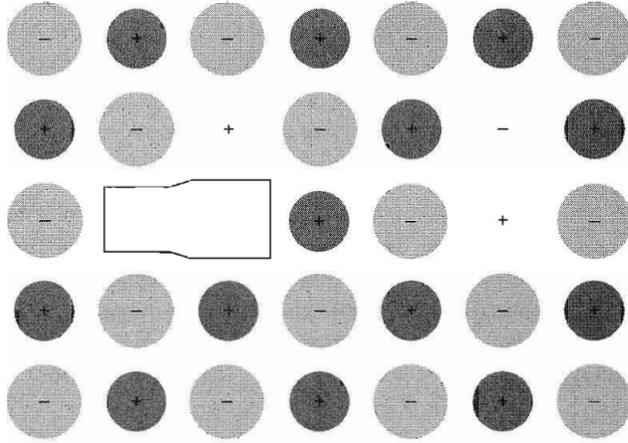


20

Point Defects

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Figure 1 A plane of a pure alkali halide crystal, showing two vacant positive ion sites, and a coupled pair of vacant sites of opposite sign.



CHAPTER 20: POINT DEFECTS

The common point imperfections in crystals are chemical impurities, vacant lattice sites, and extra atoms not in regular lattice positions. Linear imperfections are treated under dislocations, Chapter 21. The crystal surface is a planar imperfection, with electron, phonon, and magnon surface states.

Some important properties of crystals are controlled as much by imperfections as by the composition of the host crystal, which may act only as a solvent or matrix or vehicle for the imperfections. The conductivity of some semiconductors is due entirely to trace amounts of chemical impurities. The color and luminescence of many crystals arise from impurities or imperfections. Atomic diffusion may be accelerated enormously by impurities or imperfections. Mechanical and plastic properties are usually controlled by imperfections.

LATTICE VACANCIES

The simplest imperfection is a **lattice vacancy**, which is a missing atom or ion, also known as a **Schottky defect**. (Fig. 1). We create a Schottky defect in a perfect crystal by transferring an atom from a lattice site in the interior to a lattice site on the surface of the crystal. In thermal equilibrium a certain number of lattice vacancies are always present in an otherwise perfect crystal, because the entropy is increased by the presence of disorder in the structure.

In metals with close-packed structures the proportion of lattice sites vacant at temperatures just below the melting point is of the order of 10^{-3} to 10^{-4} . But in some alloys, in particular the very hard transition metal carbides such as TiC, the proportion of vacant sites of one component can be as high as 50 percent.

The probability that a given site is vacant is proportional to the Boltzmann factor for thermal equilibrium: $P = \exp(-E_v/k_B T)$, where E_v is the energy required to take an atom from a lattice site inside the crystal to a lattice site on the surface. If there are N atoms, the equilibrium number n of vacancies is given by the Boltzmann factor

$$\frac{n}{N - n} = \exp(-E_v/k_B T) . \quad (1)$$

If $n \ll N$, then

$$n/N \cong \exp(-E_v/k_B T) . \quad (2)$$

If $E_v \approx 1$ eV and $T \approx 1000$ K, then $n/N \approx e^{-12} \approx 10^{-5}$.

The equilibrium concentration of vacancies decreases as the temperature decreases. The actual concentration of vacancies will be higher than the

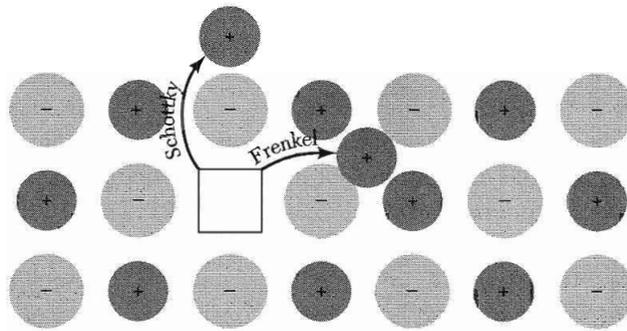


Figure 2 Schottky and Frenkel defects in an ionic crystal. The arrows indicate the displacement of the ions. In a Schottky defect the ion ends up on the surface of the crystal; in a Frenkel defect the ion is removed to an interstitial position.

equilibrium value if the crystal is grown at an elevated temperature and then cooled suddenly, thereby freezing in the vacancies (see the discussion of diffusion below).

