Some Properties of F and F-Aggregate Centers in Cesium Halides*

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(Received 12 February 1965)

Measurements of the absorption spectrum of F centers in CsI reveal structure similar to that of the F band in CsBr. Bands like the L bands in other alkali halides have been observed in CsBr and CsI. In CsBr these L bands exhibit structure similar to that of the CsBr F band. The emission of F centers in CsCl, CsBr, and CsI has been measured. The emission spectra are double Gaussian, peaking at 1.255, 0.910, and 0.740 eV in CsCl, CsBr, and CsI, respectively. The full widths at half-maximum are 0.245, 0.184, and 0.140 eV, respectively. The emission in CsBr is excited with constant quantum efficiency in all parts of the F band. The lack of structure in the emission bands can be explained by either of two descriptions of the excited F center after relaxation of the lattice has occurred. Dichroism of the M band in CsBr indicates these centers have $\langle 100 \rangle$ transition-dipole axes as expected for the van Doorn–Haven model of the M center. Other M-center transitions lie under the long-wavelength part of the F band. A large number of F-aggregate bands have been found.

I. INTRODUCTION

THE F band in cesium halides exhibits a characteristic structure at low temperatures.[1,2] Because the structure occurs in CsF,[2] which crystallizes in the NaCl structure, as well as in the three body-centered cesium halides, the structure can be attributed to the cesium ions, not to the crystal structure.[4]

A first attempt[5] to relate the F-band structure to the spin-orbit splitting of the cesium atom, the wave functions of which are used for the F-center electron, gave too small a calculated splitting. More recently Knox[6] has shown how the spin-orbit splitting of the cesium $6p$ levels could give rise to several conduction bands. From the split conduction bands he formed F-center states by the effective-mass approximation. There were three "ground" states with $1s$ wave-function envelopes, built from Γ_6^+, Γ_6^-, and Γ_8^- conduction-band functions. The former presumably lies lowest and the other two "ground"-state levels are sufficiently higher in energy that they are unoccupied at 300°K. The pertinent excited states were $2p\Gamma_6^+$, $2s\Gamma_6^-$, and $2s\Gamma_8^-$, all of which can be reached from the $1s\Gamma_6^+$ state by electric-dipole transitions. With this model there should be absorption at long wavelengths from $1s\Gamma_6^+$ to the other two "ground" states, and a structure in emission from $2p\Gamma_6^+$ to all three "ground" states. Knox also suggested that in other alkali halides the L bands[7,8] could arise from the levels that give the F band its structure in the cesium halides.

In the following we present absorption and emission data on CsI and CsBr crystals containing F centers. No structure is evident in the emission spectra. In addi-

tion, F-center emission in CsCl has been observed. We show that L bands are present in CsBr and CsI which are similar to those of other alkali halides except that they exhibit structure in CsBr. We have looked for the $1s\Gamma_6^+$-$1s\Gamma_6^-$ and $1s\Gamma_6^+$-$1s\Gamma_8^-$ transitions in the 1–35 μ region and found none.

Henry, Schnatterly, and Slichter,[9] and Moran,[10] have explained the splitting of the cesium-halide F band by using a more appropriate localized F-center electron. The splitting arises primarily from spin-orbit effects on the nearest cesium and halogen ions, as shown by Smith,[11] and also from the interaction of the F-center electron with noncubic (tetragonal) vibrational modes. Moran[10] has shown how these interactions explain not only the splittings observed in the F bands of the four cesium halides, but also changes in oscillator strengths caused by magnetic fields, observed in recent magneto-optical experiments.[12,13] In the model used in Refs. 9 and 10 there are only three transitions expected in the main absorption band, not five as in Ref. 6. The F-center luminescence spectra in CsBr and CsI also are in accord with the usual localized model for F centers.

We also present evidence that the M center in CsBr is indeed the F_2 center van Doorn and Haven[14] proposed for the other alkali halides. M-center absorption and emission in CsBr is described. A number of F-aggregate absorption bands have been found.

II. EXPERIMENTAL

Harshaw or Korth crystals were additively colored with Cs or K metal. Prior to measurements they were heated to 500°C for 1 min, then quenched on a copper block. They were exposed only to light outside the F

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[8] C. C. Klick and M. N. Kabler, Phys. Rev. 131, 1075 (1963).

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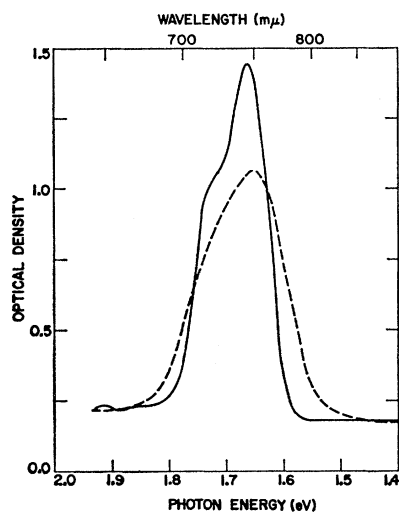[14] C. Z. Van Doorn and Y. Haven, Philips Res. Rept. 11, 479 (1956).

