Frenkel-type and Schottky-type defects

Masatsugu Sei Suzuki
Department of Physics, SUNY at Binghamton
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The simplest imperfection is a lattice vacancy, which is a missing atom or ion, known as a Schottky defect. 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 crystal. In thermal equilibrium in an otherwise perfect crystal a certain number of lattice vacancies are always present, because the entropy is increased by the presence of disorder in the structure. At a finite temperature the equilibrium condition of a crystal is the state of minimum free energy $F = E - ST$.

The probability that a given lattice site is vacant is given simply by the Boltzmann factor for thermal equilibrium at temperature T;

$$P = e^{-\beta E_V}$$

where ε_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 ratio of vacant to filled sites.

$$\frac{n}{N} \approx e^{-\beta\varepsilon_V}$$

Another type of vacancy defect is the Frenkel defect, in which an atom is transferred from a lattice site to in interstitial position, a position not normally occupied by an atom. If the number n of Frenkel defect is much smaller than the number of lattice sites N and the number of interstitial sites N', n is evaluated as

$$n \approx \sqrt{NN'} \exp(-\beta\varepsilon_I / 2)$$

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

Yakov Il'ich Frenkel (Russian: Яков Ильич Френкель) (10 February 1894 – 23 January 1952) was a Soviet physicist renowned for his works in the field of condensed matter physics. He is also known as Jacov Frenkel.

https://en.wikipedia.org/wiki/Yakov_Frenkel

Walter Hermann Schottky (23 July 1886– 4 March 1976) was a German physicist who played a major early role in developing the theory of electron and ion emission phenomena, invented the screen-grid vacuum tube in 1915 and the pentode in 1919 while working at Siemens, co-invented the ribbon microphone and ribbon loudspeaker along with Dr. Erwin Gerlach in 1924 and later made many significant contributions in the areas of semiconductor devices, technical physics and technology.

https://en.wikipedia.org/wiki/Walter_H._Schottky

1. Frenkel-type defect

((Problem))

N atoms are arranged regularly so as to form a perfect crystal. If one replaces *n* atoms among *N* atoms ($1 << n << N$) from the lattice sites to interstices of the lattice, this becomes an imperfect crystal with *n* defects of the Frenkel type. The number *N'* of the interstitial sites into which an atom can enter is of the same order of magnitudes as *N*. Let *w* be the energy necessary to remove an atom from a lattice site to an interstitial site, Show that, in the equilibrium state at temperature *T* such that $w >> k_B T$, the following relation is valid

$$\frac{n^2}{(N-n)(N'-n)} = e^{-\beta w}, \qquad n = \sqrt{NN'} e^{-\beta w/2}$$

with $\beta = \dfrac{1}{k_B T}$.

