i.e., $(V^{-1})_{ii}$ is the induced displacement on the ith component of displacement due to unit force per unit mass applied to the ith basis direction. The effective restoring force on a unit mass (including the reaction force due to the other atoms in their new equilibrium configuration) is therefore

$$\alpha = 1/(V^{-1})_{ii}. \tag{B2}$$

But α is exactly the quantity $(L - aC^{-1}a^T)$ appearing in Eq. (26), i.e.,

$$L - aC^{-1}a^T = 1/(V^{-1})_{ii}. \tag{B3}$$

Now $\langle \omega^{-2} \rangle$ is given by the trace of the inverse reduced-mass potential-energy matrix (defined with care to eliminate zero-frequency modes) divided by the order of V. Since all atoms of the perfect cubic crystal are equivalent, all the diagonal elements will be equal, giving

$$\langle \omega^{-2} \rangle = (V^{-1})_{ii}. \tag{B4}$$

Therefore we have

$$M(L - aC^{-1}a^T) = M/\langle \omega^{-2} \rangle. \tag{B5}$$

This shows that Eq. (4) is equivalent to Eqs. (25) and (26).

Optical Properties of Alkali-Halide Crystals*

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Reflectivity data from single crystals of alkali halides have been obtained in the ultraviolet region of the spectrum where excitonic and low interband transitions occur. Following recent calculations for the band structure of KCl and KI and basing our analysis on the experimental data, it has been possible to predict the properties of the band structure in other alkali halides and describe satisfactorily the low-lying transitions. Furthermore, a close relationship between the conduction band and the energy of the L bands of the F center has been established.

1. INTRODUCTION

ULTRAVIOLET absorption from thin films and reflectivity from cleaved crystals are among the most direct methods for investigating the intrinsic optical properties related to the excitation of electron states of alkali halides. As far as the absorption measurements are concerned, there exist in the literature extensive data at room temperature,[1] liquid-nitrogen temperature,[1] and 10°K.[2] On the other hand, if we except the pioneering work of Hartman et al.,[3] the reflectivity of alkali halides has not been studied extensively. Yet the important work by Philipp and Ehrenreich,[4] although confined to room temperature, has fully shown the potentiality of these measurements. At present, no systematic analysis, comparable to that relative to the absorption, is available for the reflectivity from single crystals at low temperatures. Reflectivity measurements are expected to yield details characteristic of the crystal structure more easily than absorption data from thin films. In fact, one of the experimental results derived from this assumption has been the observation of structures which are presumably to be attributed to excited levels of the Wannier type. These structures had been previously observed, with certainty, in the absorption spectra of iodides only.[2,5]

Until recently, the theoretical interpretation of the optical spectra has been based on the use of simple models for the excited states[6] and limited generally to the lowest-energy peaks. An attempt to explain the rich structure above the edge was made, not long ago, by Phillips,[7] who based his analysis on a tentative band scheme for the alkali halides. A connection with the band structure of rare-gas solids has also been anticipated, since the alkali halides may be considered a slightly more complex version of the rare-gas solids.[8]

* Preliminary data have been presented at the National Conference on Alkali Halides, Consiglio Nazionale delle Ricerche, Milano, Italy, 1966.

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[3] P. L. Hartman, J. R. Nelson, and J. G. Siegfried, Phys. Rev. **105**, 123 (1957).

[4] H. R. Philipp and H. Ehrenreich, Phys. Rev. **131**, 2016 (1963).

[5] F. Fischer and R. Hilsch, Nachr. Akad. Wiss. Goettingen, II, Math. Physik. Kl. **8**, 241 (1959); F. Fischer, Z. Physik **160**, 194 (1960).

[6] For a review of the exciton models see R. S. Knox, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl. 5.

[7] J. C. Phillips, Phys. Rev. **136**, A1705 (1964); in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 18.

[8] R. S. Knox and F. Bassani, Phys. Rev. **124**, 652 (1961); L. F. Mattheiss, *ibid.* **133**, A1399 (1964); J. C. Phillips, *ibid.* **136**, A1714 (1964); W. B. Fowler, *ibid.* **132**, 1591 (1963).

A critical review of the present status of the problem of excitations in alkali halides has been given by Bassani,[9] and important results for the conduction band[10,11] of these crystals are shown to be very useful for a reinterpretation of the optical spectra.[9] In the light of recent and fundamental calculations on the band structure of KI,[12,13] we here attempt an interpretation of our experimental results in terms of band structure and of exciton and interband transitions. By employing the atomic-energy levels of the free alkali atoms, a schematic band structure of alkali iodides, bromides, and chlorides is sketched in Sec. 2. In Sec. 3 we give our reflectivity spectra for a representative series of alkali halides at low temperatures and discuss the data in Sec. 4 in terms of exciton and interband transitions at different points in the Brillouin zone.

