Point Defects in Insulators

Lattice defects and electrons combine to form varieties of color centers.

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Over the last few years a really remarkable increase in knowledge has occurred concerning the nature of point defects in insulators. While this progress is most notable in alkali halides, important steps have also been taken with respect to silver halides, alkaline earth halides, oxides, and many other materials. But the alkali halides are clearly the pioneer materials, and it is from investigations of these solids that models, theory, and techniques have been developed for other classes of insulating solids. Because of this situation, what follows will concentrate almost completely on describing the knowledge that presently exists about point defects in the alkali halides, with only a brief mention of other materials (*1*).

Before going into this topic it may be well to compare insulators with metals and semiconductors. In all materials with a regular lattice array of atoms there is developed a grouping of energy levels permitted to the electrons. These energy ranges are called bands, and an energy band structure for an insulator is illustrated in Fig. 1. Increasing energy is plotted vertically; motion from one part to another in the crystal is plotted horizontally. Starting at the top there is a band of allowed energy levels called the conduction band. In an insulator there are normally no electrons in this band, because they can all fit into lower bands. But if an electron were excited up to one of these energy levels, it would be free to wander throughout the crystal, giving rise to electrical conduction. In metals there are more electrons than can be accommodated in the lower bands, and the conduction band is always partly filled, thus allowing conduction.

Below the conduction band is a region called the band gap which does not have any energy levels for the perfectly periodic lattice, so that electrons cannot have energies in this region. Of course, no real crystal is ever perfectly pure. Occasionally one may have a missing atom or ion—called a vacancy—or one that is shoved between others—called an interstitial. In addition, foreign elements may be introduced into the crystal or appear there inadvertently. These point defects frequently give rise to an energy level in the band gap, the electron being confined to the vicinity of the defect. Such a case is illustrated in Fig. 1 by the short line labeled *D*, and an electron (*e*) is indicated as being in the level. The defect may also have other higher levels to which the electron can be excited, as illustrated by the vertical arrow. In the alkali halides many of the point defects permit such transitions by absorption of light in the visible portion of the spectrum. As a result, these crystals appear colored, and the defects are usually called "color centers." In semiconductors the defect levels with electrons in them are usually found close to the conduction band, and thus thermal energy will excite the electrons into the conduction band at room temperature. A sort of metallic conduction results, except that the number of electrons which are free can be controlled both by controlling the number of defects and by controlling the temperature.

Below the band gap in an insulator is a filled band. All the energy positions permitted in this band have electrons in them, and no more are allowed. As a result no electron can move to a higher or lower energy position within the band. In an electric field none of the electrons can gain energy, and as a result there can be no conduction. It is this band property that characterizes insulators. If an electron is excited from the filled band to the conduction band, then the electron is free to move from one energy level to another, since the positions are unoccupied. The position in the filled band left by an electron excited to the conduction band allows some of the lower-energy electrons to gain or lose energy, and the result of this process is just what would occur if a *positive* electron were introduced into an empty band. This "positive electron" is called a "hole" and can move through the filled band just as the electron can move through the conduction band. If the free electron and free hole recombine, the original state is restored.

In metals and semiconductors a great deal has been learned about the detailed nature of the energy bands and the motion of electrons and holes, whereas properties of defects seem to be less well known and are more difficult to study. Just the opposite is true for alkali halides, where it is relatively simple to study the defects but much more difficult to obtain information about the bands.

Electron Centers

In alkali halides there is a group of defects which may arise in the pure material and which capture electrons. These electron centers can be introduced into an alkali halide in various ways, of which an especially simple one is to heat the crystal in the vapor of the alkali metal at high temperature. The first and most prominent color center produced is called the F center. It is also the simplest, the most important, and the best understood. As shown in Fig. 2, it consists of an electron trapped at the site of a missing halide ion. The F center absorbs light in the visible region of the spectrum by a process like that illustrated in Fig. 1. In addition the F center causes a perturbation of its neighboring ions so that their ultraviolet absorption is shifted slightly from the energy of the pure lattice to lower energies. This appears as an absorption band called the β band (*2*). Finally, the F center gives rise to weak absorption bands, called the L bands, between the F and β bands (*3*). These involve transitions