In ionic crystals it is usually energetically favorable to form roughly equal numbers of positive and negative ion vacancies. The formation of pairs of vacancies keeps the crystal electrostatically neutral on a local scale. From a statistical calculation we obtain

$$n \cong N \exp(-E_p/2k_B T) \quad (3)$$

for the number of pairs, where E_p is the energy of formation of a pair.

Another vacancy defect is the **Frenkel defect** (Fig. 2) in which an atom is transferred from a lattice site to an **interstitial position**, a position not normally occupied by an atom. In pure alkali halides the most common lattice vacancies are Schottky defects; in pure silver halides the most common vacancies are Frenkel defects. The calculation of the equilibrium number of Frenkel defects proceeds along the lines of Problem 1. If the number n of Frenkel defects is much smaller than the number of lattice sites N and the number of interstitial sites N' , the result is

$$n \cong (NN')^{1/2} \exp(-E_I/2k_B T) , \quad (4)$$

where E_I is the energy necessary to remove an atom from a lattice site to an interstitial position.

Lattice vacancies are present in alkali halides when these contain additions of divalent elements. If a crystal of KCl is grown with controlled amounts of CaCl_2 , the density varies as if a K^+ lattice vacancy were formed for each Ca^{2+} ion in the crystal. The Ca^{2+} enters the lattice in a normal K^+ site and the two Cl^- ions enter two Cl^- sites in the KCl crystal (Fig. 3). Demands of charge neutrality result in a vacant metal ion site. The experimental results show that the addition of CaCl_2 to KCl lowers the density of the crystal. The density

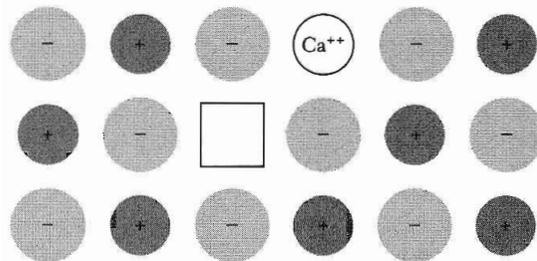


Figure 3 Production of a lattice vacancy by the solution of CaCl_2 in KCl : to ensure electrical neutrality, a positive ion vacancy is introduced into the lattice with each divalent cation Ca^{++} . The two Cl^- ions of CaCl_2 enter normal negative ion sites.

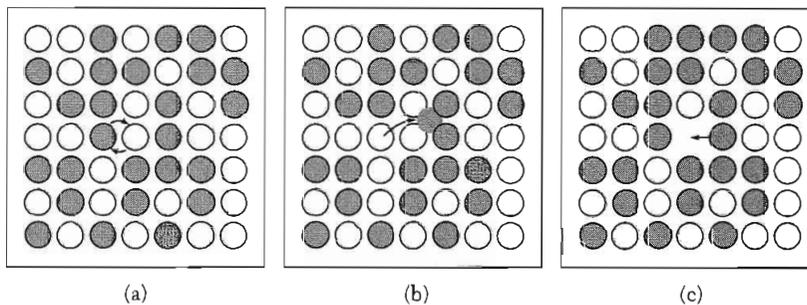


Figure 4 Three basic mechanisms of diffusion: (a) Interchange by rotation about a midpoint. More than two atoms may rotate together. (b) Migration through interstitial sites. (c) Atoms exchange position with vacant lattice sites. (After Seitz.)

would increase if no vacancies were produced, because Ca^{2+} is a heavier and smaller ion than K^+ .