After the lowest-lying peak, occurring at Γ and originating essentially from the excited s-like states of the positive ion, the closest excited states are those of d-like symmetry, of the same ion, occurring at X, as suggested by Onodera et al.[12,13]

Good evidence for the presence of states of d-like character has been suggested recently.[2] There seems to be no necessity, at least at low energies, of involving such controversial excited states as the saddle-point excitons suggested by Phillips[7] and discussed by others.[14] Finally, we attempt in Sec. 5 to relate the excited states of the F center[15] to the crystal band structure, and it is found that the lowest (L_1) band is closely related to the lowest conduction band at X. The other L bands seem to correspond to higher bands where the joint density of states is high.

2. BAND STRUCTURE

In order to interpret the optical spectra of the alkali halides, it seems useful at this point to make a short survey of the present understanding of the valence and conduction bands. Then, basing our analysis on the existing calculations for KI and KCl and on the knowledge of the excited energy levels of the alkali atoms, we shall predict the band structure of the other alkali halides.

The upper valence band, the only important valence band in the low-energy part of the spectrum, has been shown to arise from the highest filled p states of the halogen ion.[12,16,17] As shown in Fig. 1, the band is split
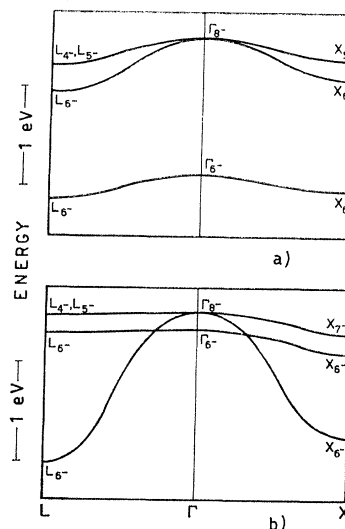
[9] F. Bassani, Lectures held at the Nato Summer School, Ghent, 1966 (unpublished).

[10] S. Oyama and T. Miyakawa, J. Phys. Soc. Japan **21**, 868 (1966).

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[13] Y. Onodera and Y. Toyozawa, J. Phys. Soc. Japan **22**, 833 (1967).

[14] C. B. Duke and B. Segall, Phys. Rev. Letters **17**, 19 (1966); B. Velicky and J. Sak, Phys. Status Solidi **16**, 147 (1966); J. Hermanson, Phys. Rev. Letters **18**, 170 (1967).

[15] F. Lüty, Z. Physik **160**, 1 (1960); G. Chiarotti and U. M. Grassano, Nuovo Cimento **46**, 78 (1966).

[16] L. P. Howland, Phys. Rev. **109**, 1927 (1958).

[17] T. I. Kucher and K. B. Tolpygo, Fiz. Tverd. Tela **2**, 2301

FIG. 1. Typical valence bands of alkali halides. (a) Iodides (Ref. 12); (b) chlorides (Refs. 16 and 17).

at the point Γ in the Brillouin zone, essentially by the spin-orbit interaction of the hole in the p state. At points along the directions of high symmetry, the upper branch of the valence band splits further into two bands. The valence bands of KCl[11,16] and KI[12] have maxima at Γ and are relatively flat, i.e., they depend very little on the wave vector $\mathbf{k}$. On the other hand, there appears to be a rather strong dependence on $\mathbf{k}$ for the lowest branch of the valence band of KCl. (Theoretical evidence for valence bands of slightly different shape, i.e., with maxima at points other than Γ, has been found for other alkali halides.[18] These crystals, however, are not discussed in the present paper.) The valence band of KI displays a spin-orbit splitting at Γ which is larger than the symmetry splitting of the upper branches at X and L. An opposite behavior is shown instead by KCl. The general trend of the valence bands of the chlorides and the iodides is described by the valence bands of KCl and KI, respectively, since the valence states are due to the hole left on negative-ion sites. A more refined statement should be based also on the results of Tolpygo,[17] which indicate a broadening of the symmetry splitting when the lattice constant of the chlorides decreases. It is obvious at this point that the valence bands of the bromides will be intermediate, as far as splittings go, between those of the chlorides and those of the iodides.

The more complex structure of the conduction bands is clearly indicated by the first detailed calculations,[10–12] which have appeared only very recently. From the calculations of Onodera et al.[12] and Oyama et al.,[10] a model conduction band for the alkali halides has been

(1960) [English transl.: Soviet Phys.—Solid State **2**, 2052 (1961)]; K. B. Tolpygo and D. I. Sheka, Fiz. Tverd. Tela **8**, 2587 (1966) [English transl.: Soviet Phys.—Solid State **8**, 2069 (1966)].