FIG. 1. *F* band in CsI. Solid line, 13°K; dotted line, 78°K.

FIG. 3. *F*-center luminescence spectra in CsBr: A, 21°K; B, 48°K; C, 58°K; D, 70°K.

band (Corning 5-58 filter) except for the light used for measurements. When they were at 15°K, room light was allowed on the crystals. Most absorption measurements were made with a Beckman DU spectrophotometer. Some later measurements were made with a Cary 14R spectrophotometer.

Luminescence was excited by a 1-kW tungsten lamp filtered through 5 cm of a 2% CuSO₄ solution, and Schott OG-1 and KG-3 filters. Luminescence was analyzed with a Bausch and Lomb grating monochromator, Schott UG-8 filter and PbS photodetector. Corrections for the relative spectral response of the detection system were applied to the data. These corrections were determined by using the analyzing system to measure the known spectral distribution of radiation from a tungsten-ribbon filament lamp at a known temperature.
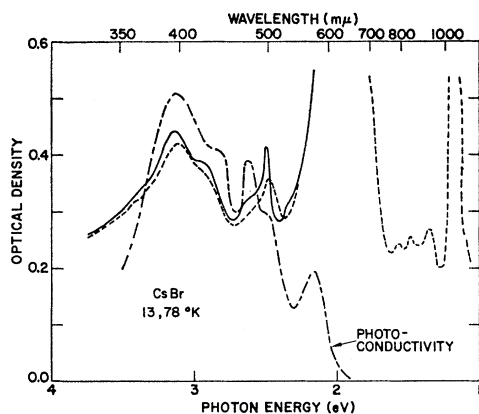

FIG. 2. Absorption in additively colored CsBr. Solid line, 13°K; dotted line, 78°K; dot-dash line, photoconductive response at 4.2°K (Ref. 17). At 78°K the *F* band (∼2 eV) peak has an optical density of ∼3. At 13°K the peaks in absorption to the left of the *F* band occur at 2.50, 2.62, ∼2.90, 3.12, ∼3.35, and ∼3.6 eV.

15 R. Berman and D. J. Huntley, Cryogenics **3**, 70 (1963).
16 D. K. Finnemore, J. E. Ostenson, and T. F. D. Stromberg, U. S. Atomic Energy Commission Report IS-1046, 1964 (unpublished).
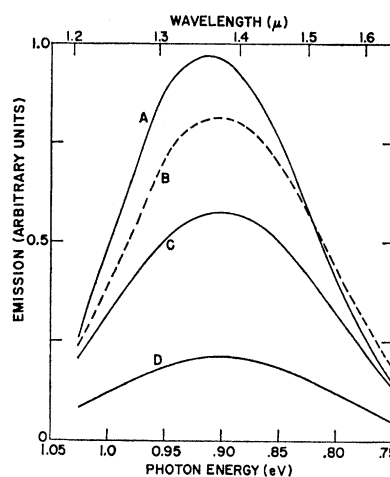
Excitation curves were obtained by setting the analyzing monochromator at the emission peak with 6-mm slits and exciting with a second, similar monochromator using a KG-3 filter and the Cu₂SO₄ solution. This was adequate for exciting in the *F*-band region but too much scattered exciting light was detected to allow excitation in the *M* bands. The relative spectral distribution of the exciting light was measured with a radiation thermocouple and the appropriate corrections applied.

Temperatures were measured with a gold (0.03% iron) versus copper thermocouple.[15,16]

III. RESULTS

1. *F* Band in CsI

Figure 1 shows the *F* band in CsI at 78 and 13°K. The peaks are at 1.655 and 1.665 eV at 78 and 13°K, respectively. The integrated area of the *F* band changes less than 2% upon cooling from 78 to 13°K, and this change could result from errors in assigning baselines. The hint of structure at 78°K changes to easily apparent structure at 13°K. The 13°K *F* band can be decomposed into two sub-bands by the method used by Rabin and Schulman.[1] These bands peak at 1.660 and 1.728 eV and have relative areas of about 2:1 (1.84:1 in this case). Their widths are 0.072 and 0.060 eV, respectively. There is some residual absorption at energies higher than 1.74 eV but its integrated area is less than ⅓th of the smaller of the two main *F*-band components. The relative areas of the two *F*-band components in CsI are about the same as those for CsBr.[1,2]

2. *L* Bands in CsBr and CsI

Figure 2 shows the absorption spectrum of a densely colored crystal of CsBr at 78 and 13°K, as well as the results of photoconductivity measurements of Ishii and Ueta.[17] It is too difficult to fix a baseline so that oscil-

17 T. Ishii and M. Ueta, J. Phys. Soc. Japan **18**, 1460 (1963).

lator strengths relative to that of the F band cannot be obtained. The bands on the high-energy side of the F band decrease when the F band is bleached and exhibit the same photoconductive behavior as the L bands in other alkali halides.[18-20] It seems reasonable to call them L bands too. The K band is not well resolved, but probably is the structure at 2.08 eV reported previously[1] as potentially part of the F band. There is another absorption component in the region 2.3–2.4 eV. Some of the L bands were also reported previously,[1,2,21] but their origin was unknown.

