, the two listed impurities having been added for a prior experiment. The RbCl samples were grown from two sources of the salt. One grade was Fairmount, cp, for which spectroscopic analysis showed 5 percent K, 0.5 percent Ba, 0.4 percent Na, 0.1 percent Cs, and lesser quantities of Li, the other alkaline earths and Pb. A purer source was Mackay "99.99 percent" for which spectroscopic analysis showed 0.3 percent K, 0.03 percent Na, and smaller quantities of Cs, and the alkaline earths.

The NaBr, KI, and RbCl crystals were grown in air from a platinum crucible by the Czochralski[29] method, with crystallization occurring on a platinum wire that was slowly withdrawn from the melt surface. The divalent impurities in these salts were reduced in concentration by a factor of two to ten in crystals grown in this manner. The CsCl specimen was grown by slowly lowering through a gradient furnace an evacuated and sealed Vycor tube containing the salt in a small spun platinum crucible with a conical bottom. All samples were annealed after growth for a 12-hour period. The air-grown crystals were readily cleaved to desired sizes. The deliquescent CsCl specimen, which did not cleave, was cut to shape and polished under silicone fluid. Similar handling precautions were taken with those of the other samples whose surfaces tended to fog easily.

The *F* band was produced in the crystals by irradiation with x-rays from a Machlett type A-2 molybdenum target tube with a beryllium window. The irradiations varied from 5 minutes to 90 minutes (40–50 kv, 20 ma) with the sample about one inch from the tube window. The ranges of time correspond to the varying darkenability of the different compounds. X-irradiation was performed in the dark, during which all samples showed a faint green or blue-green fluorescence. This effect has also been observed by Molnar[30] and attributed to impurities because the fluorescence differs in natural and synthetic NaCl. Subsequent handling of colored samples was done in the near-dark or with appropriate filters over the light source to remove *F*-band light.

Samples of KCl and RbCl were also additively colored with excess K or Na metal. A crystal somewhat larger than sample size was sealed in an evacuated Vycor tube with the metal. The metal was previously melted in a rough vacuum to draw off trapped gas. The tube, crystal, and metal were so arranged in the furnace that the crystal was kept at 660°C, while the metal was at about 300°C. After about 20 hours the tube was quenched in a brine solution. Samples suitable for measurement were cleaved from inner regions of the colored crystal.

C. Measurement Procedure

The absorption coefficients of the crystals were measured at each desired pressure, as a function of wave number, over a range embracing the whole *F* band. Readings were taken on a linear wave number scale, 250 cm^{-1} apart. To minimize the bleaching effect of the measuring light, the sensitivity adjustment on the spectrophotometer was set so that minimum slit widths were required. In this way the entire range of pressures could be explored with one x-irradiation of a sample. Such readings measured the transmission of the crystal and associated liquid and windows with respect to the reference hole which presented the same geometrical aperture. To obtain the true color-center absorption curve, a correction had to be applied for the effect

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[28] W. H. Duerig and J. J. Markham, Phys. Rev. **88**, 1043 (1952).

[29] See H. E. Buckley, *Crystal Growth* (John Wiley and Sons, Inc., New York, 1951).

[30] J. P. Molnar, thesis, Massachusetts Institute of Technology, 1940 (unpublished).

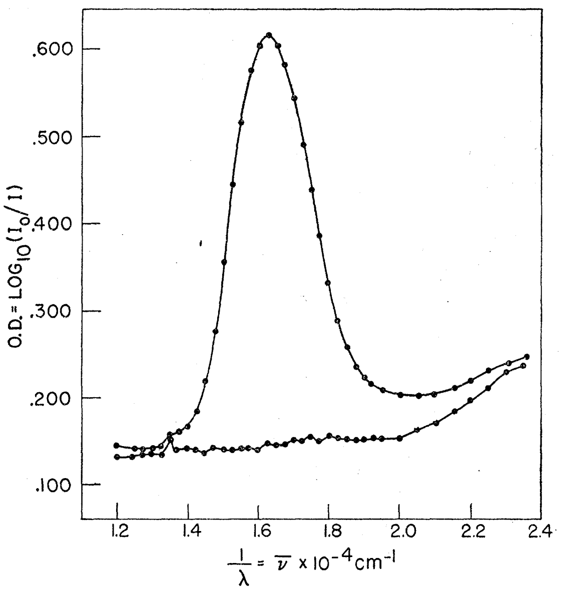

FIG. 2. Typical uncorrected F-band curve and a correction curve for the same sample.

of the blank crystal and associated apparatus. This could be measured by assembling the system with an uncolored crystal or by bleaching the x-ray colored crystal still in the bomb at the end of a pressure run. No significant differences were detected between these alternatives, if the bleaching with an ordinary incandescent lamp were sufficiently long. The latter procedure was usually adopted for the x-rayed specimens, while the former procedure was necessary for the additively colored samples. It was found that these blank absorption curves changed with pressure only by a linear displacement of the ordinate of the curve. This effect arose in part from changes in the interface reflections with the variation of the index of refraction with pressure and in part from irreversible changes in interfacial conditions induced by pressure. From this it follows that one blank absorption curve taken at one pressure was sufficient to make the necessary correction. This curve was linearly displaced to fit the colored absorption curves at one point where the F-band absorption was negligible. Figure 2 shows an uncorrected F-band curve and a correction curve taken on the same sample.

A very slow contamination of the bomb fluid took place at the violet end of the spectral range due to a dissolution of binding agents from the O-rings and piston washer. This resulted in some uncertainty in the height of the F band and gave rise to an uncertainty in the width at half-maximum, γ, of $\pm 0.004\times 10^4$ cm^{-1}.

To avoid the distortion in the position of the band maximum due to the optical bleaching during the measurements, absorption curves were taken with both increasing and decreasing wavelengths in separate runs on each compound except NaBr and KI. The corrected absorption curves were plotted with optical density (O.D. $=\log_{10}I_0/I$) as ordinate and wave number ($\tilde{\nu}=1/\lambda$) as abscissa. For each curve the band parameters were measured, that is, the peak wave number, $\tilde{\nu}_m$, and the width at half-maximum, γ. The peak wave number was determined by extrapolation on the curve formed by the mid-points of the bell-shaped band at four O.D. values, starting up from half the maximum height of the band. With this method the uncertainty in $\tilde{\nu}_m$ was usually $\pm 0.002\times 10^4$ cm^{-1}.