[18] A. B. Kunz and W. J. van Sciver, Phys. Rev. **142**, 462 (1966); A. B. Kunz, ibid. **151**, 620 (1966).

derived, and is shown in Fig. 2 in its essential features. Also indicated in the figure are the approximate charge fractions, symmetries, and their location (positive or negative ion) according to the most detailed calculations on KI.[12] Because of the known charge distribution at the points of high symmetry, it is possible to predict a band structure for several alkali halides. From Fig. 2 we see that the conduction band (see, e.g., the lowest Γ and X points) is mainly characterized by the positive ions in the lattice, since they possess most of the original charge when the crystal is excited at low energies. Therefore, if we consider the same halide of different alkalis, we can predict the relative positions of the Γ_1 and X_3 points in the conduction band by inspecting the spacings of the excited levels of different alkalis. The X_3 level, related to the d states of the cation, is expected to move slightly downward, toward the Γ_1 level, when the Rb^+ ion is substituted for K^+, and upward, when Na^+ takes the place of K^+, since the lowest d states of the alkali metals show this behavior relatively to the lowest s level of the valence electron.[19] The shape of the conduction band for alkali halides, obtained from the above arguments, can be summarized by the following points.

(i) The lowest conduction branch has an absolute minimum at Γ_1. At this point, the wave function is a superposition of s-like states with 70% of the charge located on the alkali ion and the rest on the halogen ion.

(ii) At X_3, the lowest conduction band displays another minimum built from d-like wave functions which give 80% of the charge on the alkali ion. This appears the most striking difference between previous prediction[7] and calculated band structures.[10–12]

(iii) Above these lowest branches, other conduction states with minima at higher energies are found at Γ_{12} and $\Gamma_{25'}$, and again most of the charge, with d-like symmetry, is located on the alkali ion.

(iv) The lowest band at L corresponds mainly to the d states of the alkali ion. No minimum is observed at L, but rather the bands running along different directions originating from L form a saddle point in k space.

(v) Above the first band at X_3 there is one which apparently plays an important role. In KI, the s-like X_1 state is endowed with $\simeq 70\%$ of the charge on the positive ion. As pointed out also by Onodera *et al.*,[12] it is this point which makes Na halides different from K and Rb halides because the d levels at X_3 and the s level at X_1 may change their order.

3. EXPERIMENTAL TECHNIQUES AND RESULTS

Single crystals of alkali-halide crystals have been cleaved and mounted in a double Dewar cryostat in good thermal contact with the sample holder. The

[19] *Atomic Energy Levels*, Natl. Bur. Std. (U. S.) Circ. No. 467 (U. S. Government Printing Office, Washington, D. C., 1949).
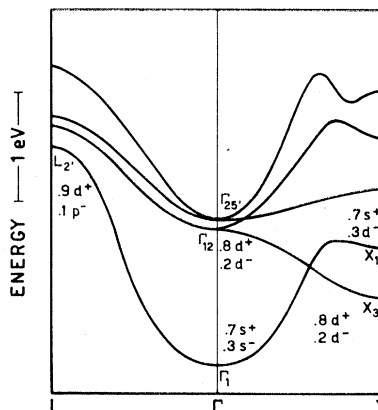

FIG. 2. Typical conduction band of alkali halides, with the indication of the approximate charge fractions, symmetries, and location (positive or negative ions) for some relevant points (Ref. 12). (See Refs. 10–13 for more details.)

measurements have been obtained at room temperature and 55°K by pumping the liquid air contained in the inner Dewar. In order to suppress, or at least to reduce, the reflection from the back surface of the samples at low extinction coefficients, this surface had been previously treated with an emery cloth. Light from a vacuum ultraviolet monochromator was reflected from the free surface of the crystals at an angle of about 20°, and therefore the data might be considered as referring to normal-incidence reflectivity. A LiF beam splitter, interposed between the cryostat and the exit slit of the monochromator, allowed direct and continuous recording of the logarithm of the reflectivity from 5 to 10 eV in about 5 min. No significant differences were observed from spectra taken, at low temperature, within a 10-min interval while the samples were kept at a pressure of less than 10^{-6} Torr. It was necessary to correct for the stray light of the monochromator, since regions of low reflectivity are encountered in the spectra of the alkali halides. A current equivalent to that due to the stray light was subtracted from the sodium-salicylate-coated photomultiplier output while recording the data.

