nents of the spin wave then exist corresponding to the phonon wavelength and the calculated excitation of the spin waves by the phonons comes out in good agreement with experiment. The dependence of the spectrum on film thickness and the apparently erratic intensities are understandable on this basis.

The effects of eddy currents are quantitatively neglected but must be taken into account for the $n=0$ mode and perhaps for higher-order modes if the film thickness is increased past 5000 Å. It is apparent that the spin-wave functions will not be exactly Hermite functions in all cases because of variations in film fabrication. It appears that more exact comparison between experiment and theory will be possible if efforts are made to produce either perfectly uniform films or films in which the internal effective field varies exactly parabolically.

ACKNOWLEDGMENTS

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APPENDIX I: THE FUNCTIONS $J_n(K)=[\psi_n(K)]^2/2^n n!$ WHERE $\psi_n(K)=\exp(-K^2)H_n(K)$.

$$J_0(K)=\exp(-K^2),$$

$$J_2(K)=\exp(-K^2)(2K^2-1)^2/2,$$

$$J_4(K)=\exp(-K^2)(4K^4-12K^2+3)^2/24,$$

$$J_6(K)=\exp(-K^2)(8K^6-60K^4+90K^2-15)^2/720,$$

$$J_8(K)=\exp(-K^2)(16K^8-224K^6+840K^4-840K^2+105)^2/40\,320.$$

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Excited States of the *F* Center

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Various L bands have been measured in KCl and KBr x rayed at liquid-helium temperature and in KCl:H x rayed at room temperature. These results argue against the suggestion that the L bands arise from complexes involving F centers and support the argument that the L bands arise from the F center itself. A charge-transfer model of the L bands is proposed in which the transitions correspond to a combination of transferring the F-center electron to a neighboring alkali ion and raising the resulting alkali atom to one of its excited states.

INTRODUCTION

FOR many years the picture of the F center in alkali halides has seemed reasonably complete.[1] The center consists of an electron at a negative ion vacancy. The principal electronic transition is seen in absorption as the F band which raises the electron to an energy level a few tenths of an electron volt below the conduction band. A weaker transition on the high-energy side of the F band is known as the K band. It also arises from the F center and is thought to involve excitation of the electron either into the conduction band or very close to it.

A startling development, due to Lüty, has been injected into this picture.[2] In additively colored potassium and rubidium salts he has found three new bands on the high-energy side of the F and K bands. These bands, called L_1, L_2, and L_3 bands, are smaller than the F band by one to two orders of magnitude but are proportional to the F band. The peak positions of the L bands vary as the host lattice is changed and follow the empirical Mollwo-Ivey relation[3] as do the F and K bands. This relationship is

$$\nu d^n=\text{const}, \tag{1}$$

where ν is the frequency of the maximum of the band, d is the lattice constant of the host material, and n is a constant which is nearly 2.

The most surprising feature of these bands is that they lie from about 0.7 to 2.5 eV higher in energy than the F band. From all that is known about the F center, these transitions would be to states well within the conduction band if the F center is the defect responsible for the bands. One might expect that photoconductivity would be observed on irradiation into these bands; this had indeed been observed by Inchauspé before the discovery of the L bands.[4] In KBr at 80°K, Inchauspé found photoconductive peaks at the L_2 and L_3 positions and has found another peak at even higher energies which has not been identified in optical absorption. Wild and Brown have examined the photoconductivity

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[1] For a recent review of the properties of the F center see J. H. Schulman and W. D. Compton, *Color Centers in Solids* (Pergamon Press Inc., New York, 1962).

[2] F. Lüty, Z. Physik **160**, 1 (1960).

[3] E. Mollwo, Nach. Ges. Wiss. Göttingen, **II**, 97 (1931); H. Ivey, Phys. Rev. **72**, 341 (1947).

[4] N. Inchauspé, Phys. Rev. **106**, 898 (1957).

of additively colored KCl at temperatures near 10°K and find distinct peaks corresponding to the L_1 and L_2 bands.[5] The quantum efficiency for photoemission on irradiation into these bands was found to be 0.04. There is no evidence that thermal activation is necessary for photoconductivity at this low temperature.

Another band, called the L_4 band, has been found in KCl at 1900 Å by Hirai and Ueta.[6] It appears to have properties similar to those of the other L bands. Also, Lüty has recently found that L bands exist for F_A centers (F centers with an alkali impurity at a nearest neighbor site).[7] If polarization is induced in the F_A band, it also appears in the corresponding L bands. Thus, there is a variety of experimental evidence that the L bands arise from F centers.