III. RESULTS

A. Pressure Dependence of F-Band Parameters

The data from the measurement of the F-band peak wave number at intervals of about 1000 atmospheres are presented in Table I and in terms of wavelength in Table II. These data represent the average of two or more runs, except in the cases of NaBr and KI for which only one run was made. The experiments were conducted at room temperature, which was constant within 1°C during any single run but which varied during separate runs from 20° to 28°C. The agreement of the atmospheric pressure values in Table II with those listed by Ivey[5] is reasonably satisfactory in most cases. The agreement is even better with the recent values of Gnaedinger[31] for the compounds which he studied. The largest discrepancy from Ivey's tabulation is in the case of CsCl, but a re-examination of the source[1] of this value suggests that our value in Table II is reliable. The values based on a single run are distorted in the direction anticipated from the optical bleaching. It should be pointed out that the reported location of the peak may be affected by the method chosen to fix its location, due to the considerable width of the room temperature bands.

In order to make a more significant physical correlation, the results are considered as a function of the crystallographic unit cell distance, a. This is calculated from the compressibility at 30°C determined by Slater

TABLE I. Pressure dependence of F-band peak wave number.

Pressure bars[a]	Peak wave number[b] 10^4 cm^{-1}						
	NaCl	NaBr[c]	KCl	KBr	KI[d]	RbCl	CsCl
1	2.147	1.865	1.787	1.593	1.446	1.578	1.656
1000	2.161	1.876	1.798	1.604	1.460	1.591	1.666
2000	2.175	1.886	1.810	1.616	1.474	1.604	1.676
3000	2.190	1.897	1.821	1.628	1.489	1.615	1.685
4000	2.203	1.909	1.832	1.640	1.503	1.624	1.693
5000	2.215	...	1.842	1.652	1.517	1.634	1.701
6000	2.226	...	...	...	...	...	...
7000	2.238	...	...	...	...	...	...
8000	2.250	...	...	...	...	...	...

[a] 1 bar $=10^6$ dynes/cm^2 $=1.01971$ kg/cm^2 $=0.98692$ atmos.
[b] $\pm 0.002\times 10^4$ cm^{-1}.
[c] Measured with increasing wavelength only.
[d] Measured with decreasing wavelength only.

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[31] R. J. Gnaedinger, Jr., J. Chem. Phys. **21**, 323 (1953).

and Bridgman, as tabulated by Birch,[32] with regard for recent corrections in the value of the compressibility of iron. For the complete data on the compressibility of RbCl, the original article by Bridgman[33] must be consulted. The effect on the elastic constants due to the presence of *F* centers is negligible for color-center concentrations encountered in usual practice. A calculation of this type has been presented by MacKenzie,[34] in which the correction term is proportional to the relative decrease in density of the material due to the presence of small cavities or vacancies. This density change has been measured in two investigations,[35,36] but it is insignificant in the case at hand. A simple correlation of the pressure data is found by plotting $\log_{10}\tilde{\nu}_m$ *versus* $\log_{10}a$ for each individual compound. The points lie along a straight line whose slope can be measured with an uncertainty of about 5 percent. Figure 3 presents typical curves from individual runs on each of the seven compounds, plotted on reduced scales. The straight lines become more clearly defined when data from several runs are considered, but these are omitted from the figure for the sake of clarity.

The quantity of interest in this method of considering the results is the parameter $n_T(P)$, which is the negative of the slope of the line, i.e., $n_T(P) = -(\partial \ln\tilde{\nu}_m/\partial \ln a)_T$. From the figure it is seen that most of the lines have nearly the same $n_T(P)$, i.e., 3.5, with the exception of NaCl which is high (4.4), and of CsCl which is low (2.8). The specific values are recorded in column 2 of Table III. The slopes did not vary outside the limits of uncertainty on different samples of the same compound, or on samples of different purity obtained from separate sources as in the case of RbCl, or on samples colored by different methods, additively or photochemically (x-ray) as in the cases of KCl and RbCl.

The widths at half-maximum at atmospheric pressure are in good agreement with previously published values, subject to the experimental uncertainties mentioned above. For five of the seven compounds studied, the width of the band does not change with pressure, within a scatter of 2 or 3 percent. For NaBr there appeared to be a decrease in band width amounting to about 10 percent in 4000 atmospheres. The experiment on NaBr left much to be desired because of a tendency of the sample to become fogged, impairing the optical measurements. In view of behavior of the five other compounds of the same structure and similar properties, the validity of this result for NaBr remains in considerable doubt. CsCl also shows a dependence of width on pressure, but in the opposite direction. The amount of the increase is about 5 percent and appeared in each of two runs on the same sample, despite a 5 percent difference in the zero pressure value of the width of the band between the two runs. The average value of this zero pressure width at room temperature is found to be $\gamma = 0.295 \pm 0.009 \times 10^4$ cm^{-1}. A value for comparison does not appear to be available in the literature. The validity of this width increase with pressure for CsCl is in doubt, as the argument employed above need not apply to a compound of different structure. Further experiments are required to confirm the result.

TABLE II. *F*-band wavelength and shift with pressure.

Crystal	λ_{max}(1 bar) A	$\lambda_{max}(1) - \lambda_{max}(5000)$ A
NaCl	4658±5	143±7
NaBr[a]	5362±6	154±8[c]
KCl	5596±6	167±9
KBr	6277±8	224±11
KI[b]	6916+10	324±14
RbCl	6337±8	217±11
CsCl	6039±7	160±10

[a] See footnote c, Table I.
[b] See footnote d, Table I.
[c] Extrapolated value.