The mechanism of electrical conductivity in alkali and silver halide crystals is usually by the motion of ions and not by the motion of electrons. This has been established by comparing the transport of charge with the transport of mass as measured by the material plated out on electrodes in contact with the crystal.

The study of ionic conductivity is an important tool in the investigation of lattice defects. Work on alkali and silver halides containing known additions of divalent metal ions shows that at not too high temperatures the ionic conductivity is directly proportional to the amount of divalent addition. This is not because the divalent ions are intrinsically highly mobile, for it is predominantly the monovalent metal ion which deposits at the cathode. The lattice vacancies introduced with the divalent ions are responsible for the enhanced diffusion (Fig. 4c). The diffusion of a vacancy in one direction is equivalent to the diffusion of an atom in the opposite direction. When lattice defects are generated thermally, their energy of formation gives an extra contribution to the heat capacity of the crystal, as shown in Fig. 5.

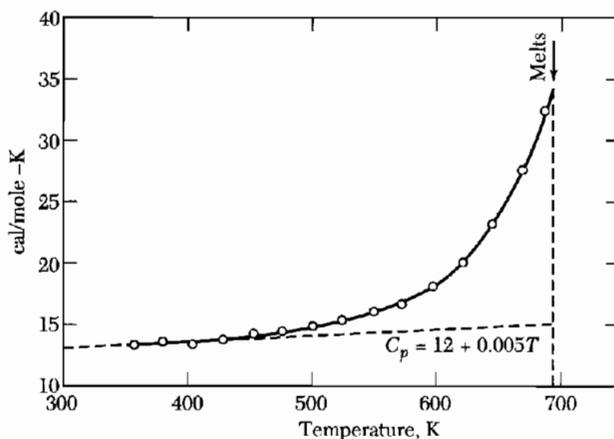


Figure 5 Heat capacity of silver bromide exhibiting the excess heat capacity from the formation of lattice defects. (After R. W. Christy and A. W. Lawson.)

An associated pair of vacancies of opposite sign exhibits an electric dipole moment, with contributions to the dielectric constant and dielectric loss due to the motion of pairs of vacancies. The dielectric relaxation time is a measure of the time required for one of the vacant sites to jump by one atomic position with respect to the other. The dipole moment can change at low frequencies, but not at high. In sodium chloride the relaxation frequency is 1000 s^{-1} at 85°C .

DIFFUSION

When there is a concentration gradient of impurity atoms or vacancies in a solid, there will be a flux of these through the solid. In equilibrium the impurities or vacancies will be distributed uniformly. The net flux J_N of atoms of one species in a solid is related to the gradient of the concentration N of this species by a phenomenological relation called **Fick's law**:

$$J_N = -D \text{ grad } N . \quad (5)$$

Here J_N is the number of atoms crossing unit area in unit time; the constant D is the **diffusion constant** or **diffusivity** and has the units cm^2/s or m^2/s . The minus sign means that diffusion occurs away from regions of high concentration. The form (5) of the law of diffusion is often adequate, but rigorously the gradient of the chemical potential is the driving force for diffusion and not the concentration gradient alone (*TP*, p. 406).

The diffusion constant is often found to vary with temperature as

$$D = D_0 \exp(-E/k_B T) ; \quad (6)$$

here E is the **activation energy** for the process. Experimental results on the diffusion of carbon in alpha iron are shown in Fig. 6. The data are represented

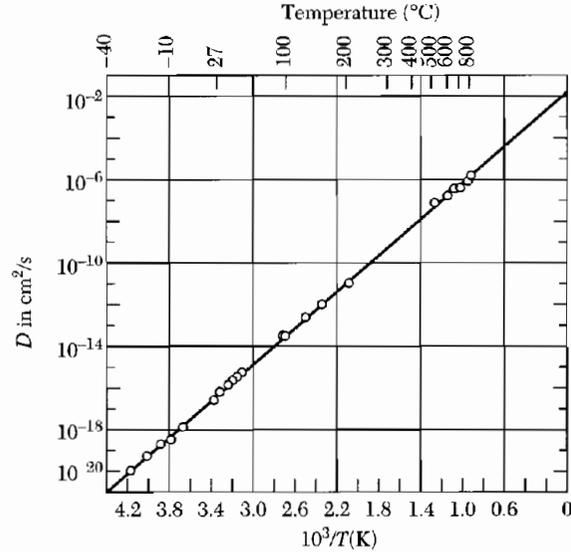


Figure 6 Diffusion coefficient of carbon in iron, after Wert. The logarithm of D is directly proportional to $1/T$.

