JOURNAL OF MATERIALS SCIENCE 8 (1973) 385–396

The entropy of binding between vacancies and solute atoms in harmonic lattices–computer experiments in linear and square lattices

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Entropy changes related to point defects within the high-temperature limit have been studied, on the basis of exact frequency spectra obtained by computer calculations, for linear and square lattices in the light of lattice vibration in the harmonic nearest-neighbour-force approximation.

The binding entropy of a vacancy-solute pair is independent of the solute mass but depends on the force-constant around the defect, whereas the entropy change due to substitution by a solute atom is dependent on the solute mass as well as the force constant. For square lattices, the displacement amplitude of atoms has been shown in connection with the localized or resonance mode, which may have implications for solute diffusion.

1. Introduction

Current theory of solute diffusion in metals requires that vacancies have some interaction with solute atoms. Such interaction affects the formation and migration of vacancies in metals depending on the valence, the atomic size and other characteristics of the solute atom. The interaction can be described in terms of the binding free energy, or the binding energy and the binding entropy between a vacancy and a solute atom. Because of the significance of these parameters, many experimental and theoretical investigations have been carried out on the binding energy [1], but very few on the binding entropy [2-4].

There have been reported two experimental methods which can give the binding energy as well as the binding entropy correctly, at least in principle. One is the measurement of the equilibrium concentration of vacancies in dilute alloys by means of simultaneous measurements of the linear dilatation and the lattice parameter change of a specimen [2]. The other is to determine the binding entropy from the resistivity measurement of quenched dilute alloys, which has been suggested by Takamura *et al* [3].

Vineyard and Dienes [5] have pointed out that the formation entropy of a point defect consists only of the vibrational entropy change and the term arising from the temperature-dependent part of the formation energy can be excluded. In the same sense, the binding entropy of a vacancy-solute pair can also be determined from the vibrational entropy change, i.e. the change in the frequency spectrum which is to be observed when free vacancies are bound to solute atoms.

Therefore, the entropy change related to the formation and the association of point defects is given by the vibrational entropy change, which is described within the high-temperature approximation by

$$\Delta S = -k \sum \ln(\omega_i/\omega_{0i}) , \qquad (1)$$

where k is the Boltzmann's constant, and ω_0 and ω are normal mode frequencies of the lattice before and after the change of state. In the harmonic lattice, the vibrational frequencies can be expressed simply by the interatomic force and the atomic mass. In a real crystal the frequency spectrum is changed with the temperature through the anharmonicity, hence the vibrational entropy change could be tem-

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perature-dependent. For simplicity, however, the anharmonicity is not taken into account in this paper.

The present paper primarily aims at knowing the change in the entropy when vacancies are associated with solute atoms, with particular reference to the change in the atomic force and the solute mass. For this purpose, computer calculations are made of the exact frequency spectra in linear and square lattices containing vacancies and solute atoms in the nearest-neighbour harmonic approximation. The calculation method used for linear lattices is the one originally suggested by Dean [6] and modified by Rosenstock and McGill [7]. For square lattices, eigenfrequencies and the belonging eigenvectors of the dynamical matrix of a system are directly calculated by means of the "threshold Jacobi method". Therefore, for square lattices not only frequency spectra but also vibrational amplitudes of atoms are obtained, which may give useful information on the solute diffusion.

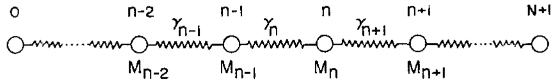

Figure 1 A linear lattice composed of $N + 2$ atoms with fixed ends. Each atom is coupled to its nearest neighbours by elastic springs obeying Hooke's law. M_n is the mass of nth atom, and γ_n denotes the force constant of the spring coupling atoms $n - 1$ and n.

2. Frequency spectra in one- and two-dimensional lattices

2.1. One-dimensional linear lattice

A linear chain of $N + 2$ atoms with fixed ends is shown in Fig. 1, in which each atom is coupled to its nearest neighbours by elastic springs obeying Hooke's law. When the nth atom of mass M_n is displaced from its equilibrium site by $U_n(t)$ at time t, the equation describing the vibrational motion is given by

$$M_n \,\mathrm{d}^2 U_n(t)/\mathrm{d}t^2 = \gamma_n \{U_{n-1}(t) - U_n(t)\} + \gamma_{n+1} \{U_{n+1}(t) - U_n(t)\}\,, \quad (2)$$

where γ_n is the force constant coupling atoms $n - 1$ and n.

By assuming the simple time dependence for the displacement as

$$U_n(t) = U_n \exp(-i\omega t)\,, \quad (3)$$

Equation 2 can be written in terms of the time-independent displacement amplitudes as

$$\gamma_n U_{n-1} + (\omega^2 M_n - \gamma_n - \gamma_{n+1}) U_n + \gamma_{n+1} U_{n+1} = 0 \;(n = 1, 2, 3, \ldots N)\,, \quad (4)$$

with $U_0 \equiv U_{N+1} \equiv 0$. Let displacements be $U_0 = 0$ and $U_1 = a$ (a is any real number), then for a given ω, displacements for the succeeding atoms, U_2, U_3, ... U_{N+1}, are calculated in succession. The values of ω which make U_{N+1} zero are the normal mode frequencies in the lattice.

Numerical calculations of exact frequency spectra in linear lattices by means of high-speed computer were first carried out by Dean [6], followed by similar work thereafter [8, 9]. Rosenstock and McGill [7] have proved that the sequence of displacements U_1, U_2, ... U_{N+1} forms a "Sturm sequence" and therefore "Sturm theorem" [10] holds; the number of sign-changes in this sequence for a given squared frequency ω^2 gives the integrated frequency spectrum, $L(\omega^2)$, which is the number of normal modes of the lattice whose frequencies are smaller than its argument. Once the integrated spectrum has been determined, the squared frequency spectrum, $D(\omega^2)$, can be obtained by

$$D(\omega^2)\,\mathrm{d}\omega^2 = L(\omega^2 + \mathrm{d}\omega^2) - L(\omega^2)\,, \quad (5)$$

where $D(\omega^2)\,\mathrm{d}\omega^2$ is the number of normal modes whose frequencies lie between ω^2 and $\omega^2 + \mathrm{d}\omega^2$.