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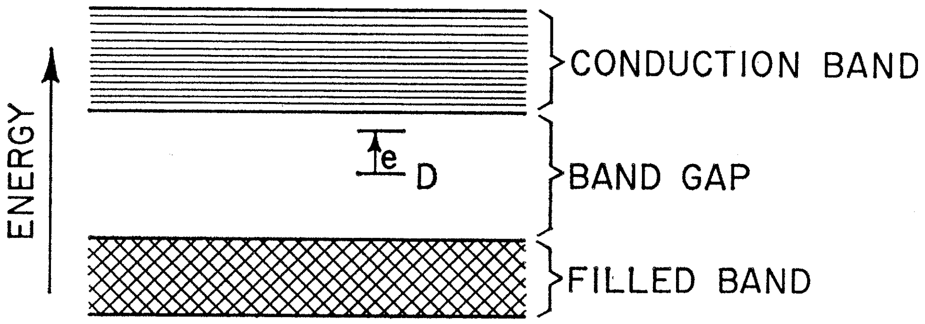

Fig. 1. Schematic representation of the electron energy band structure for an insulator. A defect, such as *D*, may introduce localized levels in the band gap, and optical transitions are possible between these levels.

of the F-center electron to excited states well inside the conduction band or perhaps even above it, in another band gap.

The model of the F center has been generally accepted for many years, and a vast array of electrical, optical, and thermal data are explained by it. Perhaps the most convincing evidence for the model arises from the study of this center by a combined electron- and nuclear-spin-resonance (ENDOR) technique. From these measurements it is possible to obtain the probability that the F-center electron will be near the nuclei of the surrounding ions out as far as the fourth or fifth nearest neighbors. These experimental results may be compared with theoretical calculations based on the F-center model. The agreement between experiments on LiF (*4*) and calculations on the F center (*5*) are quite convincing.

At temperatures near −100°C a new center may be made from the F center. If light is absorbed in the F center, its electron is raised into the conduction band by a combination of light and heat excitation. The electron is free to drift through the lattice and may be captured by another F center, which will then have two electrons (*6*). As shown in Fig. 2, this combination of two electrons at a halide ion vacancy is called an F′ center. The extra electron is held loosely, and therefore this center is stable only at low temperatures. For each F′ center formed, two F centers are destroyed, since the electron comes from one and is captured by another. Bleaching efficiencies have been measured that correspond to this picture.

If an electron is removed from the F center, what remains is only the negative ion vacancy. Since this has no electron it cannot absorb light directly. However, the vacancy does alter the normal ultraviolet absorption of the lattice near it; this lattice is seen as a band called the α band (*2*). The α center is illustrated in Fig. 2. These vacancies, or α centers, are not usually seen at room temperature, but this appears to be due to the fact that the vacancy captures an electron during the warming-up process —from the unstable F′ center, for instance.

After an alkali halide crystal has been colored by heating in alkali vapor at high temperatures and then been quenched rapidly to room temperature, it contains F centers almost exclusively. But if light is absorbed in the F band, the F band decreases and bands which absorb longer wavelengths begin to grow. First a band called the M band is seen, and then R bands, and finally N bands appear. At very long irradiations with light, these bands all bleach and the crystal is left with a light stain probably due to colloidal particles of alkali metal.

In recent years much has been learned about the nature of the M and R bands. It is now clear that the M center is composed of two adjacent F centers as shown in Fig. 2. The first evidence for this was the fact that the number of M centers is proportional to the square of the number of F centers when the F centers are distributed randomly either by rapid quenching techniques (*7*) or by being formed by treatment with x-rays at low temperatures (*8*). Such a center has an axis along the face diagonal of the crystal. Evidence for this orientation has been seen both in bleaching experiments using polarized light (*9*) and in studies of the polarized luminescence of the M center when excited with polarized light (*10*).

When more than one electron appears in a center, the electrons usually form pairs, with the paired electrons having spins in opposite directions so that the pair has a net magnetic moment of zero. It is usually necessary for a center to have an odd number of electrons before an electron-spin-resonance experiment is possible. For this reason the M center, with two electrons, has not been seen in spin resonance in its normal ground-state condition. It has recently been shown that ultraviolet irradiation of a crystal with M centers leads to the formation of an excited state with two electrons having parallel spins. Resonance studies are possible for such a center. This arrangement has a lifetime of about a minute, and enough of these excited centers can be made to permit ENDOR investigations, which fully substantiate the M-center model in Fig. 2 (*11*).

The R bands arise from the R center, which is a cluster of three F centers placed on the corners of an equilateral triangle, as shown in Fig. 2. If two of the F centers are in the plane of the paper, the third one might be in a plane of atoms just above the paper and adjacent to the other two. While such a configuration for the R center had been suspected for some time, a variety of incontrovertible data have appeared only very recently. No spin resonance is seen for this center even though it has an odd number of electrons. This appears to be due to the appearance of two interacting ground-state levels for the R center which are separated by only a small energy. If the crystal is compressed in one direction, the R center is distorted slightly and these two levels are separated by a large energy gap. It then becomes possible to see resonance in the ground state (*12*). The treatment which allowed resonance to be seen in the excited state of the M center also works for the R center, which can be excited to a condition in which the three electrons have parallel spin. Here too, ENDOR measurements substantiate the model (*13*).