Table 1 Diffusion constants and activation energies

Host crystal	Atom	D_0 $\text{cm}^2 \text{s}^{-1}$	E eV	Host crystal	Atom	D_0 $\text{cm}^2 \text{s}^{-1}$	E eV
Cu	Cu	0.20	2.04	Si	Al	8.0	3.47
Cu	Zn	0.34	1.98	Si	Ca	3.6	3.51
Ag	Ag	0.40	1.91	Si	In	16.0	3.90
Ag	Cu	1.2	2.00	Si	As	0.32	3.56
Ag	Au	0.26	1.98	Si	Sb	5.6	3.94
Ag	Pb	0.22	1.65	Si	Li	2×10^{-3}	0.66
Na	Na	0.24	0.45	Si	Au	1×10^{-3}	1.13
U	U	2×10^{-3}	1.20	Ge	Ge	10.0	3.1

by $E = 0.87$ eV, $D_0 = 0.020$ cm^2/s . Representative values of D_0 and E are given in Table 1.

To diffuse, an atom must overcome the potential energy barrier presented by its nearest neighbors. We treat the diffusion of impurity atoms between interstitial sites. The same argument will apply to the diffusion of vacant lattice sites. If the barrier is of height E , the atom will have sufficient thermal energy to pass over the barrier a fraction $\exp(-E/k_B T)$ of the time. Quantum tunneling through the barrier is another possible process, but is usually important only for the lightest nuclei, particularly hydrogen.

If ν is a characteristic atomic vibrational frequency, then the probability p that during unit time the atom will have enough thermal energy to pass over the barrier is

$$p \approx \nu \exp(-E/k_B T) . \quad (7)$$

In unit time the atom makes ν passes at the barrier, with a probability $\exp(-E/k_B T)$ of surmounting the barrier on each try. The quantity p is called the *jump frequency*.

We consider two parallel planes of impurity atoms in interstitial sites. The planes are separated by lattice constant a . There are S impurity atoms on one plane and $(S + a dS/dx)$ on the other. The net number of atoms crossing between the planes in unit time is $\approx -pa dS/dx$. If N is the total concentration of impurity atoms, then $S = aN$ per unit area of a plane.

The diffusion flux may now be written as

$$J_N \approx -pa^2(dN/dx) . \quad (8)$$

On comparison with (5) we have the result

$$D = \nu a^2 \exp(-E/k_B T) . \quad (9)$$

of the form (6) with $D_0 = \nu a^2$.

If the impurities are charged, we may find the ionic mobility $\bar{\mu}$ and the conductivity σ from the diffusivity by using the Einstein relation $k_B T \bar{\mu} = qD$ from *TP*, p. 406:

$$\bar{\mu} = (q\nu a^2/k_B T) \exp(-E/k_B T) ; \quad (10)$$

$$\sigma = Nq\bar{\mu} = (Nq^2\nu a^2/k_B T) \exp(-E/k_B T) , \quad (11)$$

where N is the concentration of impurity ions of charge q .

The proportion of vacancies is independent of temperature in the range in which the number of vacancies is determined by the number of divalent metal ions. Then the slope of a plot of $\ln \sigma$ versus $1/k_B T$ gives E_+ , the barrier activation energy for the jumping of positive ion vacancies (Table 2). Diffusion is very slow at low temperatures. At room temperature the jump frequency is of the order of 1 s^{-1} , and at 100 K it is of the order of 10^{-25} s^{-1} .