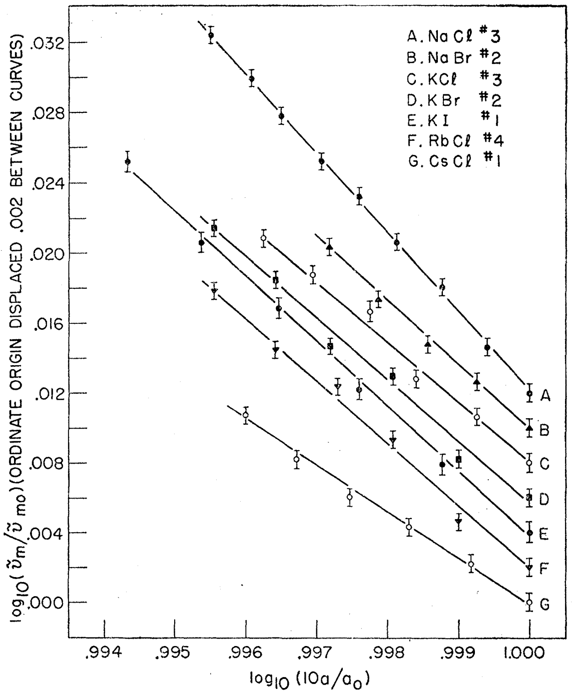

FIG. 3. Experimental curves showing dependence of peak wave number on lattice parameter. The reduced ordinates are referred to their values at atmospheric pressure.

B. Effects of Structure Transformation

Experiments were performed on colored and uncolored crystals of RbCl at pressures in excess of that required to induce the structure transformation mentioned in Sec. I. The equilibrium transition pressure is about 5000 atmospheres and the associated relative

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[32] F. Birch *et al.*, *Handbook of Physical Constants* (Geological Society of America, Special Papers, No. 36, 1942), p. 52. See also reference 27.

[33] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **67**, 345 (1932).

[34] J. K. MacKenzie, Proc. Phys. Soc. (London) **B63**, 2 (1950).

[35] Estermann, Leivo, and Stern, Phys. Rev. **75**, 627 (1949).

[36] H. Witt, Nachr. Akad. Wiss. Göttingen, Math-physik Kl. **4**, 17 (1952).

decrease in volume is about 15 percent.[23] We shall consider first some observations on uncolored crystals, made visually rather than volumetrically due to the nature of the apparatus. The indication of the transition occurs at about 6500 atmospheres, at which point the ordinarily transparent crystal abruptly becomes almost opaque as though shattered into a large number of tiny crystals. The light transmission in this state is less by a factor of 50 to 100 than that of the normal crystal. The opacity is retained at high pressure but gradually decreases as the pressure is released. At atmospheric pressure the crystal is nearly as transparent as before the transformation and is often indistinguishable from ordinary crystals in normal light. Under crossed Nicols at moderate magnification (20×), such crystals show a highly developed strain pattern of many short lines covering the whole sample. (In some cases the region near the surfaces was free of strain.) The lines lie predominantly in the {110} planes, corresponding to the slip planes and directions of alkali halides.[37] Thus the transformation is accompanied by considerable plastic flow on a local scale.

The higher transition pressure observed in this work is in agreement with previous experience with salts of less than "atomic weight" purity.[24] Thus no difference was noted when the relatively purer RbCl salt was introduced in the present experiment.

The phenomenon of opaque or shattered crystals which regain their transparency is visually similar to that observed by Kraus and Nutting[38] for the low temperature transition in ammonium chrome sulfate and selenate alums.

The crystallographic aspects of this type of structure transformation have been discussed by Buerger.[39] A contraction along a body diagonal of the face-centered cubic cell with an expansion perpendicular to that axis will transform the structure to simple cubic. Since there is no observable macroscopic distortion of the RbCl sample in the high-pressure modification, the transformation must proceed from a large number of nucleation centers, at each of which there is a choice of four possible trigonal axes along which to propagate. Thus there may be some degree of mismatch between adjoining regions characterized by different transformation axes. Associated with this mismatch, or with that between regions which have transformed and those which have not, there should be variations in the index of refraction which give rise to light scattering and to the observation of opacity.

Laue back-reflection x-ray pictures of uncolored RbCl samples which had been through the transformation generally produced patterns of smeared ring segments, if the strain extended throughout the crystal. Annealing at 300°C for one day brought about recrystallization. These results differ somewhat from findings in a recent single-crystal study[40] of the CsCl transformation to the NaCl structure at 469°C.

Observations were made on x-ray colored crystals with the hope, initially, of detecting an F band in the high-pressure form of RbCl. A rough estimate of the expected spectral location of the band can be made by assuming the approximate validity of a Mollwo-like relation for salts of the CsCl structure. The position of the F band at room temperature in CsCl is given in Table II, while the value of $\lambda_{\max}$ for CsBr at room temperature is 6750A, from measurements of Pringsheim.[41] If the peak wavelength is assumed to be proportional to some power of the interionic distance, calculation with these data yields the result that the power is about 2.6. Then, using Bridgman's data for the density of the high-pressure form of RbCl, it is estimated that the F band should be near 5200A.

The features described above for uncolored crystals remain valid for x-ray colored crystals. The optical density of the transformed crystals is about 1.5 to 2.0, which is a very insensitive region for the spectrophotometer. To reduce the light intensity passing through the reference hole, fine mesh screens were used. This reduced the apparent optical density of the crystals, but the measurements obtained were frequently erratic. Frequent development of window cracks around 7000 atmospheres also interfered with the work.

High-pressure absorption measurements taken just after the transformation revealed the F band located in its pretransition position but decreased in height by 40 percent. Returning to one atmosphere, the band retained about 50 percent of its original height. Subsequent experiments of a "before and after" type demonstrated that 85–95 percent of the band could be destroyed by subjecting the colored crystal to the two-way transformation. For these experiments, the crystals were taken to 8000 atmospheres between the two absorption curve measurements.

The explanation of this effect is readily found in the experiments of Smekal[42] and of Schröder,[43] interpreted by Seitz,[44] which show that x-ray darkened crystals are bleached by cold work. As noted above, considerable plastic deformation accompanies the structure transformation. Schröder reduced the F-band height by 20 percent with uniaxial stresses of 40–400 g/mm². A separate experiment in this study confirmed his result by reducing the band height by at least 25 percent after the application of a load of 500 g/mm² on an x-rayed KCl sample in a bath at 0°C. This result makes allow-

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[37] E. Schmid and W. Boas, *Plasticity of Crystals* (F. A. Hughes Company, London, 1950), pp. 228, 233.