The structure in the L_1 band (2.50 and 2.62 eV at 13°K) is clear. The high-energy component has the lower height, as in the F band. (Note the reversal in relative heights in the photoconductive response curve.) The L_1 band complex does not seem to exhibit the temperature-dependent area reported for the L_1 band in rubidium halides,[7] nor is its temperature shift unlike that of the F band. However, upon warming from 4 to 78°K, the L_1-band photoresponse grows with respect to the L_2-L_3-band photoresponse,[17] despite no obvious relative changes in absorption areas. The increase in L_1-band area with increasing temperature observed for some alkali halides has been attributed by Wood[22] to the mixing of two nearly degenerate electronic levels by lattice vibrations, but Wood's calculation was for the NaCl structure and may not pertain in detail to CsBr. The L_2 and L_3 bands overlap, but at least four sub-bands are discernible at ~2.90, 3.12, ~3.35, and ~3.6 eV, the latter not being evident in Fig. 2, but showing on the original recorder traces.

In CsI there is an L_1 band at 2.23 eV and an L_3 band at 2.94 eV (78°K). In between these two is a region of structureless absorption. At 78°K there is no evidence of structure in either the L_1 or L_3 band.

FIG. 5. Relative CsBr F-center emission efficiency versus temperature. The ordinate is the integrated area of the emission spectrum (Fig. 3) at temperature T divided by the area of the spectrum at 13°K.

3. F-Center Luminescence in CsBr

Figure 3 shows the F-band luminescence in CsBr as a function of temperature. The excitation spectrum for this luminescence is shown in Fig. 4. All parts of the F band excite emission with the same efficiency, for the excitation curve follows the absorption curve. The integrated areas of the emission curves are shown in Fig. 5 as a function of temperature. Following Swank and Brown,[20] this can be fit to an expression of the form [area (T)/area (0)]$=[1+A$ exp$(-\Delta E/kT)]^{-1}$. ΔE represents an energy for thermal ionization of an excited F center while A is a ratio of two characteristic times. The F luminescence in CsBr is fit by $A=4.5\times10^3$, $\Delta E=0.045$ eV, the latter in good agreement with data of Spinolo.[23] The emission curve is approximately double Gaussian (see Fig. 6) and the half-width is shown in Fig. 7.
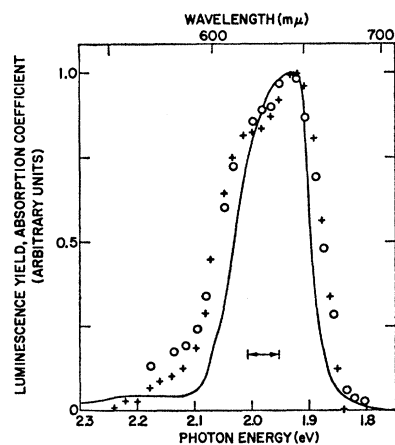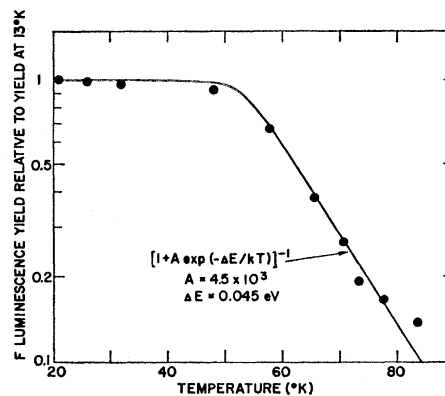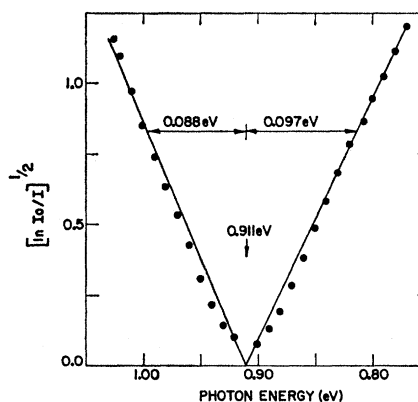

FIG. 4. Excitation spectrum for F-center luminescence in CsBr at 13°K (circles and crosses). The ordinate is emitted intensity per photon incident on the crystal. The spectral bandpass used for excitation is shown. The solid line is the absorption spectrum.

FIG. 6. $[\ln I_0/\ln I]^{1/2}$ versus photon energy for F-center luminescence in CsBr at 13°K. I_0 is the peak emission intensity and I is the emission intensity at any photon energy. If the emission is Gaussian a symmetric V should result. The skewed V is indicative of a different width for the Gaussian on each side of the maximum. The departure of the points from the V near the emission maximum is believed to be real.