There are, however, severe difficulties in accepting this interpretation, as pointed out by Gold.[8] One problem is the concept of a localized energy state in a conduction band. Can such a localized level exist? If it does exist, is the lifetime of the state sufficiently long so that transitions to it will not be made unobservable by lifetime broadening? How can the F center give rise to such excited states? Gold points out that the strength of the L bands increases in going to higher energy; this is opposite to the effect expected for a hydrogenic type of transition. He also argues against mixing of the F-center transition with a set of states such as excitons; the argument is that the energies of the L bands do not seem to fit this picture and that the Mollwo-Ivey relation implies a localized electron rather than the diffuse state characteristics of an exciton. Gold also points out that a transition to a state well inside the conduction band might be expected to lead to a photoconduction efficiency close to unity rather than the 0.04 value found by Wild and Brown.

Gold has suggested that one solution to this problem may be that the L bands do not arise from the F center itself but from some other center which is created along with the F center. The L bands have been investigated in potassium and rubidium salts colored by heating at a few hundred degrees Centigrade in the alkali vapor. Under these conditions a thermodynamic equilibrium is established and F centers are formed. Gold has proposed that smaller numbers of more complex centers may also be formed and that one of these complexes is the center responsible for the L bands. Specifically, he considers the $F_2{}^+$ center which may be formed by the combination of an F center with a negative-ion vacancy, and he argues that the number of $F_2{}^+$ centers will vary linearly with the number of F centers.

EXPERIMENTAL RESULTS

Several experiments were performed to look for L bands in material colored by x rays at liquid-helium temperature and room temperature. If the F center is the source of the L bands, the method of production should have no influence on them; but if they arise from a complex, formation by a different technique at low temperatures should cause major changes in the L bands.

At liquid-helium temperature, x rays produce F centers in a way which appears to be especially well understood. A variety of optical[9] and spin-resonance[10] studies lead to the conclusion that the F center is made in the perfect lattice by formation of an interstitial halogen atom at some distance from the F center. The x-ray production of the M center (a complex of two F centers) provides experimental evidence that there is no diffusion at liquid-helium temperature, the number of M centers formed being just what is expected from a random creation of F centers.[11] At room temperature, the situation is less clear; but even in this case the ratio of M band to F band may be changed permanently by irradiation with light so that thermodynamic equilibrium does not exist with regard to the F center.

The absorption spectrum of KCl x-rayed at liquid-helium temperature is shown in Fig. 1. For this measurement thin blocks of crystal were cleaved from material supplied by the Harshaw Chemical Company. The x-ray exposure was for 1 h from a tube with tungsten target and beryllium window run at 50 kV and 30 mA. Measurements were made on a Cary Model 14 Spectrophotometer using both the regular slide wire and a special unit which extends the range to lower optical densities by a factor of 10. Spectral measurements were made both before and after x-raying; Fig. 1 plots the difference between these runs on a logarithmic scale in

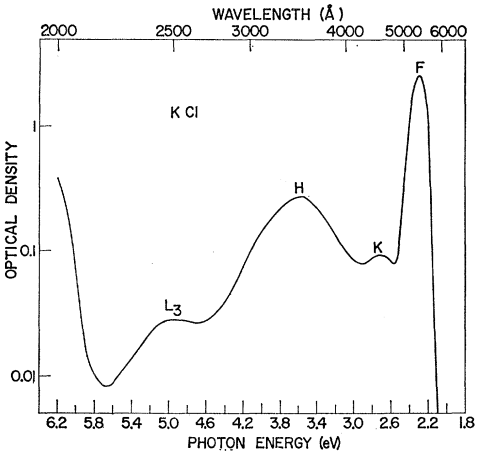

FIG. 1. The absorption of KCl is plotted on a logarithmic scale as a function of wavelength. The color centers were produced by 50-kV x rays at liquid-helium temperature and measured without warming.

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[5] R. L. Wild and F. C. Brown, Phys. Rev. **121**, 1296 (1961).

[6] M. Hirai and M. Ueta, J. Phys. Soc. Japan **17**, 566 (1962).

[7] F. Lüty, International Symposium on Color Centers in Alkali Halides, 1962.

[8] A. Gold, Phys. Rev. **123**, 1965 (1961).

[9] H. Rabin and C. C. Klick, Phys. Rev. **117**, 1005 (1960).

[10] W. Känzig and T. O. Woodruff, J. Phys. Chem. Solids **9**, 70 (1959).