By use of this procedure, frequency spectra for linear lattices containing point defects were computed. The point defects introduced into the lattices are solute atoms, vacancies and vacancy-solute pairs, whose models are shown in Fig. 2. Open circles denote host atoms of mass M, and solid circles solute atoms of mass M'. The force constant coupling two adjacent host atoms and that connecting a host atom and a solute atom are denoted by γ and γ', respectively. A vacancy is at the middle of two atoms connected by the dotted line, and the force constant coupling two atoms through a vacancy is expressed by γ_v or γ_v' for a free vacancy or a solute-bound vacancy, respectively.

The squared frequency spectrum for the perfect lattice of 2000 atoms is shown in Fig. 3a. This has the symmetric U-shaped form represented by $D(\omega^2) = N\pi^{-1}[\omega^2(\omega_m{}^2 - \omega^2)]^{1/2}$, where ω_m is the maximum frequency of the perfect lattice which is given by $\omega_m{}^2 = 4\gamma/M$, and throughout this paper M and γ are taken to be unity. The spectrum for a lattice containing 100 vacancies is shown in Fig. 3b, where $\gamma_v = 0.5$. The presence of vacancies reduces

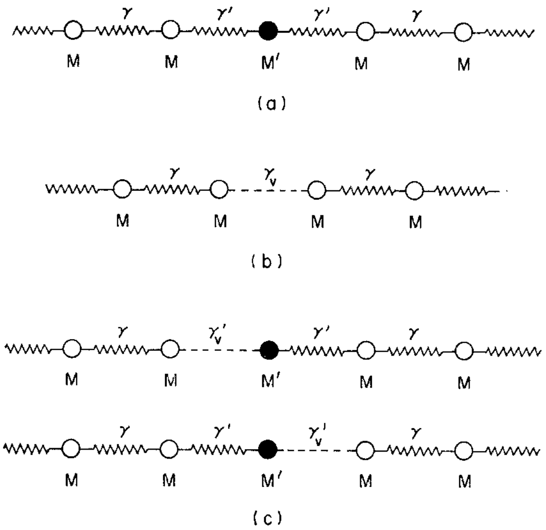

Figure 2 Point defects in linear lattice: (a) solute atom, (b) vacancy, and (c) vacancy-solute pairs. A vacancy is located at the middle of two atoms connected with a dashed line.

the high-frequency mode and makes the spectrum jaggy.

Figs. 4a to d are the spectra for different mass ratios in the lattice with randomly distributed 200 isotopic solute atoms. In order to avoid the interaction between solute atoms, they are distributed at least three atomic distances apart from each other. The mass of solute atoms is different for each spectrum but their distribution is all the same. The effect of solute mass on the spectrum is clearly visualized in these figures; in the lattice with light solutes (Fig. 4a) the so-called localized mode with frequencies higher than the maximum frequency of the perfect lattice has appeared with the intensity corresponding to the number of solutes concerned. The localized mode frequency for a light isotopic impurity ($M > M'$) is theoretically given [11] by $\omega_s{}^2 = \omega_m{}^2/[1 - \{(M - M')/M\}^2]$, which agrees with the frequency corresponding to the sharp peak in the figure. In the lattice containing heavy solutes (Figs. 4b to d), the spectra are slightly shifted, in average, to the lower frequency side, and are getting more jagged for heavier solute atoms. It should be also noted that special or forbidden frequencies [12] at which the spectrum vanishes are observed for the case of heavy solutes.

The spectra of lattices having 100 vacancies as well as 200 isotopic solute atoms are shown in Figs. 5a to d, where vacancies are distributed not to occupy the nearest-neighbour site of the solute atom. The spectra are slightly shifted to the lower frequency side and become less jagged compared with those in Fig. 4, but no remarkable change in the shape of spectra can be seen. Figs. 6a to d are the spectra of lattices containing 200 isotopic solute atoms and 100 vacancies, 50 of which are paired with solute atoms. For heavy solutes, very little difference is seen between the spectra of Figs. 5 and 6, while for light solutes there appear remarkable changes; when vacancies are bound to light solutes, the intensity of localized modes ascribed to isolated solute atoms is reduced and as much, the new localized modes arise from the solutes associated with vacancies whose frequencies lie between ω_m and ω_s.

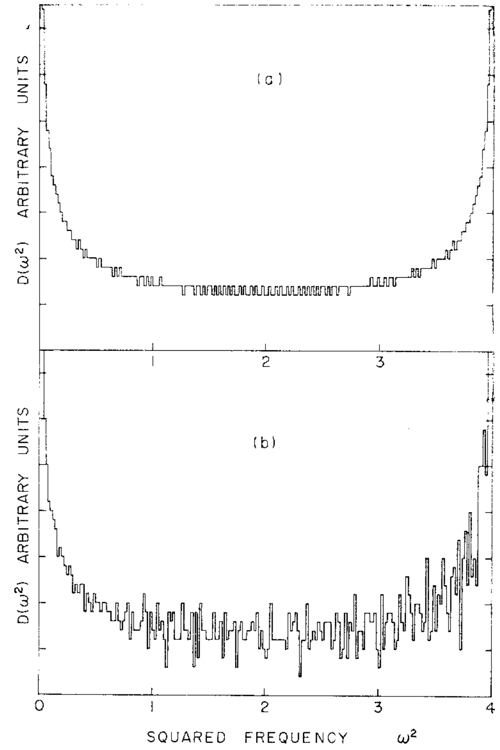

Figure 3 The squared frequency spectrum for the 2000 atoms linear lattice: (a) perfect lattice, (b) a lattice containing 100 vacancies, where $M = \gamma = 1$, $\gamma_v = 0.5$.