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[19] R. L. Wild and F. C. Brown, Phys. Rev. **121**, 1296 (1961).
[20] R. K. Swank and F. C. Brown, Phys. Rev. **130**, 34 (1963).
[21] P. Avakian and A. Smakula, Phys. Rev. **120**, 2007 (1960).
[22] R. F. Wood, Phys. Rev. Letters **11**, 202 (1963).
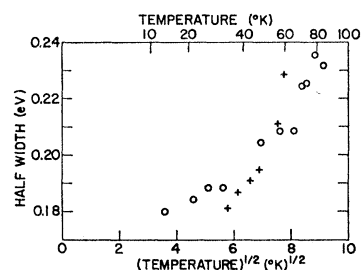
[23] G. Spinolo, Phys. Rev. **137**, A1495 (1965).

FIG. 7. Full width at half-maximum of the CsBr F-center emission versus (temperature)$^{1/2}$. The results of two runs are plotted. Because of the scale the scatter appears exaggerated. The standard deviation of the points from a smooth curve drawn arbitrarily through them is less than 0.006 eV.

4. F-Center Luminescence in CsI

Figure 8 shows the luminescence of CsI containing F centers. We assume this peak is F-center luminescence from the temperature dependence of the area and because it is excited by light in the region of the F band. Very little M absorption (assumed to be the peak at 1185 mμ[21]) was present. The integrated-area-versus-temperature curve fits closely the above-mentioned expression with $A = 7 \times 10^5$ and $\Delta E = 0.052$ eV. The shape is double Gaussian. The half-width at 14°K is 0.140 eV and tends to increase with temperature until the intensity is low and the band seems to split into two peaks. The two bands present at about 50°K are not understood. They may arise from new centers produced by bleaching the F band. These two emission peaks disappear at about 78°K. A notable feature of the F emission in CsI is the lack of temperature dependence of the energy of peak emission.

5. F-Center Luminescence in CsCl

A crystal of Semi-Elements, Inc., CsCl was x rayed at 78°K, then cooled to 15°K. Excitation in the region of its F band[1,21] produced an emission peak of width 0.24 eV centered at 1.255 eV. This peak diminished when irradiated at 15°K with F-band light, indicating optical bleaching of the F centers at this temperature. Upon warming to 78°K the 1.255-eV peak disappeared, being replaced by a strong emission peak at 1.00 eV and very weak peaks at 1.22 and 1.30 eV. No optical-absorption measurements could be made on this crystal.

6. Infrared F-Center Transitions

The model of Ref. 6 predicts two allowed transitions at wavelengths longer than the F band. We found no such transitions in either colored CsBr or colored CsI at 90°K in the region from 1 to 35 μ. Since the $1s\Gamma_6^-$ and $1s\Gamma_8^-$ levels, if present, are unpopulated at room temperature, they lie at least 0.05 eV above the $1s\Gamma_6^+$ level. Optical transitions would thus be expected at an energy greater than about 0.05 eV, or $\lambda < 25$ μ.

7. M-Band Dichroism in CsBr

A crystal with a (100) face was used. M-band (1045 mμ at 78°K) dichroism could be produced either by bleaching the F band with [010] or [001] polarized light at 190°K to form M centers, or by bleaching the M band at 190°K with [010] or [001] light. Polarized M light had no effect at 78°K where M centers do not bleach, and polarized F light at 78°K gives an F' band, not an M band.

Either [010] or [001] light gives a dichroic M band (Fig. 9), but [011] light does not, indicating that the M centers have their transition dipole parallel to $\langle 100 \rangle$ directions, not $\langle 110 \rangle$ or $\langle 111 \rangle$. $\langle 100 \rangle$ M-center axes are expected for the van Doorn—Haven model of the M band[14] in the CsBr lattice. The M dichroism is not permanent at 190°K in the dark. The weak component of the dichroic M band grows at the expense of the strong component, apparently from reorientation of the centers.

As can be seen in Fig. 9 there is dichroism in the low-energy side of the F band. This dichroism peaks at 1.86 eV and is proportional to the M-band dichroism, but of opposite sign. It probably arises from transitions to higher excited states of M centers.[24-26] The area in the region of the F band in Fig. 9 due to such M-center transitions is 1.6 times the area of the M band dichroism. A band at 1.80 eV that forms upon F bleaching is not dichroic when the M band is, nor are any of the bands between the F and M.

8. M- and "R"-Center Luminescence in CsBr

A colored CsBr crystal which had been bleached with F light at 190°K to produce M centers exhibited a complex emission spectrum at 90°K. There was no F center emission (0.90 eV peak), but there were two strong peaks at 0.975 and 0.775 eV, and a weak one at 0.85
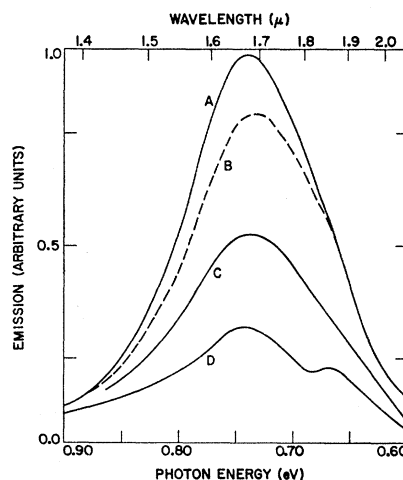

FIG. 8. F-center luminescence spectra in CsI: A, 13°K; B, 34°K; C, 44°K; D, 49°K.