It would seem likely that centers with even larger numbers of F centers can be formed, and indeed there is some evidence that a relatively weak band called the N band may consist of four F centers (*14*). But these higher aggregate centers are rather rare, and interest has centered principally on the simpler centers.

Recently both the M and R centers

have been made with one electron less than their usual number (*15*). In the case of the M center, the two F centers of which it is composed are first made to line up in a particular direction by bleaching with polarized light. Then hole trap centers are formed in ways to be described later in this article, and a hole is excited from the center and allowed to recombine with the M center, annihilating one of the M-center electrons. The resulting center is identified as arising from the M center by its orientation, which survives this treatment. It is called an F_2^+ center, since it consists of two F centers with a single positive charge as compared with the normal lattice. A corresponding R center treated similarly is called the F_3^+ center. The F_2^+ center has only one electron and it should be capable of being detected by spin resonance. This has, however, not yet been seen.

Hole Centers

All of the centers composed of electrons trapped at negative ion vacancies can also be produced by x-raying the crystal. The x-rays are absorbed by the crystal and produce high-energy primary electrons which in turn produce a large number of secondary electrons. All these electrons are free to move through the lattice and may be trapped at vacancies to form F centers or some of the more complex centers.

As was mentioned earlier, the intrinsic production of free electrons leads to the simultaneous production of free holes which have a positive charge. Just as the electron can be trapped at negative ion vacancies, so it might be expected that the hole could be trapped at positive ion vacancies. This idea dominated the early speculation about the nature of the centers involving trapped holes. It has turned out, however, that this parallelism does not exist in alkali halides and that the trapping processes for electrons and for holes are qualitatively different.

The first hole trap to be clearly understood was the V_K center, and the details of its structure came from an analysis of the elaborate spin-resonance spectrum that it shows (*16*). The resulting model of the V_K center is shown in Fig. 3. It consists of a hole which is localized between two halide ions and shared by them. An equivalent but more familiar way of describing this is to say that a molecule is formed consisting of two halogen atoms with a shared electron. In KCl, for instance, this would be a Cl_2^- molecule. The electron shared by the two chlorine atoms tends to pull the atoms together and binds them with the same sort of exchange energy that provides the binding for the H_2 gas molecule. As a result the two halogen atoms involved in the V_K center are displaced from their normal positions toward each other.

It should be noted that the V_K center, in contrast with the electron centers, does not involve any vacancies. Any time free holes are formed they are apt to be captured into the V_K configuration. However, the production of holes always means the production of free electrons, and unless these are trapped somewhere they will recombine with the holes at V_K centers, destroying the center. If appropriate traps for electrons are introduced into an alkali halide by incorporating small amounts of Ag^+, Tl^+, or Pb^{++}, large numbers of V_K centers can be formed and the optical absorption and polarization properties of the center may be studied (*17*).

The V_K center and other hole traps are best understood by starting with halogen molecules and taking the major binding forces to be those involving exchange interactions. For the electron centers we have previously discussed, the electron is held primarily by the electric charge centered at a missing-ion site, and the binding forces have a simple electrostatic nature. As a result, the electron and hole centers are not at all similar. There is no evidence, for instance, that an electron can be trapped by the perfect lattice in the way that the hole is trapped to form the V_K center.

If an alkali halide crystal is x-rayed at temperatures near those of liquid helium, another hole center is formed. It is called the H center, and its model, deduced from spin resonance (*18*) and optical experiments (*19*), is shown in Fig. 3. It is similar in some ways to the V_K center, and its optical absorption band is close to that of the V_K center. Again, it consists of a hole shared among halide ions. This time four ions are involved rather than two, but the principal inter-