2.2 Two-dimensional square lattice

As the model of two-dimensional crystals containing point defects, are chosen square lattices with the nearest-neighbour harmonic interaction. In these lattices it is assumed, for simplicity, that atomic motions in x- and y-

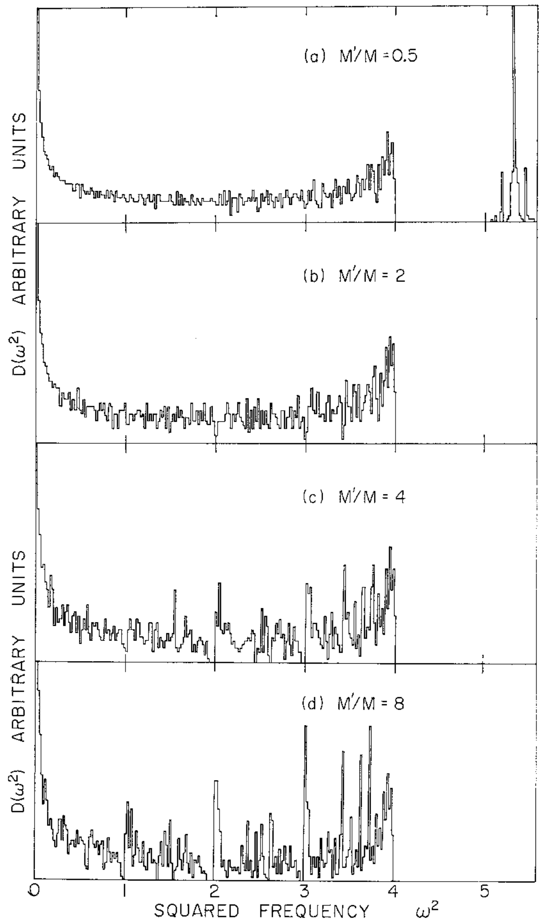

Figure 4 Frequency spectra for the 2000 atoms linear lattice containing randomly distributed 200 isotopic solute atoms, whose mass ratios M'/M are (a) $\frac{1}{2}$, (b) 2, (c) 4 and (d) 8, respectively.

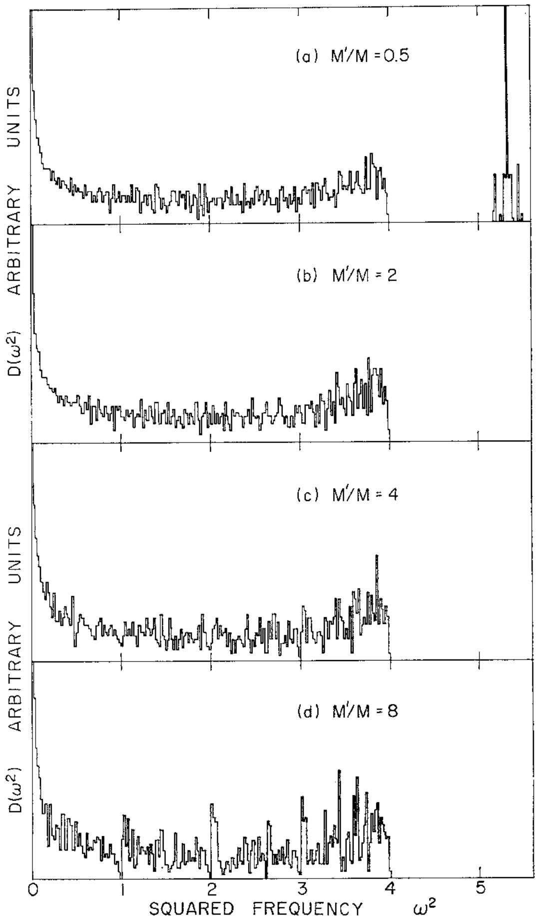

Figure 5 Frequency spectra for the 2000 atoms linear lattice containing 100 vacancies ($\gamma_v = 0.5$) and 200 isotopic solutes whose mass ratios M'/M are (a) $\frac{1}{2}$, (b) 2, (c) 4 and (d) 8, respectively.

directions are independent so as to be separately treated.

Consider a square lattice with $n \times n$ vibratile lattice points with fixed boundaries (Fig. 7), in which each atom is connected to its nearest-neighbours with central and non-central harmonic forces. In this model the time-dependent equation of motion in the x-direction of ith atom at an inner site is given by

$$\begin{aligned} M_i\ddot{U}_i =\; & \gamma_c(i, i-n)\,\{U_{i-n} - U_i\} + \gamma_c(i, i+n)\{U_{i+n} - U_i\} \\ & + \gamma_{nc}(i, i-1)\{U_{i-1} - U_i\} \\ & + \gamma_{nc}(i, i+1)\{U_{i+1} - U_i\}\,, \qquad (6) \end{aligned}$$

where $\gamma_c(i\,j)$ and $\gamma_{nc}(i,j)$ denote the central and non-central force constants, respectively, acting between a pair of atoms i and j, which are symmetric with respect to i and j. For atoms near the boundary, this equation becomes slightly modified.

Equation 6 can be written in the time independent form, by using Equation 3, as

$$\begin{aligned} \omega^2 M_i U_i =\; & -\gamma_c(i, i-n)U_{i-n} - \gamma_{nc}(i, i-1)U_{i-1} \\ & + \{\gamma_c(i, i-n) + \gamma_c(i, i+n) \\ & \quad + \gamma_{nc}(i, i-1) + \gamma_{nc}(i, i+1)\}\; U_i \\ & - \gamma_{nc}(i, i+1)U_{i+1} - \gamma_c(i, i+n)\; U_{i+n}\,. \end{aligned} \qquad (7)$$

The set of Equations 7 can be expressed compactly in matrix notation by

$$(\mathbf{M}\omega^2 - \Phi)\,\mathbf{U} = 0\,, \qquad (8)$$

where $\mathbf{M}$ is the $n^2 \times n^2$ diagonal matrix representing masses of atoms, Φ the $n^2 \times n^2$ force