[24] C. Z. Van Doorn and Y. Haven, Phys. Rev. 100, 753 (1955).
[25] H. Kanzaki, Phys. Rev. 110, 1063 (1958).
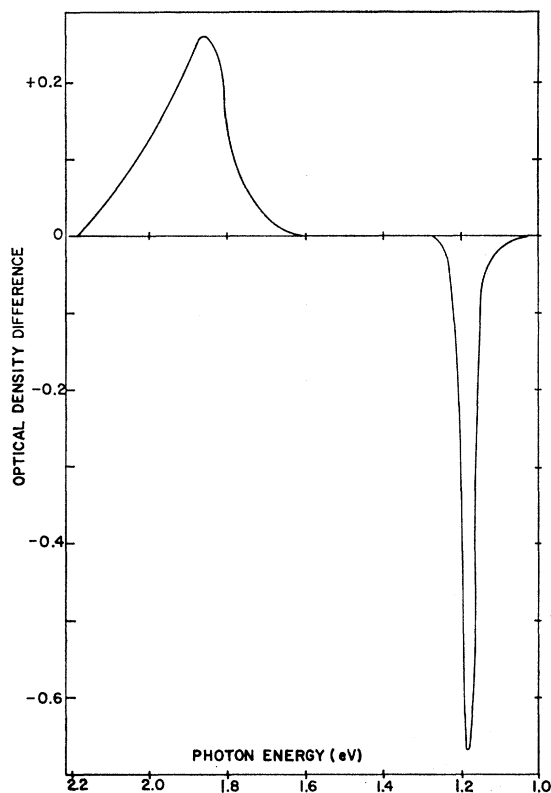[26] F. Okamoto, Phys. Rev. 124, 1090 (1961).

FIG. 9. Anisotropy in CsBr M and F bands after polarized bleach of the M band at 190°K. The ordinate is the optical density measured with the electric vector parallel to that used to bleach the M band, [010], minus the optical density with the electric vector perpendicular to that of the bleaching light, [001]. (Measurements at 78°K.)

eV. Bleaching with M light at 190°K caused the 0.975-eV emission peak to decrease slightly while the 0.775-eV peak grew a bit. The 0.85-eV peak was too weak to study. None of the above three peaks shifted upon cooling to 13°K. In another crystal bleached less heavily with F light prior to emission measurements the 0.85-eV emission was more prominent. It peaked at 0.849 eV and had a half-width of 0.090 eV (78°K). This crystal contained more M centers and fewer other aggregate centers (Sec. 10) than the previous crystal.

All of these emission spectra were obtained with excitation in the region of the F band. When the exciting light was polarized parallel to [010] in a crystal with a (100) face, the 0.975 eV emission was unpolarized while the 0.85 eV emission was almost completely polarized parallel to [001]. (The 0.755-eV band was not examined.)

Several excitation curves were run for the emission at 78°K (Fig. 10). The emission observed was a mixture of both 0.957- and 0.85-eV peaks. The excitation curve peaks at 1.86 eV, where the M centers appear to have a second transition (Sec. 7 above). This peak also corresponds to a photoconductivity peak found in crystals bleached with F light at 78°K.[17]

From its excitation spectrum and polarization characteristics, the 0.849-eV peak can be ascribed to M centers. The aggregate centers are probably responsible for the peaks at 0.975 and 0.775 eV.

9. F-M Equilibrium

An attempt was made to study the thermal equilibrium between F centers and M centers.[27] CsBr was additively colored at 500°C with potassium by the method of van Doorn.[28] The crystals were quenched to room temperature in less than 3 sec and the heights of the F and M bands measured. If the reaction $F + F \rightleftarrows M$ occurs and thermal equilibrium has been quenched in, the height of the M band should be proportional to the square of the height of the F band. In fact a linear relation, not the expected quadratic relation, was found. Van Doorn[27] takes this to indicate a quench insufficiently rapid to retain equilibrium and this is known to be the case here, for allowing the crystal to cool more slowly (up to 20 m) gave points on the same curve. Attempts to repeat the experiment by coloring at 450° were not successful.