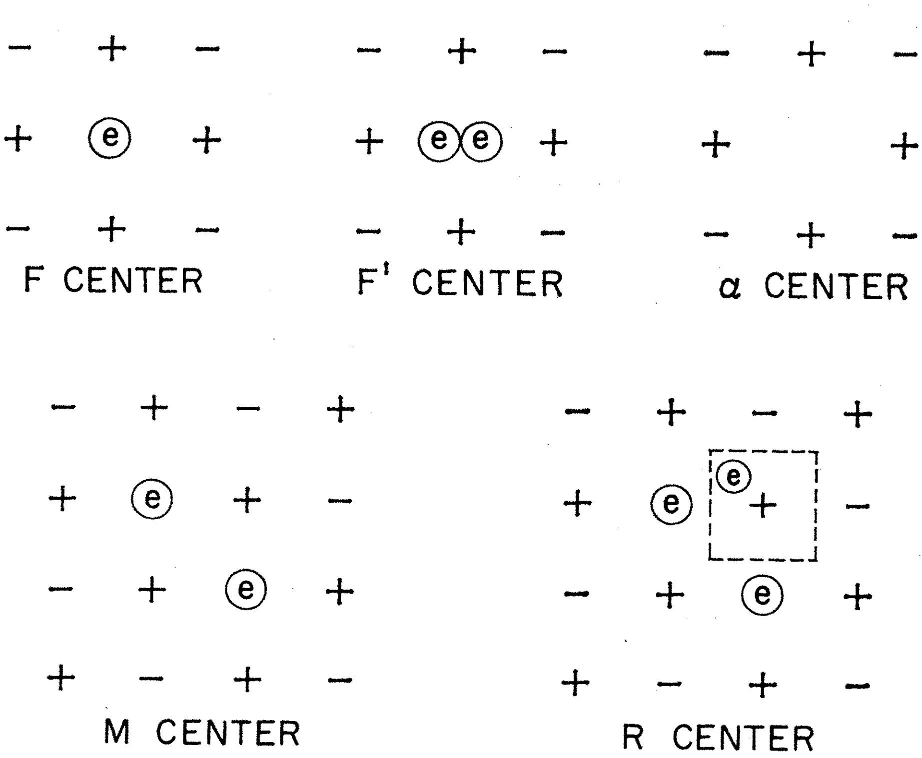

Fig. 2. The arrangement of ions and electrons for electron centers in alkali halides; + represents a positive ion, — represents a negative ion, and a circle enclosing an *e* represents an electron. The F, F′, and α centers are all built on a single vacancy with varying numbers of electrons. The M center consists of two adjacent F centers, and the R center consists of three F centers. For the R center the third F center may be considered to be in a plane above the paper and situated over the + surrounded by the dashed square. The three F centers making up the R band are then situated on the corners of an equilateral triangle.

action is still with the middle two ions. There is an important difference, however. The H center has four ions in the space where there should normally be only three. This results from removing a halide ion from its normal site and placing it in an interstitial position. Ways in which this may happen under x-ray bombardment will be discussed in later sections. The formation of the H center corresponds, essentially, to the formation of an interstitial atom. It is not very stable on warming and disappears by diffusion back to a vacant lattice site.

Optical absorption bands due to other hole trap centers have been found, but their detailed atomic composition is not yet clear. The H′ center appears at liquid-helium temperature on extended bombardment with x-rays (*20*). A weak V_1 band is often seen on treatment with x-rays at liquid-nitrogen temperature. At room temperature V_2 and V_3 bands appear both with x-ray treatment and when a crystal is heated in halogen vapor and quenched to room temperature. None of these centers appears to show spin resonance, and attempts to understand their nature have consequently had to employ less direct evidence.

Impurity Centers

All the centers described so far have been due to point defects in the pure lattice. It is possible to incorporate chemical impurities into the alkali halides and to study the properties of these centers.

Some of the first centers studied in this way were heavy-metal ions such as Tl^+, Ag^+, Cu^+, and Pb^{++}. It is often possible, as in the case of Tl^+, to attempt to correlate transitions in the solid with transitions occurring in the same ion in the gas (*21*). There are obvious differences due to the lattice in which the ion is placed: absorption and emission spectra show broad bands rather than sharp lines, and the absorption and emission are well separated in energy in the solid although they are at the same energy in the gas.

These effects for the impurities, and similar ones for centers like the F center, may be understood qualitatively by the use of a configuration coordinate diagram as shown in Fig. 4. In this kind of diagram the total energy of an impurity center is plotted as a function of some coordinate of the configuration. Often the coordinate may be taken as the distance from the impurity to its nearest neighbors. As this distance changes, the energy of the center changes, even if it is in its ground electronic state. Changes due to compression of the center and changes in electrostatic forces are some of the balancing forces which lead to an equilibrium distance for the ground state at the point *A* in Fig. 4. Thermal energy and lattice vibrations lead to appreciable oscillations of the system about the point *A*. If the system is at the configuration *A* and absorbs light, it will be raised to point *B* on the excited-state curve in such a short time that none of the nuclei will have moved. In other words, the configuration has not changed and a vertical transition to *B* results. But the distribution of electrons is different in the excited state from that in the ground state, and as a result the equilibrium position of the state, *C*, is found at a new configuration. The excited state relaxes from *B* to *C* by giving off thermal energy. In emission the process is repeated in the transition from *C* to *D* and in the release of thermal energy as the system goes from *D* to *A*. Obviously the emission energy (*C* to *D*) is not as large as the absorption energy (*A* to *B*); this accounts for the separation of absorption and emission bands. The broad absorption band arises from the thermal vibrations about the point *A*. Small variations in the coordinate lead to appreciable changes in energy since point *B* is on the side of the excited-state curve where energy is changing rapidly with configuration.

