PHYSICAL REVIEW B VOLUME 24, NUMBER 12 15 DECEMBER 1981

Brief Reports

Brief Reports are short papers which report on completed research which, while meeting the usual **Physical Review** *standards of scientific quality, does not warrant a regular article. (Addenda to papers previously published in the* **Physical Review** *by the same authors are included in Brief Reports.) A Brief Report may be no longer than 3½ printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Use of Fermi-Dirac statistics for defects in solids

R. A. Johnson
Materials Science Department, University of Virginia, Charlottesville, Virginia 22901
(Received 15 June 1981)

The Fermi-Dirac distribution function is an approximation describing a special case of Boltzmann statistics. A general occupation probability formula is derived and a criterion given for the use of Fermi-Dirac statistics. Application to classical problems of defects in solids is discussed.

As pointed out by Beshers,[1] the Fermi-Dirac distribution function is applicable to impurity atoms in a crystal in a case, for example, where the impurities interact with a stress field so that there is a spread of energies depending on position and/or orientation. The Fermi-Dirac distribution function is an approximation describing a special case of Boltzmann statistics. It is commonly derived by considering Gibbsian ensemble averages or by averaging over a large number of states of a single thermodynamic system, but it is difficult to assess the physical conditions required for these derivations to be valid. The following discussion is given to help clarify these conditions.

If a system has a number of discrete states, the probability of being in a state with energy Q_i is

$$P_i=\frac{e^{-Q_i/kT}}{\sum_i e^{-Q_i/kT}}. \tag{1}$$

The sum is over system states not energy states, because of possible degeneracies in the energy.

For a system consisting of n indistinguishable particles in m discrete particle states with energies E_j, the total energy is

$$Q_i=\sum_j f_{ij}E_j, \tag{2}$$

where f_{ij} is the number of particles in the jth particle state when the system is in the ith system state and the sum is over particle states. With a system in which (a) each particle state is either empty or occupied by one particle (i.e., f_{ij} is either 0 or 1), and (b) the E_j's are constant independent of the state of the system, the sum of the P_i's in which the kth particle state is occupied (the occupation probability of the kth state) is

$$F_k^{(n)}=\frac{nR_k^{(n)}}{\sum_j R_j^{(n)}}, \tag{3}$$

with the superscript n indicating the number of particles in the system and

$$R_k^{(n)}=R_k^{(1)}\left[\sum_j R_j^{(n-1)}-(n-1)R_k^{(n-1)}\right], \tag{4}$$

$$R_k^{(1)}=e^{-E_k/kT}. \tag{5}$$

This formulation is correct for any number of particles and states but is inconvenient to use for large m and n because mn recursion calculations must be carried out.

After some algebraic manipulation, Eq. (3) can be written in the form

$$F_k^{(n)}=\frac{1}{e^{E_k/kt}D_k^{(n)}+1}, \tag{6}$$

$$D_k^{(n)}=\frac{F_k^{(n+1)}}{F_k^{(n)}}\frac{\sum_j R_j^{(n+1)}}{(n+1)\sum_j R_j^{(n)}}. \tag{7}$$

The second term in the product on the right-hand

side of Eq. (7) is independent of the particle state k. Thus, $D_k^{(n)}$ is independent of k if the ratio $F_k^{(n+1)}/F_k^{(n)}$ is independent of k. The resulting $D^{(n)}$ is then taken as

$$D^{(n)}=e^{-\mu^{(n)}/kT}, \tag{8}$$

and

$$F_k^{(n)}=\frac{1}{e^{(E_k-\mu^{(n)})/kT}+1}, \tag{9}$$

the standard form of the Fermi-Dirac distribution function. Instead of calculating $D^{(n)}$ from the recursion relations, it can be determined through the conservation condition

$$\sum_j F_j^{(n)}=n. \tag{10}$$

In general, the Fermi-Dirac distribution function overestimates the occupation probability of the states with lowest probabilities and underestimates the occupation probability of the states with highest probabilities. The resulting errors become negligible when the ratio $F_k^{(n+1)}/F_k^{(n)}$ becomes independent of the particle state k.

If condition (a) on the system is changed to permit occupancy of each particle state by any number of particles, the only modifications in this formalism are that the minus in front of the second term in Eq. (4) becomes a plus and pluses in Eqs. (6) and (9) become minuses. Thus, the criterion for applicability of Bose-Einstein statistics is the same as for Fermi-Dirac statistics, i.e., that $F_k^{(n+1)}/F_k^{(n)}$ is independent of k.

As an example, assume there are trapping sites for impurities which are filled with one impurity. With 10 ppm trapping sites with binding energy 0.4 eV, 20 ppm trapping sites with binding energy 0.3 eV, and 30 ppm impurities, the concentration of impurities at the trapping sites is 6.95 and 2.23 ppm, respectively, at 400 K using the Fermi-Dirac formula. This value for the more tightly bound sites is almost 1% lower than that calculated with 10^6 total sites using the recursion relations and the values of $F_k^{(31)}/F_k^{(30)}$ vary by almost 3%. The same numbers can be applied to trapping sites in a semiconductor band gap. The errors due to the use of the Fermi-Dirac distribution function are minor for practical purposes in this example, but do illustrate that it is an approximate formula and must be used with care. It is clearly a better approximation than the more common procedure of incorrectly using Boltzmann statistics by taking the ratio of the occupation of the two types of trapping sites equal to the ratio of their Boltzmann factors, which gives 18.2 in this example.

Discussions with G. J. Dienes are gratefully acknowledged. This work was supported by the National Science Foundation Grant No. DMR 78-07539.

[1]D. N. Beshers, Acta Metall. 6, 521 (1958).