Mascarenhas and Rabin have x rayed CsBr at ~190°K and found the resultant M-center concentration proportional to the first power of the F-center concentration,[29] while a quadratic dependence is again expected. This result may arise from the large nonuniformity of coloration in CsBr due to the large x-ray absorption coefficient.[30]
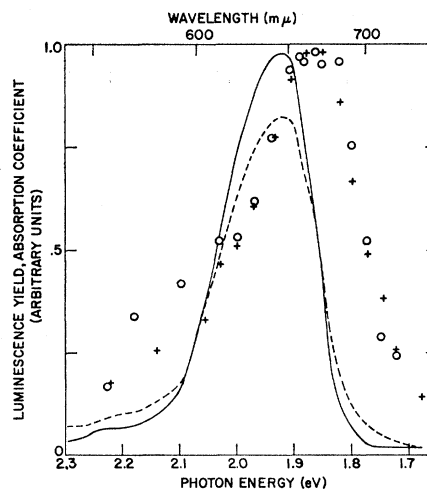

FIG. 10. Excitation spectrum for M-center luminescence in CsBr at 78°K. Circles and crosses, excitation spectrum (same ordinate as in Fig. 4); solid line, absorption spectrum at 78°K with no M centers present; dotted line, absorption spectrum at 78°K after bleach at 200°K with F light to produce M centers.

[27] C. Z. Van Doorn, Phys. Rev. Letters 4, 236 (1960).
[28] C. Z. Van Doorn, Rev. Sci. Instr. 32, 755 (1961).
[29] S. Mascarenhas and H. Rabin (private communication).
[30] S. Mascarenhas, H. Rabin, and V. B. Sverzut, Phys. Status Solidi 7, 1039 (1964).
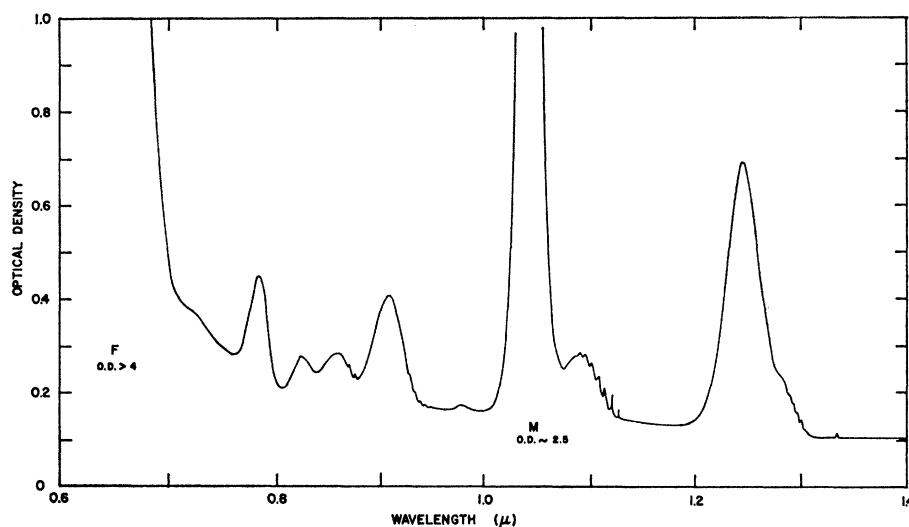
Fig. 11. Absorption spectrum at 15°K of a heavily colored CsBr crystal that had been bleached with F light at 190°K to develop F-aggregate bands.

10. Other F-Aggregate Bands in CsBr

Figure 11 shows the absorption spectrum of a heavily colored crystal that had been bleached with F light at 190°K. The measurements were made at 15°K. The bands are the F, the M, and probably F-aggregate bands.[31] At 15°K, the latter are at 720, 786, 825, 858, 908, 975, 1090, and 1246 mμ, the last having two shoulders on its long-wavelength side. There is also a shoulder on the F band at about 688 mμ. (The fine structure in the aggregate bands will be the subject of a future publication.) The band at 1090 mμ appears as an unresolved tail on the M band at higher tempera-
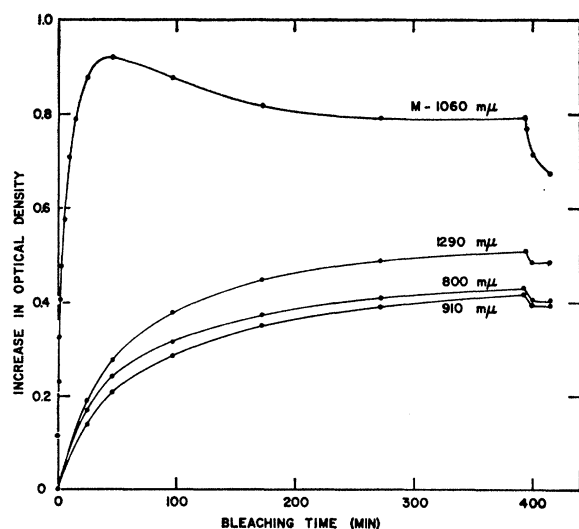

Fig. 12. Height of CsBr M band and three aggregate bands at 190°K as a function of the time exposed to F-band light. At 394 min, the F light was replaced by M-band light. An M band was present initially. The initial F band had an optical density of about 4.