The reflectivity spectra of a representative series of alkali-halide single crystals, with a band pass of approximately 6 Å, are shown in Figs. 3–9. They show well-resolved structures which often appear to be sharper than those observed in thin films at even lower temperatures.[2] As an example, the $n=2$ excitons associated with the band gap at Γ_1 of the chlorides, while absent in the spectra obtained from thin films,[2] appear clearly in our spectra on single crystals as shown in Figs. 7–9. In reflectivity measurements, both n and k, the real and the imaginary part of the refractive index, play a role, and therefore from the superposition of the peaks of both n and k we would have anticipated broader bands in the reflectivity spectra. However, the sharper behavior of some peaks, as observed here, certainly indicates that some of the band
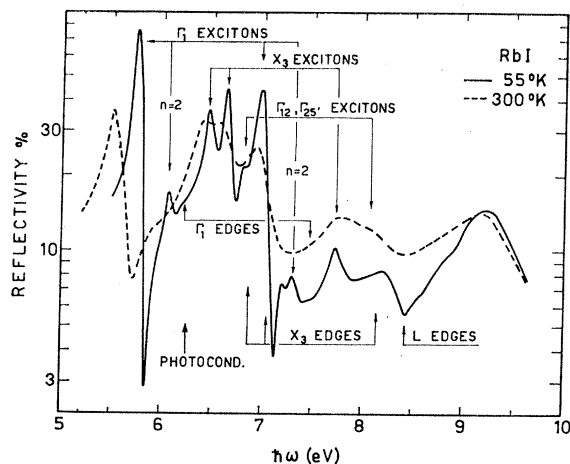
FIG. 3. Reflection spectrum at room temperature (dashed line) and at 55°K (full line) of RbI.
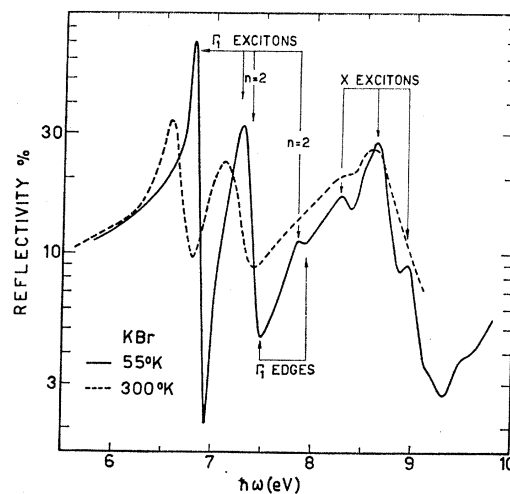

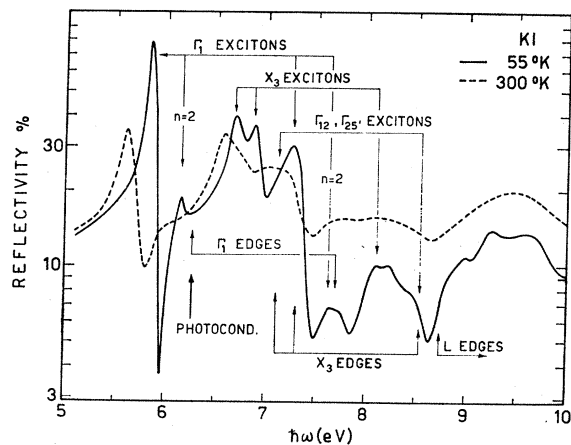FIG. 6. Reflection spectrum at room temperature (dashed line) and at 55°K (full line) of KBr.

FIG. 4. Reflection spectrum at room temperature (dashed line) and at 55°K (full line) of KI.
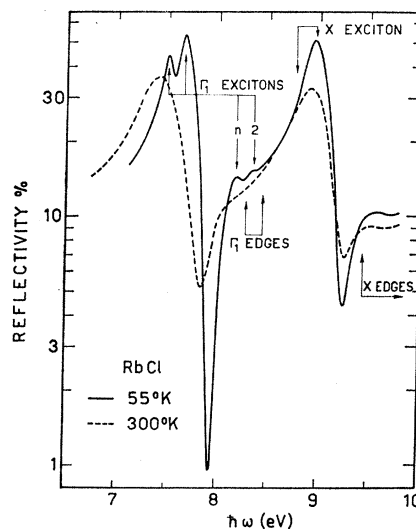

FIG. 7. Reflection spectrum at room temperature (dashed line) and at 55°K (full line) of RbCl.
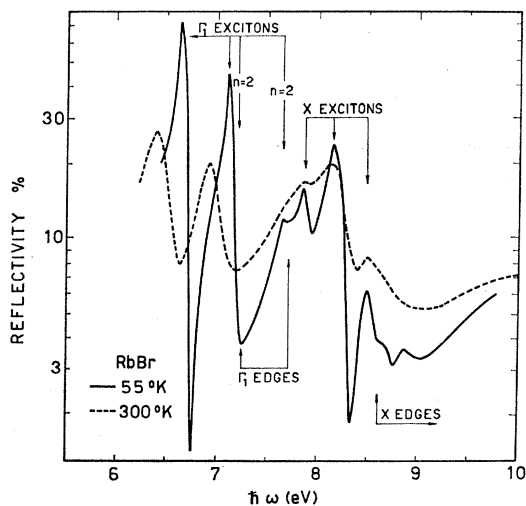

FIG. 5. Reflection spectrum at room temperature (dashed line) and at 55°K (full line) of RbBr.

broadening in the films is caused by their structure, which is less ordered than that of the crystals.