The proportion of vacancies in the temperature range in which the concentration of defects is determined by thermal generation is given by

$$f \cong \exp(-E_f/2k_B T) , \quad (12)$$

where E_f is the energy of formation of a vacancy pair, according to the theory of Schottky or Frenkel defects. Here the slope of a plot of $\ln \sigma$ versus $1/k_B T$ will be $E_+ + \frac{1}{2}E_f$, according to (10) and (12). From measurements in different

Table 2 Activation energy E_+ for motion of a positive ion vacancy

Values of the energy of formation of a vacancy pair, E_f , are also given. The numbers given in parentheses for the silver salts refer to interstitial silver ions.

Crystal	E_+ (eV)	E_f (eV)	Workers
NaCl	0.86	2.02	Etzcl and Maurer
LiF	0.65	2.68	Haven
LiCl	0.41	2.12	Haven
LiBr	0.31	1.80	Haven
LiI	0.38	1.34	Haven
KCl	0.89	2.1–2.4	Wagner; Kelting and Witt
AgCl	0.39(0.10)	1.4 ^a	Teltow
AgBr	0.25(0.11)	1.1 ^a	Compton

^aFor Frenkel defect.

temperature ranges we determine the energy of formation of a vacancy pair E_f and the jump activation energy E_+ .

The diffusion constant can be measured by radioactive tracer techniques. The diffusion of a known initial distribution of radioactive ions is followed as a function of time or distance. Values of the diffusion constant thus determined may be compared with values from ionic conductivities. The two sets of values do not usually agree within the experimental accuracy, suggesting the presence of a diffusion mechanism that does not involve the transport of charge. For example, the diffusion of pairs of positive and negative ion vacancies does not involve the transport of charge.

Metals

Self-diffusion in monatomic metals most commonly proceeds by lattice vacancies. **Self-diffusion** means the diffusion of atoms of the metal itself, and not of impurities. The activation energy for self-diffusion in copper is expected to be in the range 2.4 to 2.7 eV for diffusion through vacancies and 5.1 to 6.4 eV for diffusion through interstitial sites. Observed values of the activation energy are 1.7 to 2.1 eV.

Activation energies for diffusion in Li and Na can be determined from measurements of the temperature dependence of the nuclear resonance line width. As discussed under magnetic resonance, the resonance line width narrows when the jump frequency of an atom between sites becomes rapid in comparison with the frequency corresponding to the static line width. The values 0.57 eV and 0.45 eV were determined by NMR for Li and Na. Self-diffusion measurements for sodium also give 0.4 eV.

COLOR CENTERS

Pure alkali halide crystals are transparent throughout the visible region of the spectrum. A **color center** is a lattice defect that absorbs visible light. An ordinary lattice vacancy does not color alkali halide crystals, although it affects the absorption in the ultraviolet. The crystals may be colored in a number of ways:

- by the introduction of chemical impurities;
- by the introduction of an excess of the metal ion (we may heat the crystal in the vapor of the alkali metal and then cool it quickly—an NaCl crystal heated in the presence of sodium vapor becomes yellow; a KCl crystal heated in potassium vapor becomes magenta);
- by x-ray, γ -ray, neutron, and electron bombardment; and
- by electrolysis.

F Centers

The name *F* center comes from the German word for color, *Farbe*. We usually produce *F* centers by heating the crystal in excess alkali vapor or by x-irradiation. The central absorption band (*F* band) associated with *F* centers in several alkali halides are shown in Fig. 7, and the quantum energies are listed in Table 3. Experimental properties of *F* centers have been investigated in detail, originally by Pohl.