[38] D. L. Kraus and G. C. Nutting, J. Chem. Phys. **9**, 133 (1941); see also J. Eisenstein, Revs. Modern Phys. **24**, 74 (1952).

[39] M. J. Buerger, "Crystallographic Aspects of Phase Transformations," Chapter in *Phase Transformations in Solids* (John Wiley and Sons, Inc., New York, 1951).

[40] Menary, Ubbelohde, and Woodward, Proc. Roy. Soc. (London) **A208**, 158 (1951).

[41] P. Pringsheim (private communication). The author is indebted to Dr. Pringsheim for providing this information.

[42] A. Smekal, Z. Ver. deut. Ing. **72**, 667 (1928).

[43] H. J. Schröder, Z. Physik **76**, 608 (1932).

[44] F. Seitz, Phys. Rev. **80**, 239 (1950).

ance for the natural thermal bleaching during the period between measurements.

Experiments were also undertaken on additively colored RbCl crystals to study the effect of the structure transformation. For conventional work this type of coloration is relatively stable. In absorption measurements above the transition pressure no new band was observed, but there was evidence of a considerably reduced pretransition *F* band. "Before and after" experiments on samples colored with excess K metal produced complete destruction of the *F* band and recrystallization of the sample upon returning to atmospheric pressure. An uncolored but quenched sample did not recrystallize during such an experiment. Its behavior was identical to that of an annealed uncolored specimen.

The effect of plastic flow on additively colored crystals was investigated in an auxiliary experiment. Such work does not appear to have been undertaken in the past. KCl crystals containing excess K metal were subjected to uniaxial loads of from 200 to 500 g/mm^2, while the samples were kept at 0°C. The decrease in the height of the *F* band is negligible and there is no detectable growth of subsidiary long-wavelength bands. Compared with the effects in x-ray colored crystals, this result is somewhat surprising. In analyzing this we take note of the suggestion of Tyler,[45] based on the experiments of Gyulai and Boros,[46] that electronic processes may contribute to the enhanced conductivity due to plastic flow.[47] The latter workers, using low stresses of 100 g/mm^2, observed short decay times (10^{-3} sec) for the enhanced conductivity in alkali halide crystals. The magnitude of the effect was doubled when photochemically or additively colored crystals were studied, but the decay time was unaffected. For the present experiments, the work of Gyulai and Boros implies that the plastic flow causes the evaporation of electrons from the *F* centers. The conclusion to be drawn from the null effect observed is that the necessary rearrangements of vacancy aggregates to form *M* or other centers cannot take place in the few seconds during which the dislocations are moving rapidly. Thus the electrons are mostly retrapped in the isolated negative ion vacancies from which they were ejected.

In discussing the effect of plastic flow on x-ray colored crystals, Seitz[44] offered three tentative explanations. Only the first of these is consistent with the observations of Gyulai and Boros and with the null effect of plastic flow on additively colored crystals. This is the suggestion that the region about the vacancies associated with the color centers becomes heated when a dislocation passes very close, and that the electrons and holes evaporate and have an opportunity to recombine. The vacancies involved probably lie close to dislocations,[48] and should be in an ideal position to experience the thermal effects which accompany the motion of dislocations. Variations of the other two suggested explanations would allow a bleaching effect due to cold work in additively colored crystals, contrary to our observations.

TABLE III. Experimental and theoretical parameters describing the dependence of the *F*-band maximum on pressure and temperature.

1 Compound[a]	2 $n_T(P)$	3 $n_P(T)$	4 α_P 10^{-6} deg^{-1}	5 b/θ (cm deg)$^{-1}$	6 n_Q[b]	7 f[c]	8 n_M[d]	9 f[e]
NaCl	4.4±0.1	4.0±0.2	40±1	~0	1.5	2.9	1.94	2.3
NaCl[f]		4.4±0.2	44±1	~0				
NaBr	3.6±0.2	3.8±0.2	41±1	0.2±0.2	(1.5)	2.4	1.83	2.0
KCl	3.5±0.1	5.0±0.2	35±1	0.9±0.1	1.6	2.1	1.74	2.0
KBr	3.5±0.1	4.5±0.2	41±1	0.7±0.1	(1.6)	2.1	1.66	2.1
KI	3.7±0.1	4.4±0.2	41±1	0.4±0.1	(1.6)	2.3	1.55	2.4
RbCl	3.4±0.1	5.2±0.2	35±1	1.0±0.1	(1.6)	2.1	1.66	2.0
CsCl	2.8±0.2	4.9±0.2[g]	46±1	1.6±0.2	1.76	1.5	2.65[h]	1.0

[a] At room temperature, unless otherwise noted.
[b] Calculated from square well model; values in parentheses estimated.
[c] Using values from column 6.
[d] Derived from plot of $\log_{10}E$ *vs* a^{-1}.
[e] Using values from column 8.
[f] At 200°C.
[g] Calculated for CsBr; $\lambda_m(-190°\text{C}) = 6450\text{A}$, reference 41.
[h] Obtained by plotting data from CsCl and CsBr.

IV. THEORY

The theroretical interpretation of the shift of the absorption peak with pressure or temperature must include the effect of the variation of interatomic distance and also the effect of the interaction of the *F*-center electron with the lattice vibrations. These effects have been considered separately by various investigators, as mentioned in Sec. I, in attempts to account for the temperature shift. There does not appear to have been any attempt to combine both parts into a consistent picture. The reason for this probably lies in the difficulty in making a theoretical estimate of the relative magnitudes of the separate contributions of each effect and in the lack, up to this time, of sufficient experimental data from which to evaluate these relative contributions. The results of the present experiment provide the additional data with which to overcome this obstacle and to make empirical estimates of the magnitudes of the individual effects.