[31] H. Pick, Physik 159, 69 (1960) and references therein.

tures. Figure 12 indicates how these bands grow upon F irradiation at 190°K. As expected, the M grows first then decays. The bands at 800, 910, 1290 mμ grow more slowly and seem to grow together. (These are at 786, 908, and 1246 mμ at 15°K.) The other aggregate bands, in Fig. 11, are not resolved at 190°K. Upon irradiating with M light the M band dropped sharply while the 800, 910, and 1290 mμ bands dropped a little and then leveled off. None of the bands in Fig. 11, except the M and F, bleach optically at 190°K. Upon warming to room temperature in the dark, they all disappear, including most of the M band, leaving only an F and a small M band. They can be formed temporarily by bleaching the F band at room temperature, and are found to be resistant to optical bleach at room temperature.[32-34]

IV. DISCUSSION

Moran,[10] and Henry, Schnatterly, and Slichter[9] have explained the shape of the F band in cesium halides. Their tight-binding model adequately describes the absorption-spectrum shape. The effective-mass approximation used by Knox[6] apparently is not appropriate here. If one assigns splittings to the conduction bands according to Ref. 6 to fit experiment and assumes "ground-state" splittings of the same order of magnitude, then infrared absorption probably should occur, and structure in emission should be observed. Neither

[32] In an attempt to see whether the K' band in CsBr found by Drickamer et al., (Refs. 33, 34) could be due to plastic deformation, a CsBr crystal containing only an F band was plastically deformed 9.5% in the dark at room temperature. The result was no F band (or K'), but a broad colloid band and a large band at 910 mμ (90°K), one of the bands of Figs. 11 and 12. The K' band lies at a photoconductivity peak seen by Ishii and Ueta[17] and probably corresponds to the K band in other alkali halides.
[33] W. G. Maisch and H. G. Drickamer, J. Phys. Chem. Solids 5, 328 (1958).
[34] R. A. Eppler and H. G. Drickamer, J. Chem. Phys. 32, 1418 (1960).

were detected in the present work. A change in symmetry of several states would make such transitions unallowed, but then the structure in the F band might vanish too.

The L bands correspond to transitions to higher excited states of the F center. The small oscillator strengths are expected because of the large extent of these states. Note that L-band splittings in CsBr are about the same as the F-band splitting. The origin of the splitting appears to be spin-orbit effects and interaction with noncubic localized-lattice modes, both of which should decrease as the final state becomes more diffuse. It would appear that the higher excited states are still fairly well localized.

The structureless aspect of the CsBr F-center emission can be explained several ways. If, upon relaxation of the lattice prior to emission, the F-center "$2p$" levels remain split by spin-orbit interaction and/or by static-ionic displacements, only the lowest state will be populated at low temperatures. (There should be ample time and energy for an excited F center to come to thermal equilibrium before emission.) Then only a single emission component will be seen. At 78°K, where the emission is nearly thermally quenched, the possible occurrence of a second emission component due to higher "$2p$" levels could not be seen. On the other hand, if the excited F-center electron spreads out before emission to the extent suggested by Fowler,[35] one can expect spin-orbit effects to be negligible and the electron to interact with longitudinal-optic (LO) lattice modes rather than localized modes. In this case the "$2p$" functions become degenerate again and only one emission band will occur.

Spinolo[23] has shown that if Fowler's delocalized-excited state occurs before emission, the energy for optical ionization of the excited F center can be calculated in the effective-mass approximation. If this is close to the thermal-ionization energy ΔE, then $\Delta E \propto m^* \epsilon_0^{-2}$ where ϵ_0 is the static-dielectric constant. m^* seems to be constant for all alkali halides, for a plot of ΔE versus ϵ_0^{-2} is a fairly good straight line.[23] Our ΔE values for CsBr and CsI fall close to Spinolo's line. For CsCl a value of $\Delta E \sim 0.015$ eV is predicted. This is much smaller than for the other alkali halides and is in accord with our observation that the F band bleaches optically at 15°K. (This crystal was x rayed, and thus contained trapped holes. However, the exciting light was confined to the region 550–700 mμ, a region in which hole-excitation is unlikely. The bleaching thus seems to arise from ionization of the F center.)

By plotting the widths W of the emission curves in the form $\coth^{-1} [W(T)/W(0)]^2$ versus T^{-1} estimates of a characteristic lattice frequency for the excited state can be found.[36] For CsBr this can only be a rough

estimate for, as Fig. 7 shows, $T = 13$°K may not give the low-temperature limit of the width. For CsI the structure observed at higher temperatures precludes this estimate. For CsBr the F-center excited-state characteristic phonon energy is about 0.008 eV, about 80% of the long-wavelength LO-mode energy.

An alternative to a delocalized excited state which also yields no structure in the emission band, a large noncubic relaxation of the ions about the excited F center, cannot be ruled out. The apparent compact lattice of CsBr should still permit relaxation, for the activation energies for vacancy jumps are not very large.[37]

The Stokes shift of F-center emission in CsCl, CsBr, and CsI is not given as well by Pekar's theory[38,39] as is the shift for other alkali halides. Using room-temperature data the F emission peaks should occur at 0.45, 0.72, and 0.82 eV in CsCl, CsBr, and CsI[39] while they actually occur at 1.26, 0.91, and 0.74 eV, respectively, reversed in order from the prediction. CsCl is particularly poorly fit, the ratio of Stokes shift to the F-absorption-peak energy being in disagreement by 38%. The value of the parameter $\epsilon_0 n^{-2} - 1$, where n is the index of refraction, is larger for CsCl than for any alkali halide whose F luminescence has been measured.