Our data for potassium halides at room temperature (Figs. 4, 6, 8) are consistent with those of Philipp and Ehrenreich[4] and show peak reflectivities of about 30%. At lower temperatures, the reflectivity of the iodides and the bromides increases up to 70% or more, while for the chlorides the increment is smaller. Our values of about 55% are to be compared with the data of Hartman et al.,[3] who find values slightly above 50% for KCl, and with the KCl reflectivity measured by Tomiki,[20] who finds about 60%. This discrepancy seems to arise more from the crystal quality, which is responsible for the flatness of the cleaved surfaces, than

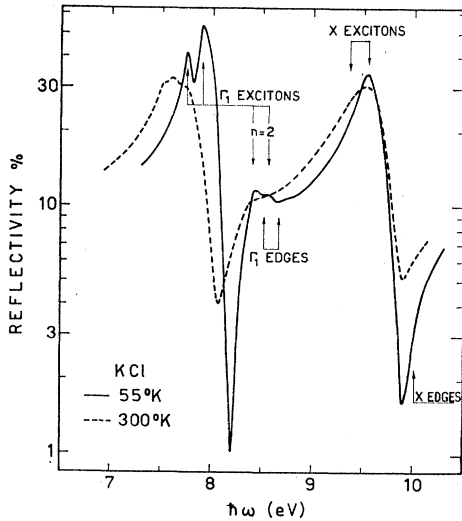[20] T. Tomiki, J. Phys. Soc. Japan 21, 409 (1966).

Fig. 8. Reflection spectrum at room temperature (dashed line) and at 55°K (full line) of KCl.
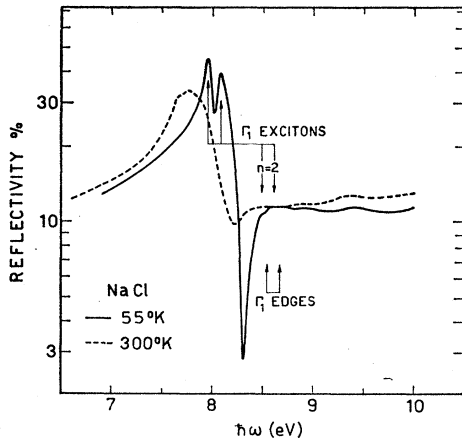

Fig. 9. Reflection spectrum at room temperature (dashed line) and at 55°K (full line) of NaCl.

from the higher temperatures employed in the present experiments. If the difference in the absolute values of the chloride reflectivities is neglected, we see that the agreement with these data is close. Finally, note in Figs. 3–9 the sharp drop in reflectivity at the high-energy side of the first exciton peak. Very low reflectivities, of about 1%, are found at the minima in the spectra.

4. DISCUSSION OF INTRINSIC SPECTRA

On the basis of the general behavior of the band structure as described in Sec. 2, and by examining of the optical data shown in Sec. 3, we have been able to reach the following conclusions, which are summarized by Fig. 10.

(i) Γ_1 excitons and interband edges. As already discussed by other workers, the first prominent peak in
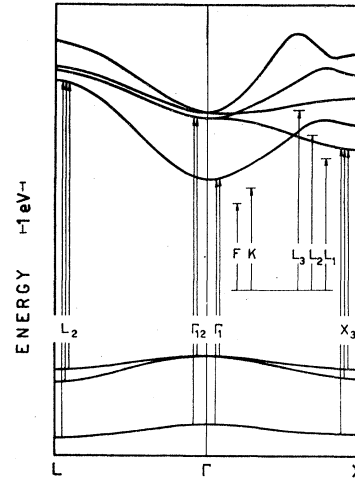

Fig. 10. Prominent interband transitions which occur in the alkali halides (energy scale referring to KI, Ref. 12). Excitons are not indicated. Transitions to the excited states of the F center are shown on the right with energies obtained from F. Lüty (Ref. 15).

the spectra, Figs. 3–9, is attributed to an exciton bound to the lowest conduction band at Γ_1 and the upper valence band at Γ_{15}. The Γ splitting guarantees the presence of a second strong exciton from the lower valence band. The spectra of all chlorides, bromides, and iodides show clearly the existence of these pairs of peaks which have been labeled Γ_1 excitons. As shown in the same spectra, we have also indicated (by $n=2$) the existence of weaker Γ_1 excitons at energies higher than those of the above doublets. The presence of these excitons, observed previously in the optical-absorption spectra of thin films of iodides and bromides only, has been found here in all of the reflectivity spectra from single crystals. The original suggestion of Fischer and Hilsch,[5] i.e., that the Wannier-Mott model describes the lowest excitation of an alkali halide, seems to find additional support from the present data. However, the simple Wannier formula for the exciton energies, based on the hydrogenic model,