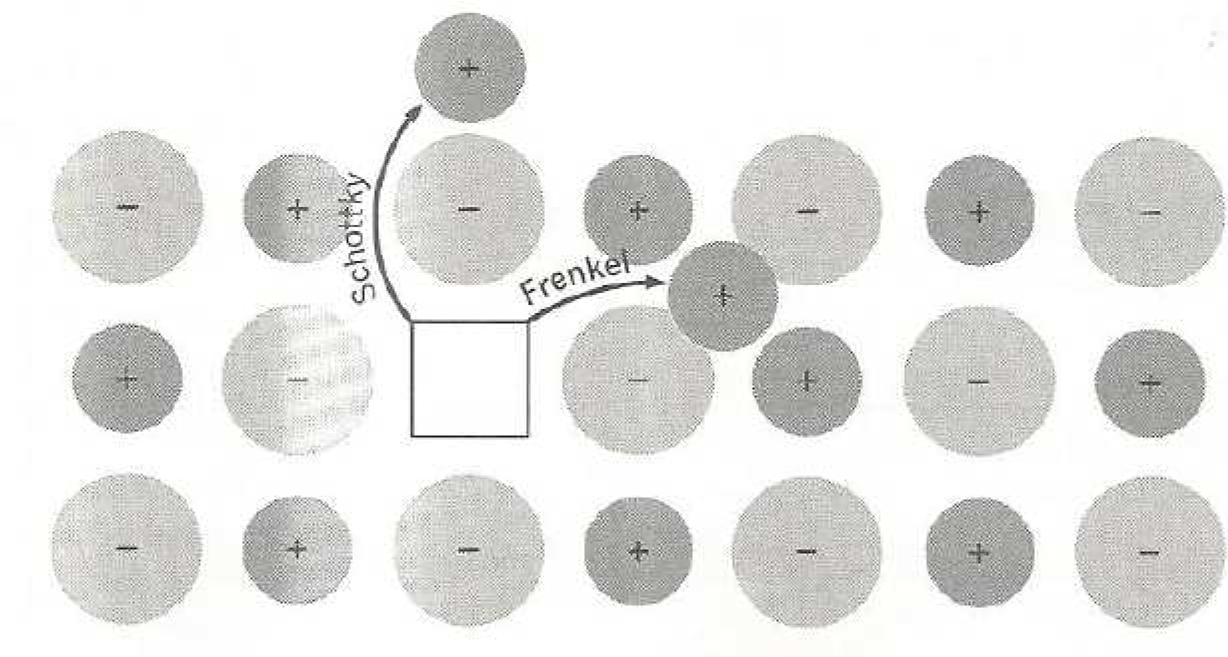

Fig. Schottky and Frenkel defects in an ionic crystal. The arrows indicate the displacement of the ions. In a Schottky defect the ion ends up on the surface of the crystal. In Frenkel defect, it removed to in interstitial position (Kittel, ISSP 4th edition).

((**Solution**))

Because $n << N$ and $n << N'$, one may assume that interstitial atoms and vacancies are separated from each other by sufficiently large distances. In this case, one can suppose that the energy of the imperfect crystal is higher than that of the perfect by the amount

$$E(n) = nw\,.$$

in which w is the energy required to create a Frenkel pair. The number of possible ways of removing n atoms from N lattice points and distributing them among N' interstitial sites is given by

$$W(n) = \frac{N!}{(N-n)!n!}\frac{N'!}{(N'-n)!n!}$$

In equilibrium the system is in the state of lowest free energy (Helmholtz free energy)

$$F(n) = E(n) - TS(n)$$

Note that

$$\frac{S(n)}{k_B} = \ln[W(n)]$$
$$= k_B\{\ln[\frac{N!}{(N-n)!n!}] + \ln[\frac{N'!}{(N'-n)!n!}]\}$$
$$= \ln N! - \ln n! - \ln(N-n)! + \ln N'! - \ln n! - \ln(N'-n)!$$
$$\approx N\ln(N) - N - n\ln n + n - (N-n)\ln(N-n) + N - n$$
$$+ N'\ln(N') - N' - n\ln n + n - (N'-n)\ln(N'-n) + N' - n$$
$$= N\ln(N) + N'\ln(N') - 2n\ln n - (N-n)\ln(N-n)$$
$$- (N'-n)\ln(N'-n)$$

The minimum of F as a function of n is given by

$$\frac{\partial F}{\partial n} = 0$$

or

$$-2\ln n + \ln(N-n) + \ln(N'-n) - \beta w = 0$$

leading to the equation

$$\frac{(N-n)(N'-n)}{n^2} = e^{\beta w}$$

Since $1 << n << N$ and $1 << n' << N$, we get the approximation as

$$\frac{NN'}{n^2} = e^{\beta w}$$

or

$$\frac{n^2}{NN'} = e^{-\beta\omega}, \qquad \text{or} \qquad n = \sqrt{NN'}e^{-\beta\omega/2}$$

The temperature dependence of the concentration n follows the Arrhenius law with the activation energy which is half the energy required for the creation of a Frenkel-pair. The factor of two in the denominator of the exponent arises because vacancies as well as interstitial atoms are distributed independently in the crystal. One therefore has two independent contributions to the entropy.