The *F* center has been identified by electron spin resonance as an electron bound at a negative ion vacancy (Fig. 8), in agreement with a model suggested by de Boer. When excess alkali atoms are added to an alkali halide crystal, a corresponding number of negative ion vacancies are created. The valence electron of the alkali atom is not bound to the atom; the electron migrates in the crystal and becomes bound to a vacant negative ion site. A negative ion vacancy in a perfect periodic lattice has the effect of an isolated positive charge: it attracts and binds an electron. We can simulate the electrostatic effect of

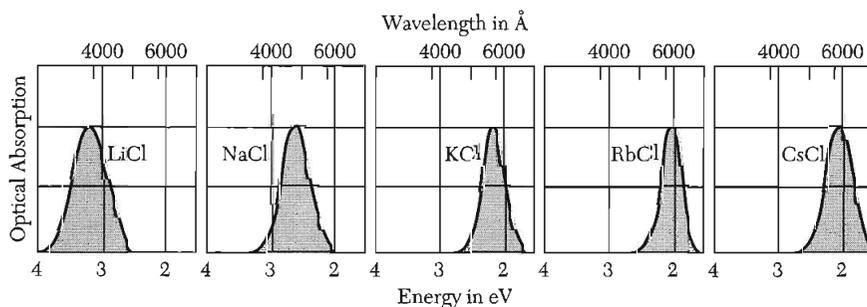


Figure 7 The *F* bands for several alkali halides: optical absorption versus wavelength for crystals that contain *F* centers.

Table 3 Experimental F center absorption energies, in eV

LiCl	3.1	NaBr	2.3
NaCl	2.7	KBr	2.0
KCl	2.2	RbBr	1.8
RbCl	2.0	LiF	5.0
CsCl	2.0	NaF	3.6
LiBr	2.7	KF	2.7

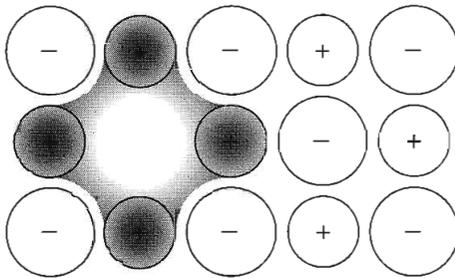


Figure 8 An F center is a negative ion vacancy with one excess electron bound at the vacancy. The distribution of the excess electron is largely on the positive metal ions adjacent to the vacant lattice site.

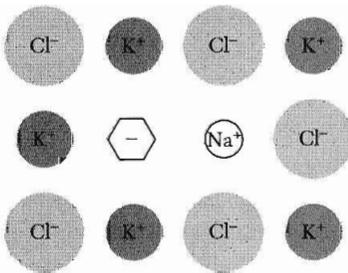


Figure 9 An F_A center in KCl: one of the six K^+ ions which bind an F center is replaced by another alkali ion, here Na^+ .

a negative ion vacancy by adding a positive charge q to the normal charge $-q$ of an occupied negative ion site.

The F center is the simplest trapped-electron center in alkali halide crystals. The optical absorption of an F center arises from an electric dipole transition to a bound excited state of the center.

Other Centers in Alkali Halides

In the F_A center one of the six nearest neighbors of an F center has been replaced by a different alkali ion, Fig. 9. More complex trapped-electron centers are formed by groups of F centers, Fig. 10 and 11. Thus two adjacent F centers form an M center. Three adjacent F centers form an R center. Different centers are distinguished by their optical absorption frequencies.

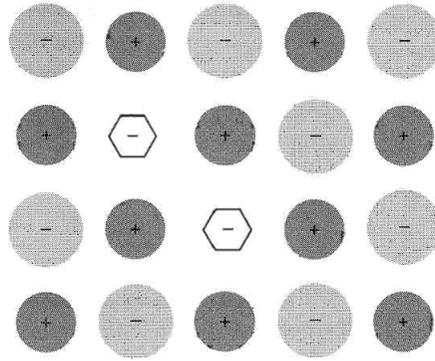


Figure 10 An M center consists of two adjacent F centers.