$$\hbar\omega_n = E_G - (\mu/\epsilon^2 n^2)\,\mathrm{Ry},$$

is not expected to be very accurate for the $n=1$ excition since its application to the spectra yields small exciton,c radii: 3.4, 4.5, and 6 Å times n^2 for RbCl, RbBr, and RbI, respectively. The reduced masses μ are 0.32, 0.27, and 0.23 free-electron masses for the Rb halides. From the measured effective masses[21] of an electron in the conduction band of KBr, it appears that the exciton mass (approximately equal to the effective electronic mass, since the hole is heavy) has been underestimated here and, as a consequence, the radii must be even smaller and the reduced masses higher than quoted above. These arguments are supported by measure-

[21] M. Mikkor, K. Kanazawa, and F. C. Brown, Phys. Rev. Letters **15**, 489 (1965).

ments on mixed alkali halides,[22] where it has been possible to use the second and third lines for determining the exciton parameters. The binding energies $G=\mu/\omega^2$ Ry of an exciton in state $n=1$ are found to be 0.68, 0.5, and 0.34 eV for the three Rb halides and, although not very accurate because of the above comments, locate the lowest Γ_1 interband transition at $\tfrac{1}{4}G$, $\simeq 0.1$ eV above the $n=2$ Γ_1 exciton, i.e., at $\hbar\omega=E_G$. The onset for photoconductivity[23] appears to fall close to these predicted band gaps. For $\hbar\omega \geq E_G$, there is the onset of the interband transitions which, according to the band structure, should be the parent of an M_0-type reflection edge resulting from a similar joint density of states originating from the valence and conduction bands at Γ. The edge corresponding to the upper valence band is clearly visible, especially in the chlorides and iodides, as shown by the spectra in Figs. 3, 4, 7–9; while the second Γ_1 edge, at least in the iodides and bromides, is somewhat difficult to isolate from other transitions. As a general remark, it appears that most of the oscillator strength has gone into the creation of small, and therefore strong, excitons which occupy a few eV of the spectra and make the interband continua weak. To be noted in the spectra of KI and RbI is the presence of low-energy peaks falling between the components of the Γ_1 spin-orbit doublet. These are discussed in the following section.

(ii) X excitons and interband edges. According to the band structure of alkali halides as shown in Fig. 10 and discussed in Sec. 2, the threefold-split valence band and the lowest conduction band at X_3 give joint densities of states characterized by singularities of type M_0. It appears, however, that the lowest branch of the valence band for the chlorides has a strong curvature, and an edge different from M_0 is expected. Since the conduction band has a minimum at X_3, and the valence band is relatively flat, we can expect that excitons might be bound to these edges. This is at first surprising, since these excitons would fall in the continuum of states above the Γ_1 point, which we observed to be fairly weak; however, the compact excited d states of the positive ions guarantee strong oscillator strength to these X exciton. Furthermore, as shown by Kaplan,[24] a Coulomb interaction between electron and hole can give rise to resonant states which are bound to conduction-band minima higher than the lowest minimum, in our case at Γ_1. These excitons are clearly seen in Rb and K halides as shown in Figs. 3–8. The d nature of these excited states is supported by the observed position in the spectra of X_3 excitons relative to that of the Γ_1 excitons. The shift of the X_3 excitons to lower energies when the atomic number of

[22] G. Baldini and K. Teegarden, J. Phys. Chem. Solids 27, 943 (1966).
[23] Y. Nakai and K. Teegarden, J. Phys. Chem. Solids 22, 327 (1961); G. R. Huggett and K. Teegarden, Phys. Rev. 141, 797 (1966).
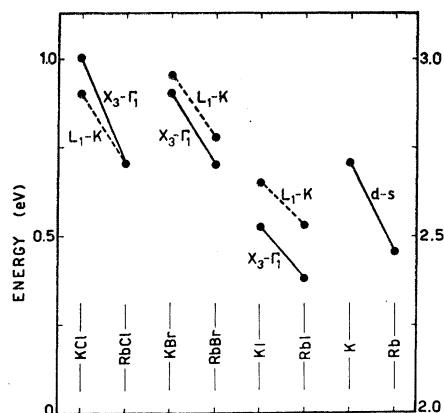[24] H. Kaplan, J. Phys. Chem. Solids 24, 1593 (1963).

FIG. 11. Peak energy difference: L_1-K (dashed line), $X_3-\Gamma_1$ ($n=2$) excitons (full line) for Rb and K halides and lowest excited d-s levels (right scale) for Rb and K atoms.

the alkali increases—as shown, e.g., by the K halides and Rb halides—agrees with the trend of the atomic d levels of the alkali metals, as indicated in Fig. 11. When the effect of different alkalis is included in the valence band, as shown by Tolpygo[17] for the chlorides, we expect that the splitting increases as the alkali becomes lighter. In agreement with these predictions, the X excitons are closer together in the Rb halides than in the K halides.