We characterize the results of the pressure experiment in terms of the parameter $n_T(P)$ listed in column 2 of Table III. Along with it we require for comparison the corresponding parameter for the temperature shift, $n_P(T) = -(\partial \ln\bar{\nu}_m/\partial \ln a)_P$. It is listed in column 3 of the same table and is evaluated for a range around room temperature except as otherwise noted. The data for the dependence of $\bar{\nu}_m$ on temperature are mainly due to Mollwo,[4] supplemented in various cases by data from

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[45] W. W. Tyler, Phys. Rev. **86**, 801 (1952).

[46] Z. Gyulai and J. Boros, Math. naturw. Anz. ungar. Akad. Wiss. **59**, 115 (1940).

[47] See reference 44 for a discussion of the earlier experiments of Gyulai and Hartly on the influence of plastic flow on conductivity.

[48] See the recent work of J. J. Markham, Phys. Rev. **88**, 500 (1952), and F. Seitz, Phys. Rev. **89**, 1299 (1953), for development of the idea that *F* centers are located near dislocations, as a consequence of their formation at incipient vacancies associated with jogs in Taylor dislocations.

Gnaedinger,[31] Molnar,[30] and Pringsheim.[41] Room temperature thermal expansion data are employed in most cases, because considerable discrepancies often appear in the values from different workers as they depart from room temperature. The values used are listed in column 4. It is seen that for most compounds the "pressure slope," $n_T(P)$, is smaller than the "temperature slope," $n_P(T)$.

We use a high-temperature representation for the F-center energy at the peak of the absorption curve, E, in the form

$$E = E_0[R(a)] - bT/\Theta(a). \qquad (1)$$

A suitable modification may be made for the low-temperature region. E_0 is the energy at absolute zero and is a function of the distance parameter, R, which in turn depends on the interionic distance, a, in the bulk crystal. The distance R is the significant parameter in determining the energy E_0, and its interpretation depends on the model employed to calculate the F-center energy levels. In a continuum model R may be the radius of the potential well of the vacancy, or in a molecular orbital model it may be the actual distance of the first neighbor ions from the center of the vacancy after relaxation has taken place. The form of the second term in Eq. (1) has its basis in the work of Huang and Rhys[16] and of Muto.[12] Huang and Rhys assume that the predominant coupling between electron and lattice is produced by the long-range Coulomb interaction between the F-center electron and the electric polarization associated with the single-frequency longitudinal optical vibrations of the lattice. They use this coupling to account for the temperature broadening of the band. They find, however, as has been confirmed in the more general treatments of Lax[17] and of O'Rourke,[18] that this idea does not give rise to any shift of the absorption peak with temperature. To rectify this, they use an idea (previously put forth by Muto) that when an F center changes its state the lattice frequency is altered by a small amount. This small frequency change, proportional to b in Eq. (1), does not appear in the harmonic forces approximation usually used to describe the lattice. Thus the parameter $\Theta(a)$, in our expression for the energy, is the characteristic temperature related to the longitudinal optical vibration frequency of the lattice. This temperature is sufficiently close to the usual Debye temperature that we need not distinguish them.

For the shift of the absorption band peak with pressure we must form the derivative $(\partial \ln E/\partial \ln a)_T$ from Eq. (1). Thus we have:

$$\left(\frac{\partial \ln E}{\partial \ln a}\right)_T = -n_T(P) = \left(\frac{\partial \ln E}{\partial \ln \Theta}\right)_{T,R} \frac{d \ln \Theta}{d \ln a} + \left(\frac{\partial \ln E}{\partial \ln R}\right)_{T,\Theta} \left(\frac{\partial \ln R}{\partial \ln a}\right)_T. \qquad (2)$$

From the Grüneisen relation we obtain:

$$d \ln\Theta / d \ln a = -3\gamma_G, \qquad (3)$$

where γ_G is the Grüneisen constant. The term $(\partial \ln R/\partial \ln a)_T$, the ratio of the relative change in R to the relative change in a at constant temperature, is equal to the ratio of the effective isothermal compressibility around the F center to the isothermal compressibility of the bulk material. There are several ways of estimating this, but we shall consider it as unknown and designate it by the symbol f_T. The derivative $(\partial \ln E/\partial \ln R)_{T,\Theta} = (d \ln E_0/d \ln R)$ may also be estimated in a number of ways. A particular model may be assumed for the F center, from which the energy levels may be calculated in terms of their dependence on R, and thus the value of the derivative may be calculated. We designate the negative of this derivative by the symbol n_Q. As an alternative the slope of a plot of the experimental values of $\log_{10}E$ *versus* $\log_{10}a$ may be employed, if it is assumed that the factor which relates the equilibrium values of R and a does not vary rapidly from one compound to another. Such a plot should be made using the values of E and a at absolute zero or as an intermediate compromise, using values which correspond to the characteristic temperature, Θ. The negative of the slope of this plot we call n_M, to distinguish it as a different way of estimating n_Q. This matter will be discussed further in the following section.

For the present, we shall use values calculated from an exceedingly simple continuum model, namely that which represents the F center as an electron trapped in a spherically symmetric square potential well. The radius of the well R is chosen equal to the interionic distance a. The depth of the well is chosen so that the energy difference between the ground s state and the excited p state is equal to the observed F-center energy. To evaluate the variation of E_0 with R, it is assumed that the well depth is inversely proportional to its radius R. The results of such a calculation are that the values of n_Q are 1.5, 1.6, and 1.76 for NaCl, KCl, and CsCl, respectively. Thus we obtain for the pressure shift:

$$n_T(P) = 3\gamma_G bT/E\Theta + n_Q f_T. \qquad (4)$$

The shift of the absorption band peak with temperature is derived in an analogous fashion, by forming $(\partial \ln E/\partial \ln a)_P$. From Eq. (1) we obtain:

$$\left(\frac{\partial \ln E}{\partial \ln a}\right)_P = -n_P(T) = \left(\frac{\partial \ln E}{\partial T}\right)_{\Theta,R} \left(\frac{\partial T}{\partial \ln a}\right)_P + \left(\frac{\partial \ln E}{\partial \ln \Theta}\right)_{T,R} \frac{d \ln \Theta}{d \ln a} + \left(\frac{\partial \ln E}{\partial \ln R}\right)_{T,\Theta} \left(\frac{\partial \ln R}{\partial \ln a}\right)_P. \qquad (5)$$