This simple picture has been extended to include the fact that if the system is a vibrating system it should have discrete energy levels. This refinement allows the model to describe low-temperature data where such quantum effects become important.

Although this model is very simple, it has been useful in a number of cases in describing the processes occurring in a center. Theoretical calculations of the configuration coordinate diagrams have been made for thallium in potassium chloride (*22*) and for the F center in lithium chloride (*23*).

Other impurity centers which have been extensively studied include H^-, OH^-, and O_2^-. A similar series is currently of great interest: SH^-, S^{--}, and S_2^-. Recently NO_2^- ions (*24*) and Sm^{+3} ions (*25*) have been extensively studied for the great wealth of detail in their optical spectra and for the information this gives about the interaction of the center and the lattice in which it is embedded. Alkali impurities can be seen if they are neighbors to an F center. They modify the F-center properties slightly and are called F_A centers (*26*). If a divalent ion such as Ca^{++} is incorporated in an alkali halide, a positive ion vacancy is also created to keep the crystal electrically neutral. At room temperature and below, the Ca^{++} and its vacancy are normally neighbors since there is a charge attraction between them. On x-ray treatment at low temperature a center has been seen which has been identified as a V_K center attached to this divalent ion-vacancy complex (*27*). At higher temperatures it appears that the addition of an F center to the same divalent ion-vacancy complex leads to still another center, called the Z_1 center (*28*). The study of the production, properties, and interaction of these impurity centers is a large and active field.

Radiation Effects

Having listed and described briefly the large number of point defects about which there is important information, we shall turn to the problem of how defects are formed by ionizing radiation. In particular we shall restrict our consideration to the case of very low temperatures produced by liquid helium. In the room-temperature region the effects of radiation are very complex because many parameters are important. Trace amounts of impurities frequently have an important effect, as does the amount of plastic strain suffered by the crystal. To further complicate affairs, the coloration depends not only on the dose of radiation received by the crystal but also on the rate at which the dose is supplied. While important steps have been made in understanding some of these effects, the processes of coloration at room temperature are far from clear.

At low temperatures, many of these complications disappear. The coloration is almost entirely independent of impurities, strain, and the rate at which the dose is applied (*29*). This leads fairly directly to the conclusion that the ionizing radiation produces color centers in the pure lattice. At low temperatures F centers and H centers, among others, are formed, and this pair is particularly simple. It was mentioned earlier that the H center corresponds to an interstitial halogen atom. If this combines with an F center, which is a halogen vacancy with an electron, the perfect lattice is reformed. It is believed that the F and H centers are formed together in pairs by the radiation; the halide ion is ejected into an interstitial position but leaves an electron behind in the vacancy, thus directly forming these centers. If the halide ion is ejected into an interstitial position but does not lose an electron to the vacancy, another pair of centers is formed. The vacancy gives rise to the α band, as was mentioned earlier, and recent work indicates that the interstitial ion gives rise to a band at 2300 Å in KBr (*30*). The ratio of α centers to F centers is about 8 to 1 in KBr that has been x-rayed at liquid-helium temperature.

The fact that ordinary x-rays are able to create interstitial ions is very surprising. Theoretical estimates of the energy necessary to make an interstitial ion are about 25 electron volts, and measurements in metals and semiconductors support this estimate. When ordinary x-rays are absorbed, fast electrons are emitted, and it is these electrons which cause the interstitial to be formed. In metals and semiconductors interstitials are formed by the transfer of momentum from a high-speed particle to the atom, which recoils into an interstitial position. But this process could produce a recoil energy of only a fraction of an electron volt in some cases encountered for alkali halides, and this is far less than the estimated minimum value. In addition, the efficiency of the process is very high in alkali halides, exceeding that in metals and semiconductors by a factor of 100 or more.