[11] B. J. Faraday, H. Rabin, and W. D. Compton, Phys. Rev. Letters **7**, 57 (1961).

order to show both strong and weak bands. In the spectrum of Fig. 1 there are easily identified the *F*, *K*, and *H* bands. It is proposed that the band near 5.0 eV is the L_3 band which Lüty finds at 4.95 eV at liquid-nitrogen temperatures.[2] The ratio of *F*-band height to L_3-band height is 136 in Lüty's data. In Fig. 1 the height of the L_3 band is difficult to determine because of the overlap of the *H* band. If one takes the height of the absorption at 5.0 eV as the height of the L_3 band, the ratio of *F*- to L_3-band height is 88. Since the L_3 band is overestimated here and since there may be small changes in the band widths between liquid-nitrogen and liquid-helium temperatures, there appears to be reasonable agreement both in wavelength and in magnitude between Lüty's L_3 band and the L_3 band of Fig. 1.

Similar results for KBr are given in Fig. 2. The material was x-rayed at liquid-helium temperature and then warmed to 30°K in order to reduce the intensity of the unstable bands at 2200 and 2300 Å.[12] The sample was then recooled with liquid helium and measured. There are bands identified as the *F*, *K*, *H*, and α bands. The band at about 4.4 eV agrees well with the L_3 band given by Lüty as 4.5 eV.[2] The ratio of *F*- to L_3-band height is 78 in Lüty's data. From Fig. 2 it is 38, again making no correction for overlapping bands or the effects of differing temperatures. Here again the agreement is felt to be good. It should be mentioned that both of these L_3 bands were seen by Duerig and Markham in early studies of the coloration of alkali halides at low temperatures.[13]

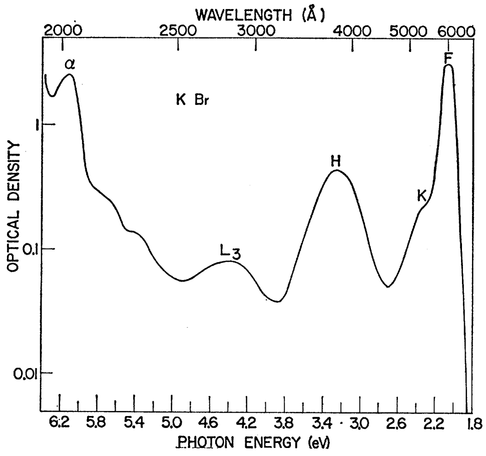

FIG. 2. The absorption of KBr is plotted on a logarithmic scale as a function of wavelength. Coloration was produced by x rays at liquid-helium temperature, the sample was warmed to 30°K to reduce the two bands near 2300 Å, and then the sample was cooled once more for the optical measurements.

The L_1 and L_2 bands cannot be seen in Figs. 1 and 2 because of the large *H* band characteristic of low-temperature coloration by x rays. To avoid this difficulty, measurements were made on KCl:H x-rayed at room temperature. Under these conditions a very large *F* band is formed but no *M* band, indicating that the formation of the F_2 complexes is inhibited by the hydride ion. The absorption spectrum shown in Fig. 3 was measured at liquid-helium temperature for KCl:H x-rayed at room temperature. The faint band marked L_1 appears to agree with the L_1 band given by Lüty as appearing at 3.6 eV. The *F* to L_1 band height is 220 from Lüty's data and is crudely estimated to be 400 from the data of Fig. 3 if background corrections are made.

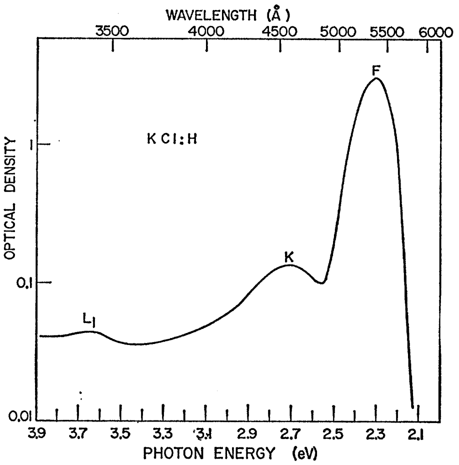

FIG. 3. The absorption of KCl:H is plotted on a logarithmic scale as a function of wavelength. The sample was x-rayed at room temperature and then cooled to liquid-helium temperature for the optical measurement.

From the experimental work one may conclude that *L* bands are seen in alkali halides x-rayed at low temperatures under conditions which are unfavorable for the formation of complexes. The peak positions of these bands agree with those formed at high temperatures, and the ratio of the *F*-band height to the height of these bands agrees within the limit of precision imposed by the overlapping of bands. Thus, it seems extremely unlikely that the *L* bands arise from complexes; it appears from abundant evidence that they must arise from the *F* center.