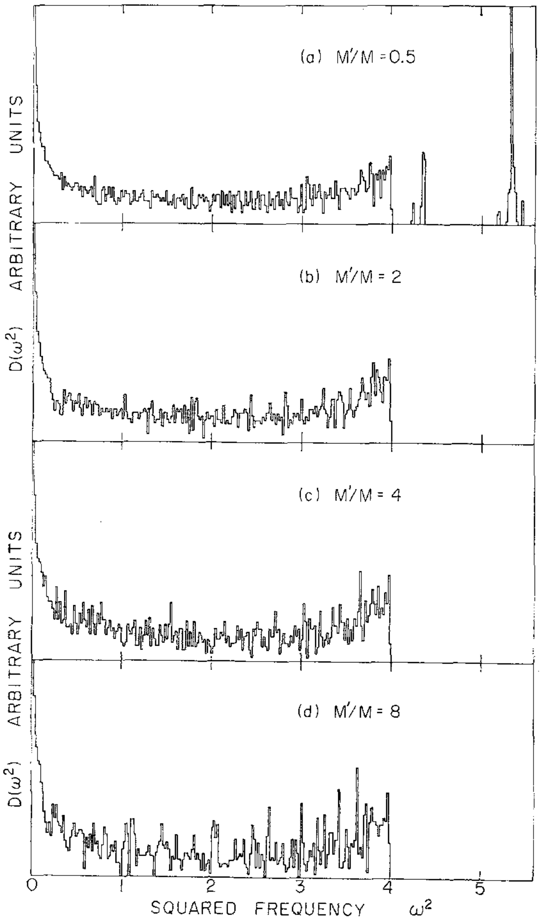

Figure 6 Frequency spectra for the 2000 atoms linear lattice containing 200 isotopic solutes and 100 vacancies 50 of which are located at nearest-neighbour sites of solute atoms ($\gamma_V = \gamma_V' = 0.5$).

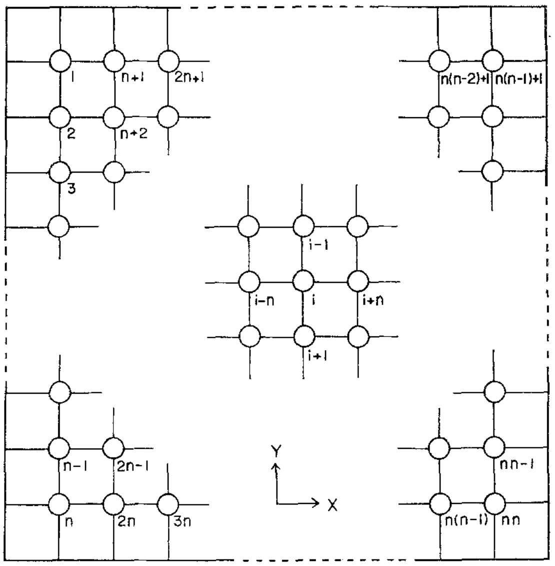

Figure 7 The site labelling scheme for the square lattice having $n \times n$ lattice points.

constant matrix which is symmetric, and **U** the n^2 dimensional column vector denoting the x-component of displacement of atoms. The elements of the force constant matrix are given explicitly by

$$\left.\begin{aligned} \Phi_{i,\,i} &= \gamma_c(i, i-n) + \gamma_c(i, i+n) \\ &\quad + \gamma_{nc}(i, i-1) + \gamma_{nc}(i, i+1)\,, \\ \Phi_{i,\,i\pm n} &= \Phi_{i\pm n,\,i} = -\gamma_c(i, i\pm n), \\ \Phi_{i,\,i\pm 1} &= \Phi_{i\pm 1,i} = -\gamma_{nc}(i, i\pm 1), \\ \Phi_{ij} &= 0 \text{ for } j \neq i, i\pm 1, i\pm n\,. \end{aligned}\right\} \tag{9}$$

With a little algebra one obtains

$$(\mathbf{I}\omega^2 - \mathbf{D})\,\mathbf{M}^{\frac{1}{2}}\mathbf{U} = 0\;, \tag{10}$$

where **I** is the $n^2 \times n^2$ unit matrix, and symmetric matrix $\mathbf{D} = \mathbf{M}^{-\frac{1}{2}}\boldsymbol{\Phi}\,\mathbf{M}^{-\frac{1}{2}}$ is called the dynamical matrix of the crystal whose elements are given explicitly by

$$D_{ij} = (M_i\, M_j)^{-\frac{1}{2}}\, \Phi_{ij}\,. \tag{11}$$

It is understood from Equation 10 that the squares of the normal mode frequencies are the eigenvalues of the matrix **D** and the mass-modified displacement amplitudes, $\mathbf{M}^{\frac{1}{2}}\mathbf{U}$, are the eigenvectors of the matrix. The same type of equation can be composed for the y-component.

The method of calculating the frequency spectrum of the two- or three-dimensional lattice was developed by Dean and his collaborators [13, 14], and Payton and Visscher [9], which is based on the negative eigenvalue theorem introduced by Dean and Martin [13]. In the present work, however, eigenvalues and eigenvectors of the dynamical matrix have been directly calculated by means of "threshold Jacobi method" on the digital computer FACOM 230-60 at KUDPC. This is because the limited capacity of the computer with respect to the number of memories as well as the computing time allows us to treat only a small crystal composed of a small number of lattice points, say, $n = 10$. Furthermore, exact eigenvalues are needed in order to obtain the exact vibrational entropy of the system.

The model of defects introduced is illustrated in Fig. 8, in which open circles denote solvent atoms, solid circles solute atoms, and vacant

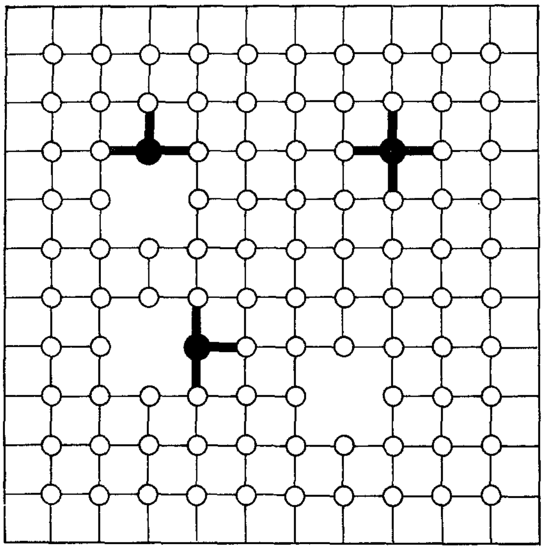

Figure 8 Point defects in the square lattice. Open circles denote host atoms, solid circles solute atoms and vacant lattice sites vacancies.