In the iodides, the X excitons appear as doublets just after the first Γ_1 edge, and as another peak whose energy is tentatively located at $\simeq 8$ eV. In the bromides, the three X excitons are still resolved, but have changed their spacing in accordance with the changes in the valence band (see Fig. 1), while for the chlorides, instead, the splitting of the two close X excitons disappears into a broad band. It appears from the spectra of K and Rb halides that the region immediately above the lowest Γ_1 band gap is again characterized by excitonic peaks rather than by interband transitions which usually give rise to smoother optical spectra. For the Cs halides,[2] it has been observed that the d excitons have come very close to the lowest Γ_1 exciton, as expected from the low-lying d level of Cs. The Na halides,[2] on the other hand, lack the d excitons at low energies, as has been anticipated on the basis of the d levels of atomic sodium, which are more energetic than those of K and Rb. As pointed out in Sec. 2, the X_3 branch of the conduction band may have moved close to or above the X_1 point, shifting the transitions to the X_3 edge toward higher energies and making the excitons weaker. The broad and almost flat spectrum of NaCl up to 10 eV shows that no d excitons are found in NaCl at these energies (Fig. 9), but only at ≈ 11 eV is the onset of a strong absorption observed in the spectrum.[2]

As for the Γ_1 excitons, it is likely that higher excitons associated with a pair of bands at X may arise. The presence of these $n=2$ d excitons seems at present hard

to ascertain, since other structures are displayed by the spectra in the region of the proper energy. Therefore, the onset of interband transitions at X has been tentatively located on the basis of binding energies of the X excitons similar to those of the Γ_1 excitons.

(iii) Transitions at Γ_{12} and $\Gamma_{25'}$. From the conduction-band structure of the alkali halides it appears that other excitons and interband transitions may arise from the Γ_{12} and $\Gamma_{25'}$ points in k space. The continua due to the lower bands beginning at Γ_1 and X_3 have been seen to be weak, and therefore the probable presence of other excitons of d symmetry could be concluded. We have indicated the possible candidates in the spectra of KI and RbI, Figs. 3 and 4, without making a distinction between Γ_{12} and $\Gamma_{25'}$, since there is little experimental evidence for structure except that observed in thin films of RbI (see Ref. 2 and Fig. 3).

(iv) Higher interband edges. At energies higher than those corresponding to the Γ_{12} and $\Gamma_{25'}$ we see (Figs. 2 and 10) the presence of high densities of states which correspond to other conduction branches at X and to the conduction band at L. The lowest point at L, corresponding again to a high fraction of the charge located on the d orbitals of the positive ions, has been discussed in connection with metastable excitons bound to saddle points in k space.[7,14] It is not necessary to introduce such controversial excitons, since there are other states, as discussed above, which are responsible for the observed structures at low energies. The contribution of this L point should involve only M_1 or M_2 edges rather than exciton peaks, and the expected onset of these edges is indicated in some of the spectra. For energies higher than those considered here, the interpretation of the optical spectra[4] seems very hard, since several bands are available[10–12] and, at the same time, the spectra show broad structures. As discussed in Ref. 3, the transitions from the valence band are exhausted between 10 and 15 eV, and plasma oscillations of the valence electrons occur at that energy.

5. EXCITED STATES OF THE F CENTER

It is well known that electrons bound to negative-ion vacancies (F centers) possess energy levels which, excited by light, give rise to absorption bands lying in the visible and near-uv part of the spectrum.[15] Of these bands, labeled F, K, L_1, L_2, and L_3 in order of increasing energy, the F and K bands correspond to transitions from the ground state to the $2p$ and $3p+4p\cdots$ excited states of the F center.[25] Since photoconductivity in colored crystals occurs at energies slightly larger than that of the K band,[26] it appears that the L_1, L_2, and L_3 bands must fall in the continuum of the conduction states of the crystal. The presence of such states in

the conduction band has been discussed,[27] but no direct evidence of a correlation between the optical data for the colored crystals and the band structure had been established so far.

In order to test the assumption that the L_1 band is correlated with the band structure, we have compared the exciton spectrum with the F-center absorption. Since the X-point excitons, as discussed in Sec. 4, are the strongest transitions after the Γ excitons, we have assumed that the L_1 band might be related to the lowest conduction band at X. In Fig. 11 we give the energy differences between the L_1 and K bands, and those between the X_3 and Γ_1 ($n=2$) excitons in K and Rb halides. The agreement is close, but we must recall that the valence band plays a role, through its k dependence, in the exciton spectra; while for the F center, since it is localized, the ground state can be assumed flat, as indicated in Fig. 10. The data of Fig. 11 indicate that the L_1 level is slightly higher than the X_3 exciton level, since the upper branch of the valence band at X is $\simeq 0.2$ eV lower than at Γ.