The term $(\partial T/\partial \ln a)_P$ which appears here is the reciprocal of the isobaric linear thermal expansion coefficient, α_P. Similar to its counterpart in the pressure shift, the term $(\partial \ln R/\partial \ln a)_P$ is equal to the ratio of the effective thermal expansion coefficient around the *F* center to the bulk value of the thermal expansion coefficient. We designate this factor by the symbol f_P. The expression for the temperature shift is then given by

$$n_P(T)=b/E\Theta\alpha_P+3\gamma_G bT/E\Theta+n_Q f_P. \tag{6}$$

We may consider that the thermal expansion of a solid arises from the effect of an outward thermal pressure set up by the anharmonicity of the vibrations of the atoms of the solid. This thermal pressure acts against the same forces as does the external pressure considered with respect to the compressibility of a solid. Since the thermal expansion is particularly dependent on the nonlinearities in these forces, we may expect that the effective thermal expansion factor, f_P, is at least as large as the effective compressibility factor, f_T, in the neighborhood of the *F* center. We lack, however, a method of evaluating this difference in detail. Consequently, we may not make too great an error if we assume that the two factors are approximately the same. If we then drop the subscripts from these two factors in Eqs. (4) and (6), we may combine these two expressions to obtain the result:

$$b/E\Theta\alpha_P=n_P(T)-n_T(P). \tag{7}$$

In this way the quantity b/Θ may be calculated from the experimental data on the pressure and temperature shifts of the *F*-band absorption maximum. These values are listed in column 5 of Table III. Making a substitution back into Eq. (4), the value of the factor f may be obtained. The magnitude of this factor will depend directly on the value used for the term n_Q. Using the calculations from the square well continuum model, the values of f listed in column 7 of Table III are obtained. If values of n_Q obtained from a different method are used, a new set of values for f will result.

In the preceding analysis we have presented a simple approach in which the temperature and pressure dependence of the *F*-band absorption peak are treated in a unified manner. The conclusion is reached that the shift of band with pressure is due mainly to the dependence of the energy on interatomic distance, with a small contribution, amounting to 5 percent at most, arising from the interaction with optical lattice vibrations. The temperature shift is governed by the same factors as the pressure shift, plus an additional term, as large as 40 percent, arising from a further contribution from this same electron-lattice interaction.

We turn now to a consideration of the width of the *F* band. This problem is rather unsettled. As pointed out in Sec. I, two explanations have been offered by separate groups of investigators. We have mentioned the long-range electron-optical lattice vibration interaction used by Huang and Rhys. This coupling gives rise to a broadening of the absorption band. Lax and O'Rourke have shown that a simple formula describes this width, in the approximation in which all lattice modes have the same frequency (that of the longitudinal optical vibrations). If we call γ_1 the width at half-maximum due to this mechanism, we have from O'Rourke:[18]

$$\gamma_1=2(2\ln 2)^{\frac{1}{2}}\hbar\omega[S\coth(\hbar\omega/2kT)]^{\frac{1}{2}}, \tag{8}$$

where ω is the frequency just mentioned, S is the net number of vibrational quanta involved at the absorption maximum, and the numerical factor in front converts the root-mean-square value of the distribution to the width at half-maximum, on the assumption that the distribution is approximately Gaussian. The width γ_1 is independent of the parameter b introduced in Eq. (1).

The second contribution to the broadening arises when we consider that the local deformation of the lattice causes variations in the gap between the electronic energy levels. In an adiabatic approximation, we may say that absorption takes place when the wavelength of light coincides with the energy gap determined as a function of the displacement of the surrounding ions. Several versions of this approach have appeared.[9,19,20] Their principal achievement has been the demonstration that the finite width of the *F* band at low temperatures may be accounted for by the zero-point vibrations of the neighboring ions. The idea which is common to all is that the mean square fluctuation in the *F*-center energy is determined by the mean square fluctuation in a suitable radius for the vacancy.

A factor which has been overlooked in these versions is the role of shear waves in causing a broadening. When the region of the vacancy is distorted from its spherical shape, it is reasonable to expect a change in the *F*-center energy, at least through an interaction with the angular momentum of the excited p state. The continuous variation of the nonspherical distortion would then contribute to the band width. Since we lack a detailed calculation of this effect, we may account in a rough way for the two shear modes by multiplying the contribution to the width from the radial distortions by the factor $\sqrt{3}$.

Both explanations of the band width seem to be valid. Consequently, we would like to combine their separate contributions to obtain the total band width. Since they appear to be independent, and assuming, for simplicity, that each gives rise to a Gaussian shape, we must add them as the square root of the sum of the squares of the individual widths.

To be specific, we consider a very simple calculation for the local deformation width. The coupling in this case is to the acoustical modes of the lattice. From the Einstein formula for fluctuations, we may write for the mean square fluctuation in the volume around the *F* center:

$$\langle(V-V_0)^2\rangle=V_0\chi_{\mathrm{eff}}kT, \tag{9}$$

where V_0 is the equilibrium value of this volume, χ_{eff} is the effective compressibility around the *F* center, and kT is the Boltzmann constant times the absolute temperature. This expression assumes that the temperature is sufficiently high that equipartition of energy has occurred. This formula gives values differing by only a few percent from a more rigorous formula containing a Debye function and the zero-point energy explicitly. The corresponding fluctuation in the F-center energy is obtained from a Taylor expansion about its mean value. We next consider that the volume is a sphere of radius R, that the effective compressibility χ_{eff} is greater than the bulk compressibility χ_0 by the factor f, that the shear modes are accounted for by the simple factor $\sqrt{3}$, and that the conversion factor from root mean square to width at half-maximum is that for a Gaussian shape. Thus we obtain for γ_2, the deformation width:

$$\gamma_2 = E n_Q[(2\ln 2) f \chi_0 kT/\pi R^3]^{\frac{1}{2}}. \tag{10}$$

For KCl at room temperature, using $n_Q = 1.6$, a calculation from Eq. (10) gives $\gamma_2 = 0.20 f^{\frac{1}{2}}$ ev.