PROPOSED MODEL

In this section a model will be proposed for the *L* bands which explains in a qualitative way some of the difficult problems associated with these bands. The model uses the idea of charge transfer which was first introduced by Hilsch and Pohl in discussing the fundamental absorption edge of alkali halides.[14] In that case the transition was thought of as taking an electron from a halide ion and placing it on a neighboring alkali ion, thus, leaving both ions in states of atomic character. With this simple model, energies were computed which

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[12] C. C. Klick and D. A. Patterson Phys. Rev. **130**, 2169 (1963).

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

[14] R. Hilsch and R. W. Pohl, Z. Physik **57**, 145 (1929); **59**, 812 (1930).

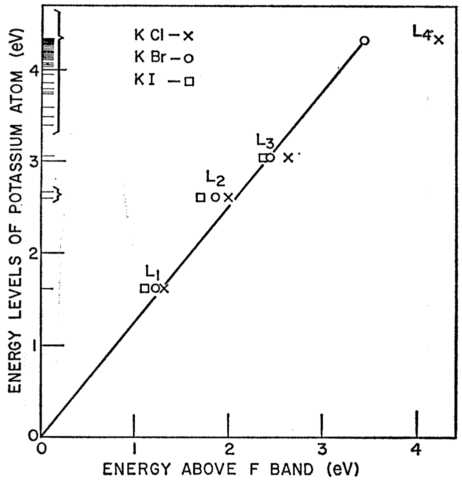

FIG. 4. The atomic energy levels for K° are given on the ordinate. On the abscissa is plotted the difference in energy between the various L bands and the F band for alkali halides with potassium ions.

agreed reasonably well with experiment. Furthermore, this model provided a simple picture to account for the observed splitting of the exciton bands. When an electron is transferred, the resulting halogen atom may exist in either of two states differing in energy by the spin-orbit splitting of the atomic ground state. These characteristic halogen doublets are, in fact, observed in the exciton spectra of alkali halides.[15] This charge-transfer model of the exciton has also been used to discuss the perturbation of excitons by nearby vacancies and F centers.[16]

On the basis of a charge-transfer model, the F-band transition would be considered as taking the electron from the vacancy and placing it on a neighboring alkali ion to form an alkali atom. The K band, which is only a few tenths of an electron volt different in energy than the F band, is considered to be essentially the same transition as the F band. For the F and K transitions the alkali atom is formed in its ground state. At higher energies the charge transfer could leave the alkali atom in an excited state. The L_1 band could result from this type of transition, leaving the alkali atom in its lowest excited state. Higher excited states of the alkali atom would correspond to the L_2, L_3, and L_4 bands.

The model implies that the energies corresponding to the L bands are given approximately by the sum of the F-band energy and the excitation energy of the alkali atom. For a series of alkali halides with the same alkali ion, subtracting the energy of the F band from that of the L bands should give differences which do not vary greatly from one alkali halide to another and agree moderately well with the spectroscopic energy levels for the specific alkali. In Fig. 4 data are presented for KCl, KBr, and KI. The abscissa is the energy difference between the L bands and the F band for each material[2]; the energy levels of the potassium atom are plotted on the ordinate. There are very many levels near the ionization limit and these could not all be drawn. The levels identified as L_1 in the figure cluster around 1.2 eV. According to the proposed model they should correspond to the 1.6 eV first excited state energy of the K^0. Since the potassium atoms are imbedded in a dielectric, this much change in the transition energies does not seem unreasonable. Also, the spread in L_1 energies is fairly small, being about 0.2 eV. The L_2 points are drawn as arising from the next two atomic levels near 2.6 eV. Here again the spread in points is small. The L_3 points are drawn at the energy of the next higher level but the larger number of atomic levels with increasingly close spacing makes the level assignment less reliable. The last points at the highest energies corresponds to a photoconductive peak seen by Inchauspé in[4] KBr and the L_4 band of Hirai and Ueta for[6] KCl. It has arbitrarily been assigned to the ionization limit for potassium. The straight line connects the KBr point with the origin and indicates that the L bands may be reasonably well accounted for as combined F-band and potassium-atom transitions if the potassium-atom transition energies are reduced by about 25%.

In Fig. 5 similar data is given for RbCl, RbBr, and RbI. The assignment of rubidium atomic levels to the L bands is identical with that for potassium, and again the L_3 assignment is unsure because of the large number of levels at the higher energies. The solid curve joining the points would indicate that agreement between the model and the data might be obtained if the atomic levels were compressed by about 35% for the rubidium salts.