The M center seems to be similar to that in other alkali halides and to have similar properties. Our data are not deemed accurate enough to let us determine the M-band oscillator strength with respect to that of the F center. The M absorption under the F band (Fig. 9) lacks a simple shape and may be due to several transitions. The F_2 model of the M center in CsBr has D_{4h} symmetry, not D_{2h} as in KCl, so the second and third excited states are degenerate, not split as in KCl. There seem to be other nearby excited states in Fig. 9. From the photoconductivity work[17] these states have an appreciable probability of being ionized at 4°K.

Not much can be said about the aggregate bands of Fig. 11. They grow from F and M centers, but are rather difficult to study since they do not bleach optically. It is not possible to relate them to R_1, N, and O bands[31] in, e.g., KCl. Furthermore other aggregate bands exist in KCl,[26,40] and A centers[41,42] cannot be ruled out.

V. SUMMARY

F centers in cesium halides appear to be similar to those in other alkali halides except for the larger spin-orbit constant and interaction with noncubic vibrations.

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Higher excited states exist in CsBr and CsI with energies and oscillator strengths similar to those of F centers in other alkali halides. In CsBr these excited states also split similarly to the excited states of the F-band transition. The F-center emission spectra indicate that the excited state prior to emission is probably like that of F centers in other alkali halides. The M center in CsBr

is probably the F_2 center as in other alkali halides. It has one or more transitions overlapping the F band. The aggregate bands are many and are not well characterized.

Mössbauer Fractions and Specific Heats of Diatomic Lattices

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(Received 5 February 1965)

A simplified analysis using one-parameter models (like the Debye model for monatomic lattices) without details of the normal-mode spectrum (acoustic, optic) is proposed and applied to the alkali iodides. The theoretical basis is the insensitivity of $\langle x^2 \rangle$ and $\langle p^2 \rangle$ of a given lattice atom to changes in masses of other lattice atoms. The calculations utilize simple relations between the Mössbauer fraction and the specific heat of an alkali iodide crystal and the corresponding properties of a fictitious monatomic iodine crystal where all the atoms have the iodine mass but the forces between atoms are those of the alkali iodide crystal. A Debye model for the fictitious crystal is used to fit experimental data. A good fit is obtained with one parameter, the Debye temperature of the fictitious crystal.

A NUMBER of calculations have been made for specific models of the Mössbauer effect for a source which is not in a homogeneous lattice.[1] These results indicate that the Mössbauer fraction depends strongly on the mass of the source and the force constants binding the source atom and is almost independent of the properties of the rest of the crystal. A general justification of this effect has been given[2] and leads to the following simple rule for calculating Mössbauer fractions and thermal shifts in nonhomogeneous lattices. One can calculate these properties using a model of a fictitious homogeneous crystal in which all the masses are the same as that of the Mössbauer source atom while leaving the forces the same as in the original crystal.

Recent experiments[3] have measured the Mössbauer effect in an iodine isotope in all the alkali iodides. Their result, that f remains essentially constant from LiI to CsI, is in agreement with the general rule above. Since the force constants of all the alkali iodides are not very different from one another, the rule states that the f factor for all of these alkali iodides can be calculated from similar fictitious homogeneous iodine crystals in which the forces and structure are those of the corresponding alkali iodide crystals.[4]

The above simple rule can easily be extended to apply to other properties of the crystal such as the specific heat as well as the Mössbauer fraction and thermal shift. Since these Mössbauer properties depend on the mean-square position and mean-square momentum fluctuations of the Mössbauer atom, the latter can also be calculated from a fictitious homogeneous lattice as can also the mean-kinetic and mean-potential energies.

Using the above rule we can write that the mean-square momentum of an iodine atom in an alkali iodide crystal denoted by aI at a temperature T is equal to the mean-square momentum of an atom in a fictitious iodine lattice at temperature T:

$$[p_1{}^2(T)]^{a\mathrm{I}} = [p^2(T)]^{\mathrm{I}}. \tag{1}$$

The same argument can be applied to the mean-square momentum of the alkali atom, which is equal to the mean-square momentum of an atom in a fictitious homogeneous alkali crystal with the same force constants as the alkali iodide crystal and the fictitious iodine crystal:

$$[p_a{}^2(T)]^{a\mathrm{I}} = [p^2(T)]^{a}. \tag{2}$$

The two fictitious homogeneous crystals are simply related since they have exactly the same forces and differ only by a change in the mass of the constituent

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[4] Although these crystals have different structures and lattice constants, the only similarity required between the corresponding fictitious iodine crystals is that they have nearly equal character-

istic temperatures. This is indicated by the near equality of the nearest-neighbor force constants, and verified for the cases of NaI, KI, and RbI by the analysis of specific-heat data in this paper. A similar analysis for LiI and CsI will be of interest when experimental data are available.