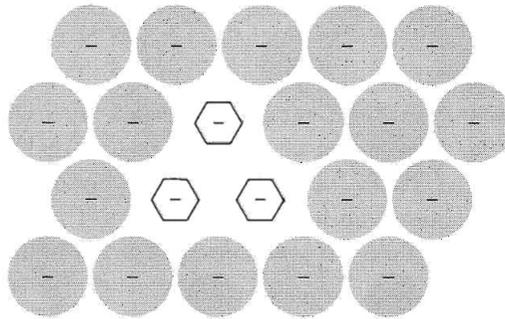


Figure 11 An R center consists of three adjacent F centers; that is, a group of three negative ion vacancies in a $[111]$ plane of the NaCl structure, with three associated electrons.

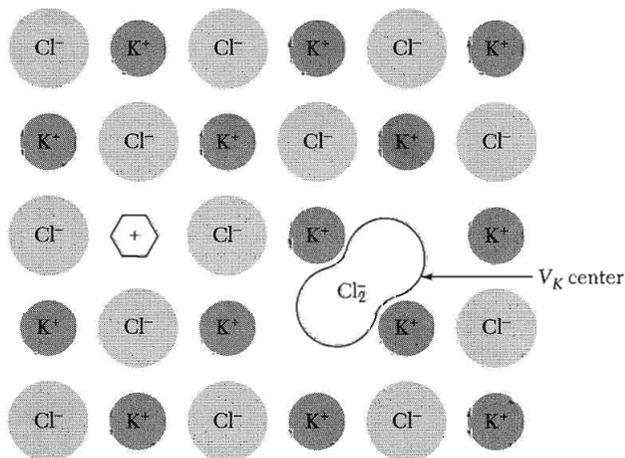


Figure 12 A V_K center formed when a hole is trapped by a pair of negative ions resembles a negative halogen molecule ion, which is Cl_2^- in KCl. No lattice vacancies or extra atoms are involved in a V_K center. The center at the left of the figure probably is not stable: the hexagon represents a hole trapped near a positive ion vacancy; such a center would be the antimorph to an F center. Holes have a lower energy trapped in a V_K center than in an anti- F center.

Holes may be trapped to form color centers, but hole centers are not usually as simple as electron centers. For example, a hole in the filled p^6 shell of a halogen ion leaves the ion in a p^5 configuration, whereas an electron added to the filled p^6 shell of an alkali ion leaves the ion in a p^6s configuration.

The chemistry of the two centers is different: p^6s acts as a spherically symmetric ion, but p^5 acts as an asymmetric ion and, by virtue of the Jahn-Teller effect, will distort its immediate surroundings in the crystal.

The antimorph to the F center is a hole trapped at a positive ion vacancy, but no such center has been identified experimentally in alkali halides; in insulating oxides the O^- (called V^-) defect is known. The best-known trapped-hole center is the V_K center, Fig. 12. The V_K center is formed when a hole is trapped by a halogen ion in an alkali halide crystal. Electron spin resonance shows that the center is like a negative halogen molecular ion, such as Cl_2^- in KCl. The Jahn-Teller trapping of free holes is the most effective form of self-trapping of charge carriers in perfect crystals.

Problems

1. **Frenkel defects.** Show that the number n of interstitial atoms in equilibrium with n lattice vacancies in a crystal having N lattice points and N' possible interstitial positions is given by the equation

$$E_I = k_B T \ln [(N - n)(N' - n)/n^2] ,$$

whence, for $n \ll N, N'$, we have $n \approx (NN')^{1/2} \exp(-E_I/2k_B T)$. Here E_I is the energy necessary to remove an atom from a lattice site to an interstitial position.

2. **Schottky vacancies.** Suppose that the energy required to remove a sodium atom from the inside of a sodium crystal to the boundary is 1 eV. Calculate the concentration of Schottky vacancies at 300 K.
3. **F center.** (a) Treat an F center as a free electron of mass m moving in the field of a point charge e in a medium of dielectric constant $\epsilon = n^2$; what is the $1s-2p$ energy difference of F centers in NaCl? (b) Compare from Table 3 the F center excitation energy in NaCl with the $3s-3p$ energy difference of the free sodium atom.