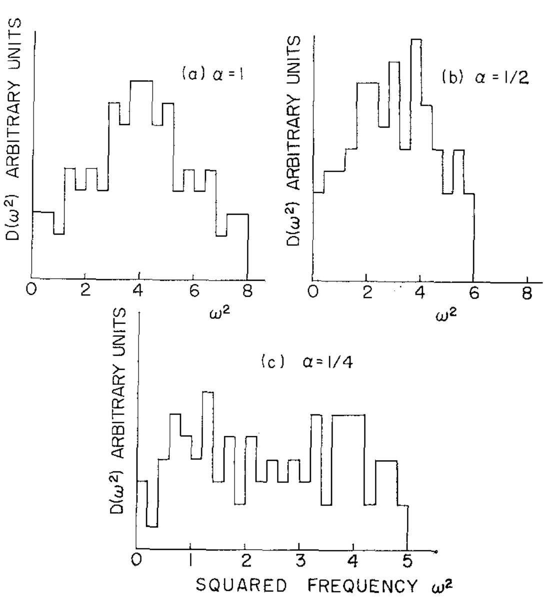

Figure 9 Squared frequency spectra for the perfect square lattice of 10 × 10 atoms. The ratio of the non-central force constant to the central force constant, α, is 1 for (a) $\frac{1}{2}$ for (b) and $\frac{1}{4}$ for (c), respectively.

lattice sites vacancies. The force constant connecting two adjacent host atoms is denoted by γ_c or γ_{nc} for the central or non-central force, respectively, and that joining a host and a solute by γ_c' or γ_{nc}'. Here it is assumed that at a vacancy all the springs are completely cut off and also that any relaxation of atomic configuration around it does not occur. For simplicity, two parameters α and β are adopted, which are given

$$\alpha \equiv \gamma_{nc}/\gamma_c = \gamma_{nc}'/\gamma_c', \; \beta \equiv \gamma_c'/\gamma_c = \gamma_{nc}'/\gamma_{nc}. \quad (12)$$

The squared frequency spectrum, $D(\omega^2)$, for the perfect square lattice is shown in Fig. 9, where in (a) α is 1, (b) $\frac{1}{2}$ and (c) $\frac{1}{4}$. The maximum frequency is given by

$$\omega_m^2 = 4(\gamma_c + \gamma_{nc})/M = 4\gamma_c(1 + \alpha)/M\,. \quad (13)$$

Taking M and γ_c as unity, the values of ω_m^2 become 8, 6 and 5 for $\alpha = 1, \frac{1}{2}$, and $\frac{1}{4}$, respectively. The spectrum for $\alpha = 1$ (Fig. 9a) is symmetric to the middle of the allowed frequency range, and has the maximum at the centre in contrast with the case of one-dimensional lattice. For the case of $\alpha < 1$ (Figs. 9b and c), the spectrum is expected to have two main peaks which, however, are not clearly observed in the figures presumably because of the smallness of number of lattice points.

Figs. 10(i), (ii) and (iii) represent the effect of the mass of isotopic solutes ($\beta = 1$) in lattices having (i) six solutes, (ii) six solutes and four vacancies and (iii) two solutes and four pairs of vacancy-solute, respectively. In each case mass ratios M'/M are (a) $\frac{1}{2}$, (b) 4 and (c) 8. In the case of light solutes (Figs. 10a of (i) to (iii)), there can be seen localized modes referred to as P_1 and P_2. Mode P_1 is associated with isolated solutes and P_2 with solutes bound to vacancies. On the other hand, in the case of heavy solutes (Figs. 10b and c of (i) to (iii)) there appear resonance modes indicated by P_3 and P_4, whose frequencies are lower for heavier solutes. Modes P_3 and P_4 correspond to isolated solutes and solutes bound with vacancies, respectively, but unfortunately P_4 is too close to P_3 to be separated. Fig. 11 shows the effect of the force constant ratio in a lattice containing two isolated solutes and four pairs of vacancy-solute. For small force constant ratios localized modes do not appear in spite of the light mass of solutes ($M'/M = 0.5$), instead, resonance modes come out (see peaks P_3 and P_4 in Fig. 11a for $\beta = 0.1$). For larger values of β, however, localized modes do appear and their frequencies become higher as the value of β increases.

The emergence of localized and resonance modes is closely related to mass ratio M'/M and force constant ratio β; for smaller mass ratio or greater force constant ratio the frequency of the localized mode becomes higher, while the resonance mode frequency is lowered for larger mass ratio or smaller force constant ratio. It is also understood that the frequency of resonance modes or localized modes arisen from solute atoms associated with vacancies is lower than that from isolated solutes.

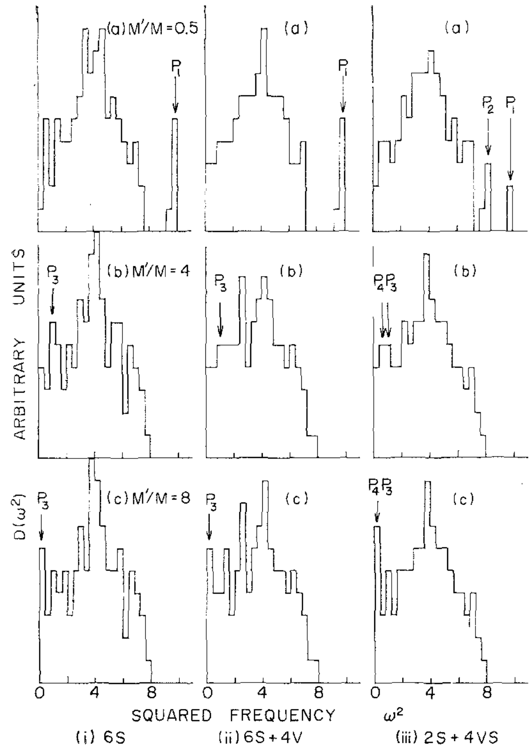

Figure 10 Squared frequency spectra for square lattices of $\alpha = 1$ containing (i) six solute atoms, (ii) six solutes and four isolated vacancies, and (iii) two solutes and four pairs of vacancy-solute, respectively. Solute atoms are isotopic (i.e. $\beta = 1$), and their mass ratios are taken as (a) $\frac{1}{2}$, (b) 4 and (c) 8. P_1 and P_3 denote the localized and resonance modes, respectively, arisen from isolated solutes, and P_2 and P_4 those from solutes bound with vacancies.