The situation proposed here is similar to that described by Zwerdling, Button, Lax, and Roth[17] for boron- and aluminum-doped silicon. They found

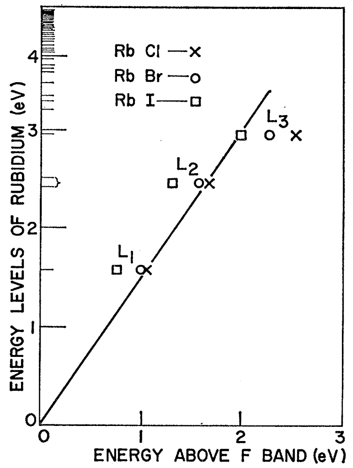

FIG. 5. The atomic energy levels for Rb° are given on the ordinate. On the abscissa is plotted the difference in energy between the various L bands and the F band for alkali halides with rubidium ions.

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[15] J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. **116**, 1099 (1959).

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[17] S. Zwerdling, K. J. Button, B. Lax, and L. M. Roth, Phys. Rev. Letters **4**, 173 (1960).

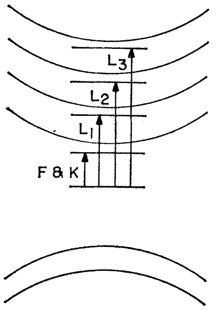

FIG. 6. A schematic energy-band picture of the model proposed for the L bands.

evidence that impurity levels occurred not only in the forbidden gap above the highest valence band but also in the valence band above the splitoff band. One can also describe the F-center model proposed here on the basis of a band model. In Fig. 6 the separation of the two valence bands represents the splitting of the halogen levels seen in exciton spectra. The ground state of the F center is in the forbidden gap, and the F- and K-band transitions are lumped together in transitions to an excited state near the minimum of the lowest conduction band. The lowest conduction band corresponds to the alkali atom in its lowest energy state and higher bands correspond to higher excited states. Excited states of the F center exist near each of these higher bands and transitions from the ground state of the F center to them result in the various L bands.

It might be expected that the existence of the various conduction bands would result in discrete band absorption at energies above the fundamental edge. Since the spectra of various alkali atoms are similar, it might also be expected that various alkali halides having the same halide ion would possess similar absorption spectra in this region. A very complex spectrum is indeed seen in absorption beyond the fundamental edge, but different alkali halides with the same halide do not possess spectra which are strongly similar.[15] This may in part be due to variations in the strengths of transitions, which do not appear to yield to simple analysis. The strength of the lowest energy line of the halogen doublet, for instance, should be twice that of the higher line on the basis of simple considerations of multiplicity, but this relation is not observed in the exciton splitting in many materials.[15]

If the F center is excited to one of the L levels, it may return to the ground state in several ways. The electron may make a horizontal transition to a conduction band state of high crystal momentum and appear as a high-energy conduction electron. Another possibility for de-excitation is that the alkali atom makes a transition to the ground state giving up the energy as radiation. This might account for the observed low quantum efficiency for photoconductivity. Lüty has apparently observed luminescent radiation at about 2 eV on exciting in the L bands,[7] but the details of this luminescence are not yet available. Timusk and Martinessen have reported luminescence at 2.9 eV in KCl and 2.4 eV in KBr on exciting at energies above the band gap.[18] They also find similar luminescence on exciting in the α band, which creates an exciton near a negative ion vacancy. It seems possible that some of these luminescent emission bands could arise from transitions involving the higher excited states of the F center. It would be instructive to look for others in ranges extending to the near infrared and at low temperatures.

CONCLUSION

Experiments reported here show the appearance of L bands in alkali halides x-rayed at room temperature and liquid-helium temperature. From these experiments it is concluded that the source of the L bands is the isolated F center rather than some complex of which the F center is a part.

A model for the L bands is presented which interprets them as being combinations of the usual F-band transition, which transfers the F-center electron to a neighboring alkali ion, and the raising of the resulting alkali atom to various excited states. The argument for this model rests primarily on the close relationship between the lowest energy steps of alkali atoms and the difference in energy between the F band and the higher L bands. Furthermore, it does offer a qualitative picture of a simple kind upon which experiments and calculations may be devised. Certainly both are needed to ascertain the validity of the model. It would be especially valuable to know from theory where the higher conduction bands lie in alkali halides and whether or not the scheme of Fig. 6 is reasonable. Also, it would be very useful if the oscillator strengths for the transition proposed here agree with those observed for the L bands.

ACKNOWLEDGMENTS

We are indebted to Dr. James H. Schulman for detailed discussions of this work.

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