Several suggestions have been made concerning more indirect ways in which x-rays may produce interstitials. One suggestion for which there is experimental evidence (*31*) is that each of two neighboring halide ions loses an electron and that this "pair" leads to interstitial formation. If the pair forms a halogen molecule that becomes localized at one of the two halide sites, a vacancy and an interstitial are formed (*32*). Some evidence exists that K-shell ionization of the halide ion also makes a contribution to interstitial formation (*33*). In this case it is possible for the halide ion to lose several electrons and to reverse the sign of its charge. In an ionic crystal such an ion would tend to be expelled from its normal lattice position.

Another problem in low-temperature coloration is the large number of α centers (negative ion vacancies) compared with F centers. Since the negative ion vacancy can be shown to have a high cross section for capture of an electron, there must be forces that prevent it from doing so at low temperatures. Two mechanisms have been proposed, and it seems likely that both are important. It has been shown that in a high electric field a negative ion vacancy cannot capture an electron long enough to form an F center. If an interstitial halide ion is within a few lattice distances of a vacancy, its field can keep the vacancy from becoming an F center (*34*). The other mechanism involves a strong luminescence which is produced in alkali halides by x-rays at low temperatures and which is due to the recombination of an electron and a hole at a V_K center. In several alkali halides this luminescence spectrum overlaps

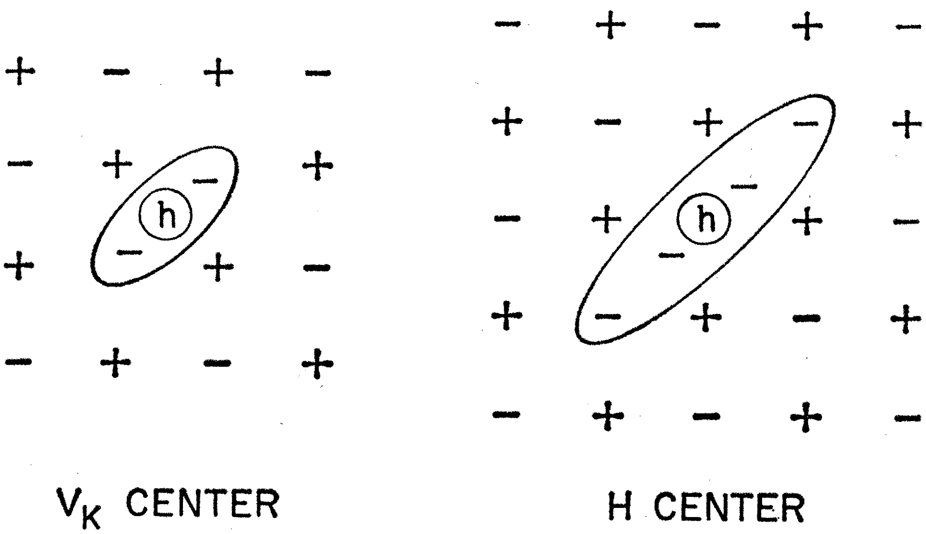

Fig. 3. The two best-known hole centers. The V_K center does not involve either vacancies or interstitial ions; it is self-trapped. The H center involves an interstitial halogen atom. The hole is represented by a circle enclosing an *h*.

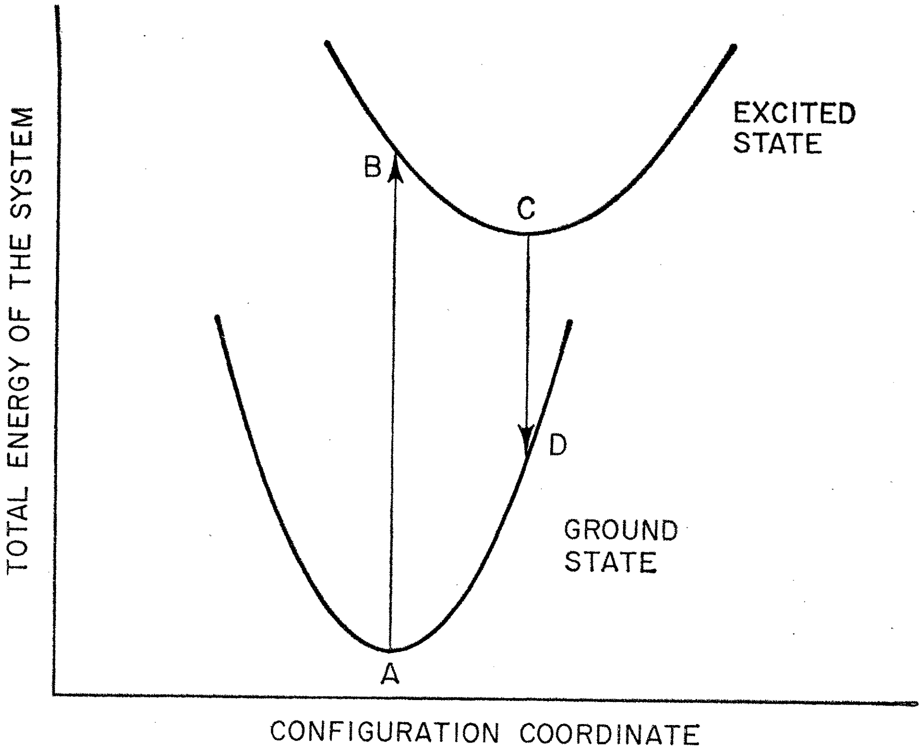

Fig. 4. A configuration coordinate diagram.