We are now able to combine γ_1 and γ_2. For KCl under the same conditions, Eq. (8) gives $\gamma_1 = 0.088 S^{\frac{1}{2}}$ ev, where S is still undetermined. One possible procedure is to fit these results to the observed total band width, γ, after choosing a suitable value of f, say 2. This produces an estimate of S such that $S = 5.4$. If we had ascribed the full width to the interaction with optical lattice vibrations, with Huang and Rhys, the value of S required would be 16 for KCl. On the other hand, Huang and Rhys estimate from Simpson's wave functions for NaCl that S should be about 4. Thus our simple model for the deformation width, using a value for f consistent with the pressure shift data, enables us to make a reasonable estimate of the parameter S in the Huang-Rhys contribution to the width.

The preceding discussion of the theories of the width of the F band serves principally to illustrate that there is considerable room for a careful theoretical analysis of the problem.

Of particular interest in the present research is the fact that the observed F-band width did not change with pressure for most of the compounds studied. Using the various expressions for the width, either separately or in suitable combination, it may be predicted that the width should increase about 1 or 2 percent in 5000 atmospheres. In view of the uncertainties described in measuring the width, such an increase could not be detected.

V. DISCUSSION

Several points in the preceding section require further consideration. It is not difficult to understand why the term $f_T = (\partial \ln R/\partial \ln a)_T$, in Eq. (2), may be greater than unity.[21] R represents a measure of the radius of a spherical cavity from which matter has been removed, i.e., a halogen ion, while a is the normal interionic distance in the crystal at a great distance from the cavity. The ion which previously occupied this region exerted a repulsive force on the surrounding material. The electron which replaces the negative ion does not exert this repulsion in a first approximation. Thus when the crystal is subjected to an external pressure, it is natural to expect that the cavity will contract more when it is empty than when it is occupied by matter. This line of reasoning suggests that it may be fruitful to consider the crystal as a continuous elastic medium. From this point of view the problem at hand reduces to the simple calculation of the radial strain in a shell bounded by concentric spherical surfaces. The solution of this problem provides an independent estimate of $f_T \approx f$. The details may be obtained from any standard textbook on elasticity, e.g., Love.[49] The radius of the internal sphere is R and the internal pressure is taken to be zero. We let the radius of the external sphere become infinite and equate the pressure on its surface to the pressure applied externally to the crystal. Thus we obtain:

$$(\Delta R/R)/(\Delta a/a) = (\partial \ln R/\partial \ln a)_T = 1 + (3K/4\mu), \tag{11}$$

where the crystal is treated as an isotropic body describable by two elastic constants: K, the bulk modulus, and μ, the shear modulus. The ratio (K/μ) may be calculated from the experimental data,[32] using an average of the two shear moduli c_{44} and $\frac{1}{2}(c_{11} - c_{12})$ for μ. An alternate way to obtain this ratio is to assume that Poisson's ratio is $\frac{1}{4}$ for these crystals, from which we can readily find $(K/\mu) = (5/3)$. In this approximation the result is $f = 2.25$, while the values obtained from the experimental data range from about 2.13 to 2.25. The results of this independent estimate of f are in approximate agreement with those obtained from the pressure-temperature shift theory in the preceding section.

From another point of view we may expect that f should be smaller for CsCl since it has a more closely packed structure than the other compounds. The ions may be treated as hard spheres and the distance that the nearest neighbors can move toward the center of the vacancy without coming into contact may be calculated for the two structures involved. Thus for Cs and Cl ions it is found that they may move nearly twice as far when arrayed in the NaCl structure as when in the CsCl structure. This is a very crude approach, but it does serve to indicate why the f values for CsCl may be lower, as found in Table III.

We now consider in further detail the various ways of estimating the quantity n_Q which appears throughout the theory of the pressure and temperature shift. It was emphasized earlier that the values calculated for f from the theory depend on the values used for this quantity. If some model for the F center is assumed for which the energy levels can be calculated, then n_Q may be computed readily. The various continuum models that have been used lend themselves to an easy calculation of this term. Before adopting the square well model described in the preceding section, calcula-

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[49] A. E. H. Love, *The Mathematical Theory of Elasticity* (Cambridge University Press, Cambridge, 1927), p. 142.

tions were made with Simpson's[8] model using the revised potential well depth suggested by Krumhansl and Schwartz,[11] and with Pincherle's[10] model which simplifies the calculations of the Simpson model. In the Pincherle calculation the potential well has a flat bottom out to a radius R and has a simple or slightly modified Coulomb dependence at large distance. In our calculation with this model the well depth was chosen so as to reproduce the experimentally observed energy difference between the two states, as was done in the square well model. In obtaining n_Q, the well depth was assumed to vary inversely with the radius R, again as in the square well model. This assumption is certainly a reasonable one, for the principal contribution to the depth is the Madelung energy which is controlled mainly by the distance to the nearest neighbors, and the secondary contribution is the energy of polarization of the surroundings, which is inversely proportional to the well radius. The result of this calculation for NaCl is $n_Q=1.53$ when the static and high-frequency dielectric constants are held fixed, and 1.50 when they are allowed to vary with pressure. An earlier calculation with Simpson's model with more restricted conditions gave a result of about 1.3. The similarity of these results led to the adoption of the square well model which is the easiest to handle numerically. For the present experiment, involving a relatively large scale effect, it is felt that the continuum represents a suitable approximation with which to treat the problem.

Recent evidence, noted in Sec. I, has pointed to the importance of the molecular orbital model of the F center. This model has found its greatest success in explaining hyperfine interactions in electron spin resonance experiments. The only quantitative calculation[9] of F-center energy levels with this model is not presented in a way which may be readily adapted to the type of calculation just described. It will be seen below, however, that certain conclusions may be drawn from that work.