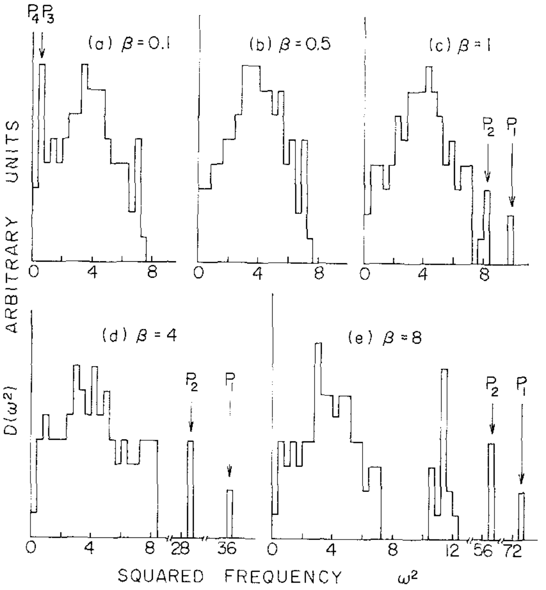

Figure 11 Squared frequency spectra for square lattices of $\alpha = 1$ containing two solute atoms and four pairs of vacancy-solute. The solutes have force constant ratios $\beta = 0.1 \sim 8$ and mass ratio of $M'/M = \frac{1}{2}$. P_1 and P_3 denote the localized and resonance modes, respectively, for isolated solutes, and P_2 and P_4 those for solutes bound with vacancies.

It is also interesting to know the displacement amplitude of atoms in square lattices. Fig. 12 shows the atomic displacement for the x-component in arbitrary units which corresponds to the four normal mode frequencies for the perfect lattice of $\alpha = 1$. It is clear that the low frequency mode has the long wavelength and atoms vibrating in this mode move in co-operation with surrounding atoms, whereas atoms vibrating in the high frequency mode move in the opposite direction to each other. In any case, however, atomic displacements have point symmetry to the centre of the crystal. Fig. 13 shows the displacement of atoms in a lattice containing vacancies, which has no remarkable difference from that of the perfect lattice.

Atomic displacements in a lattice containing vacancy-solute pairs whose frequency spectrum was given in Fig. 11a are shown in Fig. 14 for six normal mode frequencies. The frequency, $\omega^2 = 0.46396$, is the one belonging to resonance mode P_4, i.e. the mode associated with solute-vacancy pairs; solute atoms located at nearest-neighbours of vacancies have large amplitudes. On the other hand, for frequency $\omega^2 = 0.79186$ belonging to resonance mode P_3, the isolated solute atom shows the large amplitude. The mode with frequency $\omega^2 = 0.69965$ which lies between the above two resonance modes has also large amplitudes for both kinds of solutes. The force constants around solutes are taken as so small ($\beta = 0.1$) that for high frequency modes such as those with frequencies $\omega^2 = 4.11172$ or $\omega^2 = 7.06487$ the amplitude becomes very small at the site of solute atoms.

Fig. 15 indicates the atomic displacement in a lattice containing isotopic light solutes ($M'/M = 0.5$, $\beta = 1$), whose frequency spectrum was already shown in Fig. 11c. The first two low-frequency modes are inband modes, which show no singularity around defects. The mode with frequency $\omega^2 = 8.18829$ is the localized mode, P_2, arisen from solute atoms associated with vacancies, while the localized mode with frequency $\omega^2 = 9.71621$, P_1, is the one from isolated solutes. It is clearly seen that the displacement amplitude in these localized modes is large at the site of solutes and rapidly decreases with increasing distance from the solute.

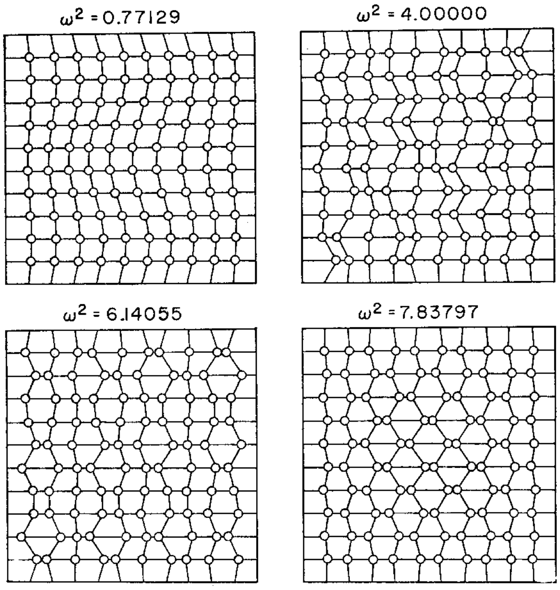

Figure 12 Atomic displacements in the x-direction for the perfect square lattice of $\alpha = 1$, in arbitrary units. See also the frequency spectrum shown in Fig. 9a.

3. Vibrational entropy change due to point defects

By knowing the normal mode frequencies themselves or frequency spectra in lattices containing point defects, the vibrational entropy change on introducing or forming the defects and on binding of them can be evaluated. Equation 1 is rewritten as

$$\Delta S = S - S_0 = -\tfrac{1}{2}k\sum \ln(\omega_i^2/\omega_{0i}^2)\,, \quad (14)$$

with

$$S = -\tfrac{1}{2}k\sum \ln\omega_i^2 = -\tfrac{1}{2}k\int D(\omega^2)\ln\omega^2\,d\omega^2\,. \quad (15)$$

For simplicity, term S is defined as the vibrational entropy of the lattice, S_P as the entropy of the perfect lattice, and S_S, S_V, S_{V+S} and S_{VS} the entropies of lattices in which solute atoms, vacancies, vacancies and isolated solutes, and vacancy-solute pairs are introduced, respectively.