the F-center absorption band, and the luminescent light may bleach some of the F centers, leaving α centers (*35*).

In general, there is a satisfying amount known about radiation effects in alkali halides at low temperatures. Identification of the bands is nearly complete, some mechanisms of formation of interstitials have been worked out, and interactions between centers have been studied. Determined attempts are now being made to extend this study into the more difficult high temperature ranges.

Recent Activity

This review of point defects in alkali halides would hardly be complete without mention of three areas in which there has been a great deal of recent interest: the interaction of lattice vibrations with defects, the excited state of the F center, and theoretical developments.

One would expect the various color centers to interact with the vibrations of the lattice, and studies of such effects have been made over a number of years with the use of the configuration coordinate diagram. Experimentally, the variation of the width of the absorption and emission bands is determined as a function of temperature, and from these data the frequency of the important vibrational modes may be determined. This frequency is not quite that expected from the pure lattice, possibly because the presence of the defect disturbs the lattice in its vicinity (*36*). It has also been shown that the introduction of H^- and D^- into alkali halides gives rise to sharp infrared absorption bands as a result of the vibrations of these ions with the lattice (*37*). More recently, the introduction of a complex center such as NO_2^- has both given a very detailed spectrum in the near infrared, owing to its own absorption (*24*), and introduced sharp lines into the far infrared region, indicative of important modifications of the vibrational spectrum (*38*). Also, lines have been observed at the long-wavelength tail of some complex color centers such as the R centers (*39*). In some cases there are one, two, three, and so on, phonon lines as well as the zero lines (*40*). These lines are extremely sharp and correspond to the electronic transition in the center coupled with the creation of zero, one, two, . . . quantized bits of lattice vibrations, or phonons. From the difference in energy of these lines the frequency of the lattice vibrations involved in the particular transition can be obtained. A large experimental and theoretical effort is being marshalled to understand these effects.

Recently, information has been obtained on the excited state of the F center by investigation of the magneto-optical properties of this center (*41*). The excited state is not single but is split by a small energy. Ordinarily this splitting would be too small to be observed as a direct energy difference, but it does lead to rotation of the plane of polarization of transmitted light if a magnetic field is applied, and this can be measured with considerable accuracy. Here again, intensive theoretical study has been undertaken to understand this splitting of the excited state in a quantitative way (*42*).

A great deal of effort has recently been expended on calculating the configurations and energies of the states of the F centers (*23, 43*). This is a complex problem because the electron is spread over the nearest neighbors as well as being in the vacancy. In the excited state, polarization effects among the electrons of the neighboring ions have been shown to have very important effects in spreading the electron over a volume enclosing several hundred ions. Also, the positions of the neighboring ions are shifted from their usual ones in the perfect lattice. Since this shift is different for the ground and the excited state, it must be evaluated in each case, and these shifted positions must be used in the final calculation of the F-center properties. As a result of these calculations, theory and experiment are in substantial quantitative agreement.

A considerable effort has gone into studies of silver halides such as AgCl, alkaline earth fluorides such as CaF_2, and oxides such as MgO. One might expect that these other ionic insulators would have properties very similar to those of the alkali halides. While centers corresponding to the F center have recently been identified in some of these materials, the principal coloration properties seem to be associated with impurities. The reasons for this situation can only be guessed at, and it is possible that they are different for different materials. As a result, each of these classes of materials presents a new and interesting challenge in its own right. Once the nature of point defects and their production in materials other than alkali halides becomes really well established, comparisons between these materials should be very valuable in establishing generalized rules and mechanisms for the appearance of point defects in insulators.