The alternative to calculating n_Q from a specific model is to obtain it from a plot of experimental data, as mentioned in Sec. IV. We then replace n_Q by n_M in Eqs. (4) and (6). Assuming that a straight line may be drawn through the points on a $\log_{10}E$ *versus* $\log_{10}a$ plot, we might be tempted to adopt Ivey's value for its slope, namely $n_M=1.84$. If the data is plotted corresponding to the Debye temperature for each compound, we find that a better straight line may be drawn for which $n_M=1.6$. Actually, the notion of a straight line on such a plot is more fiction than fact. Plotting the data for the chloride, bromide, and iodide of sodium, potassium, and rubidium, with $\log_{10}E$ and $\log_{10}a$ as ordinates, we find that curves (not straight lines!) having approximately the same shapes may be drawn through the points with a common cation. Without knowing the exact shape of these curves, defined by only three points, some sort of compromise must be adopted to estimate the values of n_M, which change from compound to compound. It would be desirable to find a suitable choice of ordinates on which a straight line could be drawn with some reliability. In attempting to do this, it was found that a plot of $\log_{10}E$ *versus* a^{-1} produces a line which is at least as good as the $\log_{10}E$ *versus* $\log_{10}a$ "straight line." Evaluating the n_M parameters from this plot gives a variation from compound to compound in the same direction as found with the curves above. Considering all these alternatives, it is important to note that they do not differ significantly from one another in the results that they give. Also, these results are not particularly different from those found with the various models. To show approximately how these alternatives vary, we have tabulated values of n_M and f in columns 8 and 9 of Table III as obtained from the plot of $\log_{10}E$ *versus* a^{-1}.

An additional observation may be made in connection with the graphical way of estimating $n_M \approx n_Q$. We may plot the results of the molecular orbital calculation of Inui and Uemura on a $\log_{10}E$ *versus* $\log_{10}a$ graph. Using their model IV with a potential due to 26 neighboring ions, the data for LiCl, LiBr, and LiI fall on a rather good straight line with $n_M=1.43$. This bit of evidence, in general agreement with what has gone before, may be taken as support for our contention that no startling deviation is to be expected from the molecular orbital model, and that the continuum model is a useful approximation for this experiment.

By introducing the factor f, and making use of the lattice interaction constant b, we are able to develop a reasonably consistent account of the behavior of F-center absorption as a function of pressure and temperature. The factor f, as derived in the theory, is in satisfactory agreement with an estimate of its value from elasticity theory. Also, it is used in a simple theory of the band width, which combines the two proposed mechanisms of broadening, in such a way as to give a reasonable value for the number of vibrational quanta involved in broadening by interaction with optical lattice vibrations. The coupling constant b/Θ does not vary too greatly, if we exclude the sodium salts and CsCl. As used by Huang and Rhys and others, it would appear that negative values for b/Θ are inadmissible theoretically. Also, since the errors almost overlap in the case of NaCl, there is no strong experimental evidence that these values are negative. Thus, we say $b/\Theta \sim 0$ for NaCl, when small negative values would result from the calculation. Perhaps some experimental uncertainty, unknown to us, may account for the discrepancy. Another possibility is that the theory has not included some term which, although it may be small, may be sufficient to account for the different behavior of NaCl and NaBr in contrast to the other compounds. The term in b appears to be the only satisfactory suggestion, thus far offered, which is capable of treating the difference in the pressure and temperature shifts. In the Huang and Rhys approximation this term involves only the optical lattice vibrations. It is possible that future investigation will reveal that a similar contribution involving the acoustical lattice vibrations must be taken into account. In any case, however, such a term would not affect the qualitative conclusions which are made above, but would affect their quantitative interpretation.

VI. ACKNOWLEDGMENTS

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The Superconductivity of Some Transition Metal Compounds*

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About eighty transition metal compounds comprising borides, carbides, nitrides, oxides, silicides, and germanides of metals of Groups 4A, 5A, and 6A were tested for superconductivity down to 1.20°K, using a magnetic method. Among the specimens were most of the known compounds of the above type not examined magnetically for superconducting behavior by previous workers, and in all cases the structures were checked by x-ray diffraction analysis. The following eleven new superconductors were discovered, with the transition temperatures (°K) shown in parentheses: W_2B (3.10°), Nb_2C (9.18°), Ta_2C (3.26°), Nb_4N_3 (7.2°), V_3Si (17.1°), V_3Ge (6.01°), Mo_3Si (1.30°), Mo_3Ge (1.43°), α-$ThSi_2$ (3.16°), β-$ThSi_2$ (2.41°), and W_3Si_2 (2.84°). These compounds include the first superconducting germanides, V_3Ge and Mo_3Ge, which, together with V_3Si and Mo_3Si, crystallize in the cubic β-tungsten structure. The transition temperature of V_3Si is apparently the highest known for any binary superconducting compound.

I. INTRODUCTION

It is well known that there exists a group of compounds of transition metals with nonmetals, typified by the borides, carbides, and nitrides of "A group" transition metals, which possess most of the properties of metals or alloys. These compounds show metallic luster and have thermal and electrical resistivities of the same order of magnitude as those for pure metals, together with a positive temperature coefficient of electrical resistivity. In many cases they are known to have high hardness values, high moduli of elasticity, high melting points, and relatively high strengths at elevated temperatures, properties which cause them to be of considerable technological importance.[1] At the time of the first extensive crystal structure determinations for these substances, carried out by Hägg,[2] it seemed appropriate to call them "interstitial" compounds, implying that the nonmetal atoms merely fit into interstices in the metallic lattice, thereby slightly modifying the properties of the pure metal. More recent investigations have shown that for borides the interstitial picture is inadequate owing to the tendency of the boron to form chains, nets, and three-dimensional networks,[3] while even for carbides and nitrides it is the exception rather than the rule for the lattice of metal atoms in the compound to be identical with the lattice of the pure metal.[4]

Among the typically metallic properties of transition metal compounds one may include the fact that many become superconducting at temperatures of a few degrees absolute. This behavior was first discovered during the extensive investigations of Meissner and his co-workers over twenty years ago.[5–7] Unfortunately, Meissner's results were obtained using electrical resistance measurements, which have since been shown to yield unreliable results with impure specimens. The

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[1] The term "hard metals" is often applied to this whole group of materials. See P. Schwarzkopf and R. Kieffer, *Refractory Hard Metals* (Macmillan Company, New York, 1953).

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