The discrepancy between the exciton level and the F-center level at X_3 can probably be ascribed to the difference between the electron-hole and the electron-vacancy interaction. Calculations on this point are necessary. It is interesting that the X_3 excitons and the lowest d level of the alkali ions appear to be related to the Γ_1 excitons and s level, respectively, as shown in Fig. 11. As discussed in Sec. 4 (ii), resonant states may arise at minima which lie in the continuum of the conduction band,[24] and therefore from the above data it seems plausible to attribute the L_1 band to a resonant state at X_3.

Other minima are found in the conduction band at $X_1, \Gamma_{12}, \Gamma_{25'}, X_2$, etc. Applying the same argument to the other L bands, we can assume that the L_2 and L_3 peaks originate from some of these minima. Also reported in Fig. 10 are the excited states of the F center in KI. Their energies indicate that also the L_2 band (apparently dependent upon the alkali ion) is related to a resonant state at X (X_1), and that the L_3 band, which is usually the strongest, is perhaps connected with higher points such as Γ_{12}, Γ_{25}.

From the discussion of Sec. 4 (ii), in which the absence or weakness of the d excitons in NaCl was explained, it appears that the L bands should be hard to detect, as confirmed by optical-absorption experiments. There is, however, evidence for structure of the type due to the L bands in the photostimulated thermoluminescence of NaCl.[28] Definite conclusions on this point do not seem possible at present, and therefore it is believed that the problem should be investigated both experimentally and theoretically.

[25] N. F. Mott and R. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940), p. 114; G. Spinolo and D. Y. Smith, Phys. Rev. **140**, 2121 (1965).

[26] R. L. Wild and F. C. Brown, Phys. Rev. **121**, 1296 (1961); R. S. Crandall and M. Mikkor, *ibid*. **138**, A1247 (1965).

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6. CONCLUSIONS

The analysis of the optical properties of alkali-halide crystals at low energies, attempted on the basis of recent band-structure calculations, has yielded a satisfactory description of the low-lying excited states. Excitonic structures deriving from different points in the Brillouin zone, mainly at Γ and X, have been found responsible for the observed peaks. Interband transitions seem to be weak in this region and are masked by the strong exciton peaks. Data up to higher energies for K halides, as those given by Philipp and Ehrenreich,[4] although obtained at room temperature, should help in understanding the electronic structure of these crystals. However, it appears a difficult task to attribute all the transitions to well-defined interband edges or excitons unless new methods can be employed to sort out all the bands.

Some comments are in order for other crystals, such as the Cs halides.[29] According to the discussion of Sec. 6, the d states if the alkali metals cause the conduction band to shift, and since Cs has a very low d level, the presence of lines close to the first exciton peak can still be ascribed to minima of the conduction band related to these states. In the case of the fcc CsCl structure, as assumed by Eby et al.[1] for room-temperature-deposited films, the minimum at X_3 seems to be responsible for the peak at ~ 8 eV. This point is in good quantitative agreement with the relative position of the atomic levels in Cs, as can be easily shown by employing the same arguments used for the other alkali halides. It is also expected that the spectra of the simple cubic Cs halides arise from transitions of

the same kind. However, points other than X should probably be held responsible for these d-like excitons.[30] This behavior of the conduction band could perhaps explain at least part of the structure observed in the F band of the Cs halides.[31]

Furthermore, the conclusions found for the alkali halides, when applied to the isoelectronic rare-gas solids, suggest that also in these solids excitons deriving from the threefold valence band at X are responsible for the structure at 9.8, 10.4, and 11.2 eV in solid Xe and similar structures in dilute alloys.[32] This interpretation is consistent with the fact that these peaks derive from atomic d states[2] shown to be associated with the point X.[12]

Finally, the intimate relation between the excited states of the F center and the "intrinsic states of the fcc crystals," derived from the experimental data, suggests that the L bands could yield useful indications about the conduction-band structure of the alkali halides.

Note added in proof. Recent reflectivity measurements on KI and RbI have been presented by Roessler and Walker [D. M. Roessler and W. C. Walker, J. Opt. Soc. Am. **57**, 677 (1967)]. Their interpretation is consistent with our discussion.

[29] J. C. Phillips, Phys. Rev. **136**, A1721 (1964).

[30] We are grateful to Professor Onodera for clarifying comments on the band structure of Cs halides.
[31] See, e.g., P. R. Moran, Phys. Rev. **137**, A1016 (1965), and references therein.
[32] G. Baldini, Phys. Rev. **128**, 1562 (1962); **137**, A508 (1965); J. C. Phillips, *ibid.* **136**, A1714 (1964).