References

1. A complete and readable account of the work in this field up to 1962 is given by J. H. Schulman and W. D. Compton, *Color Centers in Solids* (Pergamon, New York, 1962). The reader is referred there for more complete references. The papers cited below are intended to serve as introductions to the various topics and to point out some of the more recent studies.
2. C. Delbecq, P. Pringsheim, P. Yuster, *J. Chem. Phys.* **19**, 574 (1951).
3. F. Lüty, *Z. Physik* **160**, 1 (1960).
4. W. C. Holton and H. Blum, *Phys. Rev.* **125**, 89 (1962).
5. B. S. Gourary and F. J. Adrian, in *Solid State Physics*, F. Seitz and D. Turnbull, Eds. (Academic Press, New York, 1960), vol. 10.
6. H. Pick, *Nuovo Cimento* **7** (No. 2), 498 (1958).
7. C. Z. van Doorn, *Phys. Rev. Letters* **4**, 236 (1960).
8. B. Faraday, H. Rabin, W. D. Compton, *ibid.* **7**, 57 (1961).
9. M. Ueta, *J. Phys. Soc. Japan* **1**, 107 (1952).
10. J. Lambe and W. D. Compton, *Phys. Rev.* **106**, 684 (1957).
11. H. Seidel, *Phys. Letters* **7**, 27 (1963).
12. D. C. Krupka and R. H. Silsbee, *Phys. Rev. Letters* **12**, 193 (1964).
13. H. Seidel, M. Schwoerer, D. Schmid, *Z. Physik* **182**, 398 (1965).
14. S. Schnatterly and W. D. Compton, *Phys. Rev.* **135**, A227 (1964).
15. I. Schneider and H. Rabin, *Phys. Rev. Letters* **13**, 690 (1964).
16. T. G. Castner and W. Känzig, *J. Phys. Chem. Solids* **3**, 178 (1957).
17. C. J. Delbecq, B. Smaller, P. H. Yuster, *Phys. Rev.* **111**, 1235 (1958).
18. W. Känzig and T. O. Woodruff, *J. Phys. Chem. Solids* **9**, 70 (1958).
19. W. D. Compton and C. C. Klick, *Phys. Rev.* **110**, 349 (1958).
20. B. J. Faraday and W. D. Compton, *ibid.*, in press.
21. F. Seitz, *J. Chem. Phys.* **6**, 150 (1938).
22. F. E. Williams, *ibid.* **19**, 457 (1951).
23. R. F. Wood and H. W Joy, *Phys. Rev.* **136**, A451 (1964).
24. T. Timusk and W. Stande, *Phys. Rev. Letters* **13**, 373 (1964).
25. W. E. Bron and W. R. Heller, *Phys. Rev.* **136**, A1433 (1964).
26. K. Kojima, N. Nishimaki, T. Kojima, *J. Phys. Soc. Japan*, **16**, 2033 (1961); F. Lüty, *Z. Physik* **165**, 17 (1961) .
27. W. Hayes and G. M. Nichols, *Phys. Rev.* **117**, 993 (1960).
28. H. Härtel and F Lüty, *Z. Physik* **182**, 111 (1964).
29. H. Rabin and C. C. Klick, *Phys. Rev.* **117**, 1005 (1960).
30. G. Kurz and W. Gebbhardt, *Physica Stati Solidi* **7**, 351 (1964); N. Itoh, B. S. H. Royce, R. Smoluchowski, *Phys. Rev.* **137**, A1010 (1965).
31. V. H. Ritz, *Phys. Rev.* **133**, A1452 (1964).
32. C. C. Klick, *ibid.* **120**, 760 (1960).
33. J. Sharma and R. Smoluchowski, *ibid.* **137**, A259 (1965).
34. F. Lüty, *Halbleiter Probleme* (Vieweg, Braunschweig, 1961), vol. 6, p 238.
35. M. N. Kabler, *Phys. Rev.* **136**, A1296 (1964).
36. G. A. Russell and C. C. Klick, *ibid.* **101**, 1473 (1956).
37. G. Schaefer, *J. Phys. Chem. Solids* **12**, 223 (1960).
38. K. F. Renk, *Physics Letters* **14**, 281 (1965); A. J. Sievers and C. D. Lytle, *ibid.*, p. 271.
39. D. B. Fitchen, R. H. Silsbee, T. A. Fulton, E. L .Wolf, *Phys. Rev. Letters* **11**, 275 (1963).
40. C. B. Pierce, *Phys. Rev.* **135**, A83 (1964).
41. J. Mort, F. Lüty, F. C. Brown, *ibid.* **137**, A566 (1965); J. Margerie and R. Romestain, *Compt. Rend.* **258**, 4490 (1964).
42. D. Y. Smith, *Phys. Rev.* **137**, A574 (1965); C. H. Henry, S. E. Schnatterly, C. P. Slichter, *ibid.*, p. A583.
43. W. B. Fowler, *ibid.* **135**, A1725 (1964).