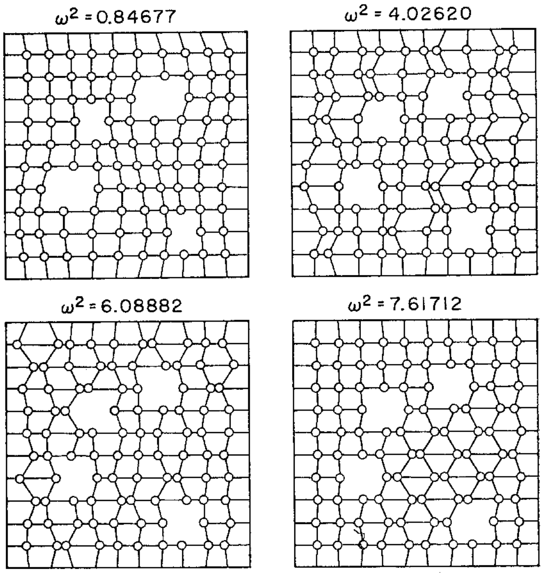

Figure 13 Atomic displacements in the x-direction in the square lattice containing four vacancies, in arbitrary units.

Entropy changes due to the substitution by a solute, ΔS_S, the formation of a vacancy, ΔS_V, and the association of a vacancy with a solute, $\Delta S_{VS}{}^B$, are calculated in linear and square lattices having the nearest-neighbour harmonic force, with particular reference to the solute mass and the force constant around defects. These entropy changes are defined respectively by

$$\left.\begin{aligned} \Delta S_S &= (S_S - S_P)/n_S\,, \\ \Delta S_V &= (S_V - S_P)/n_V\,, \\ \Delta S_{VS}{}^B &= (S_{V+S} - S_{VS})/n_{VS}\,, \end{aligned}\right\} \quad (16)$$

where n is the number of the defects specified by the subscript.

3.1 One-dimensional linear lattice

In Fig. 16, the entropy change due to substitution by a solute atom is shown as a function of the mass ratio and the force constant ratio. It is clear that the change in the force constant is more effective for the entropy change than that in the mass, and as easily understood, the mass and the force constant act in the opposite direction in such a way that heavy mass or weak force constant increases the entropy change and

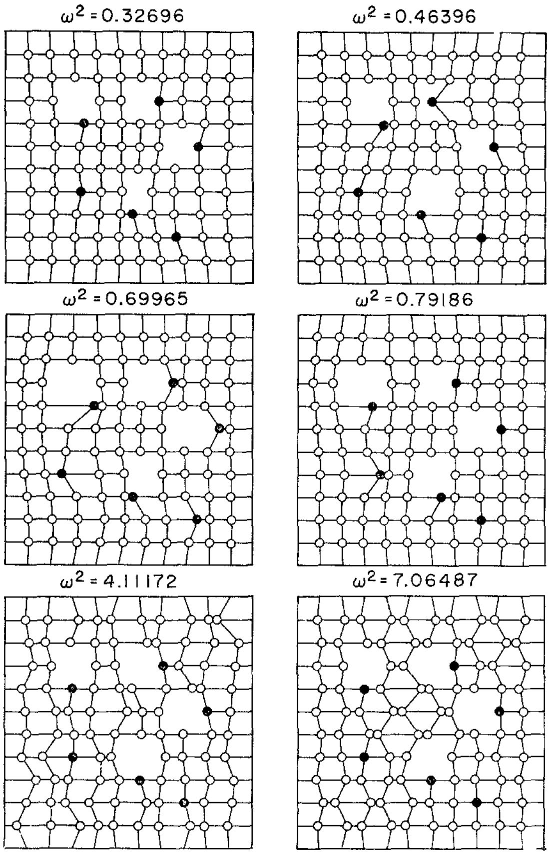

Figure 14 Atomic displacements in the x-direction in the square lattice containing two isolated solutes and four pairs of vacancy-solute, in arbitrary units. See also the spectrum shown in Fig. 11a. $\omega^2 = 0.46396$ is the resonance mode frequency arisen from solutes bound with vacancies (mode P_4), and $\omega^2 = 0.79186$ is that from isolated solutes (mode P_3).

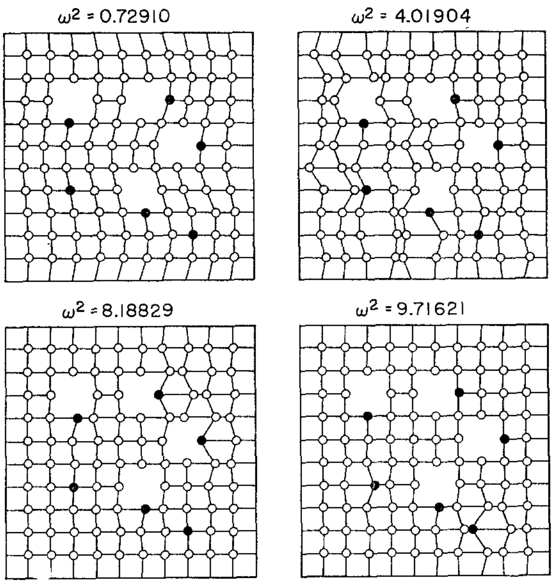

Figure 15 Atomic displacements in the x-direction in the square lattice containing light isotopic solutes and vacancy-solute pairs, in arbitrary units. See also the spectrum shown in Fig. 11c. $\omega^2 = 8.18829$ is the localized mode frequency arisen from solutes bound with vacancies (mode P_2), and $\omega^2 = 9.71621$ is that from isolated solutes (mode P_1).

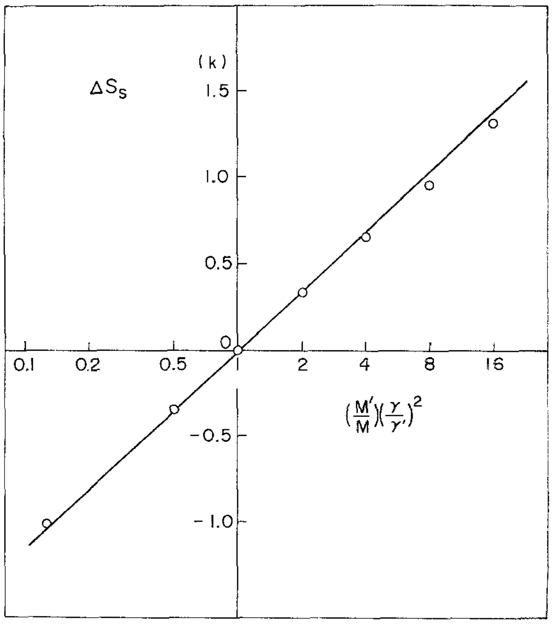

Figure 16 The entropy change due to the substitution by a solute atom in a linear lattice.

vice versa. The calculated values are well represented by the form

$$\Delta S_S = \tfrac{1}{2}\, k \ln(M'/M) - k \ln(\gamma'/\gamma)\,. \quad (17)$$

Fig. 17 shows the entropy change for the formation of a vacancy. The values are larger when the force constant around a vacancy, γ_V, is smaller and are expressed by the form

$$\Delta S_V = -\tfrac{1}{2}\, k \ln(\gamma_V/\gamma)\,. \quad (18)$$

In this figure a negative value is shown for the case of ratio γ_V/γ being greater than unity that may not be practical, although the increase in the force constant around a vacancy in some symmetry direction has been suggested by Land and Goodman [15].