((Microcanonical ensemble))

$$\begin{aligned}\frac{S(n)}{k_B} &= \ln W(n) \\ &= N\ln(N) + N'\ln(N') - 2n\ln n - (N-n)\ln(N-n) \\ &\quad - (N'-n)\ln(N'-n)\end{aligned}$$

The energy is

$$E(n) = nw\,.$$

Then the entropy is expressed as a function of E,

$$\begin{aligned}S(E) &= k_B \ln W(n) \\ &= k_B[N\ln(N) + N'\ln(N') - 2n\ln n \\ &\quad - (N-n)\ln(N-n) - (N'-n)\ln(N'-n)] \\ &= k_B[N\ln(N) + N'\ln(N') - 2\frac{E}{w}\ln\frac{E}{w} \\ &\quad - (N-\frac{E}{w})\ln(N-\frac{E}{w}) - (N'-\frac{E}{w})\ln(N'-\frac{E}{w})]\end{aligned}$$

for $n = \dfrac{E}{w}$. The temperature T is related to the entropy S as

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right) = \frac{k_B}{w}[\ln(N-\frac{E}{w}) + \ln(N'-\frac{E}{w}) - 2\ln\frac{E}{w}]$$

or

$$\frac{(N-n)(N'-n)}{n^2} = e^{\beta w}$$

since $E = nw$. For $n << N$ and $n << N'$ we have

$$n = \sqrt{NN'}e^{-\beta w/2}.$$

2. Schottky type defect

((Problem))

If n atoms in a perfect crystal formed by N atoms ($1 << n << N$) are displaced from lattice sites inside the crystal to lattice sites on the surface, it becomes imperfect, having defects of the Schottky type. Let w be the energy necessary to displace an atom from the inside to the surface. Show that in the equilibrium state at temperature T satisfying $w >> k_B T$ one has

$$\frac{n}{N+n} = e^{-\beta w} \quad \text{or} \qquad n = Ne^{-\beta w},$$

if one can neglect any effect due to the change in the volume of the crystal.

((**Solution**))

When n atoms are displaced to the surface, there are n holes and N atoms in $N+n$ lattice points. Thus the entropy is

$$\begin{aligned} S(n) &= k_B \ln[\frac{(N+n)!}{N!n!}] \\ &= k_B[\ln(N+n)! - \ln N! - \ln n!] \\ &\approx k_B[(N+n)\ln(N+n) - N - n - N\ln N + N - n\ln n + n] \\ &= k_B[(N+n)\ln(N+n) - N\ln N - n\ln n] \end{aligned}$$

where $\frac{(N+n)!}{N!n!}$ is the number of ways of distributing holes and atoms. Since the energy is

$$E(n) = nw.$$

So the Helmholtz free energy is

$$\begin{aligned} F(n) &= E(n) - TS(n) \\ &= nw - k_B T[(N+n)\ln(N+n) - N\ln N - n\ln n] \end{aligned}$$

From the condition that F having a minimum, we get

$$\frac{\partial F(n)}{\partial n} = w - k_B T[\ln(N+n) - \ln n]$$
$$= w - k_B T \ln(\frac{N+n}{n})$$
$$= 0$$

Hence, we have

$$\frac{N+n}{n} = e^{\beta w}$$

or

$$\frac{n}{N+n} = e^{-\beta w}$$

((**Micro-canonical ensemble**))

$$S = S(n)$$
$$= k_B \ln[\frac{(N+n)!}{N!n!}]$$
$$= k_B[(N+n)\ln(N+n) - N\ln N - n\ln n]$$

$$U = E(n) = nw$$

From the definition of temperature, we get

$$\frac{1}{T} = \frac{\partial S}{\partial U}$$
$$= \frac{\partial n}{\partial U}\frac{\partial S}{\partial n}$$
$$= \frac{k_B}{w}\ln\left(\frac{N+n}{n}\right)$$

or

$$\ln(\frac{N+n}{n}) = \beta w$$

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