Regarding the entropy change for binding between a solute and a vacancy (Fig. 18) with which the present authors are much concerned, it has been made clear that the binding entropy

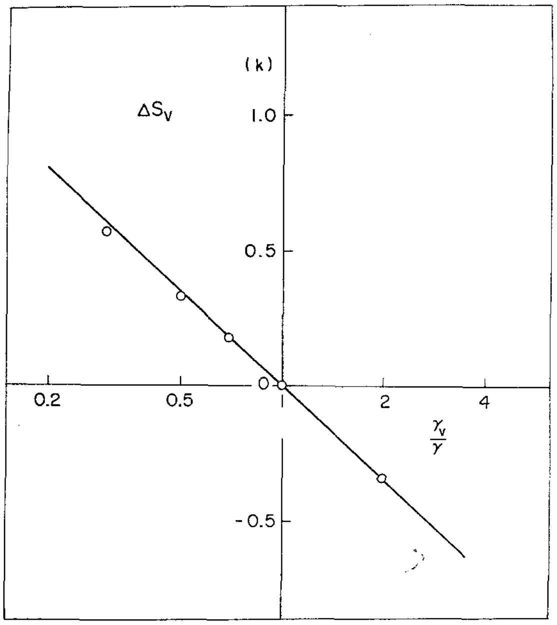

Figure 17 The formation entropy of a vacancy in a linear lattice.

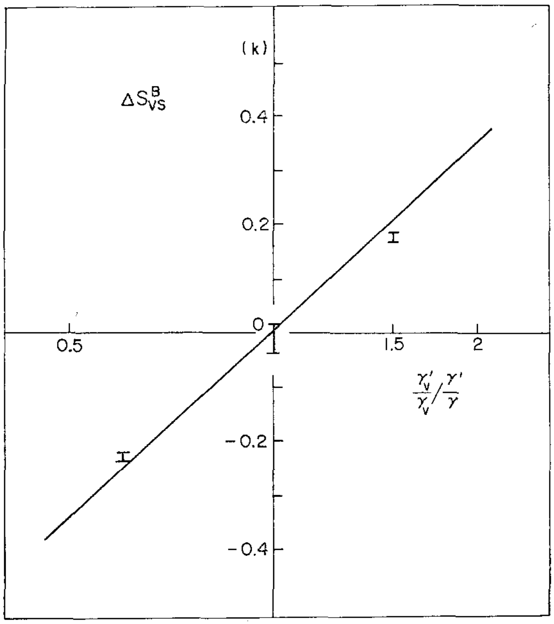

Figure 18 The entropy of binding between a vacancy and a solute atom in a linear lattice. Note that the entropy is independent of the solute mass. The range of scatter of the values is due to different combinations of solute masses and force constants.

change is independent of the solute mass but is affected by the change in the force constant, as expressed by the following relationship

$$\Delta S_{\mathrm{vs}}{}^{\mathrm{B}} = \tfrac{1}{2}k\ln\left(\frac{\gamma}{\gamma'}\cdot\frac{\gamma_{\mathrm{v}}'}{\gamma_{\mathrm{v}}}\right) = \tfrac{1}{2}k\ln\left(\frac{\gamma_{\mathrm{v}}'}{\gamma'}\Big/\frac{\gamma_{\mathrm{v}}}{\gamma}\right). \tag{19}$$

In Fig. 18 is indicated the range of scatter of the calculated values which is due to different combinations of solute masses and force constants.

3.2 Two-dimensional square lattice

The entropy of the two-dimensional square lattice is calculated from eigenfrequencies themselves of the dynamical matrix by use of Equation 15 as

$$S = -\tfrac{1}{2}k\left\{\sum_{x\text{-comp}}\ln\omega_i{}^2 + \sum_{y\text{-comp}}\ln\omega_i{}^2\right\}. \tag{20}$$

The entropy change for substitution by a solute atom, ΔS_{S}, is shown in Fig. 19 as a function of force constant ratio β, where mass ratio M'/M is taken as a parameter. Each curve is found to be fitted completely with that for $M'/M = 1$ by shifting it parallel to the ordinate, having the form

$$\Delta S_{\mathrm{S}} = k\ln(M'/M) + f(\alpha, \beta). \tag{21}$$

Here f is a monotonically descending function of α and β, which cannot be analytically expressed in a simple form. Function f is positive when $\beta < 1$, zero when $\beta = 1$, and negative when $\beta > 1$. Since the function depends very little on α, only the case for $\alpha = 1$ is shown in the figure. In two-dimensional lattices too, as in linear lattices, the value of ΔS_{S} increases with increasing the mass ratio and with decreasing the force constant ratio.

The vacancy-solute binding entropy, $\Delta S_{\mathrm{vs}}{}^{\mathrm{B}}$, is given in Fig. 20, which is also a descending function of α and β like the function f, and also little depends on α. Binding entropy $\Delta S_{\mathrm{vs}}{}^{\mathrm{B}}$ changes its sign at $\beta = 1$ from the positive to the negative as the value of β increases, and is independent of the solute mass.

4. Discussion and summary

Entropy changes related to point defects within the high temperature limit were investigated for linear and square lattices in the light of lattice vibration in the harmonic nearest-neighbour-force approximation. The entropy changes were derived from the computer calculation of exact frequency spectra. The computer experimental results about the entropy changes were found to have the following tendencies.

The entropy change due to substitution by a

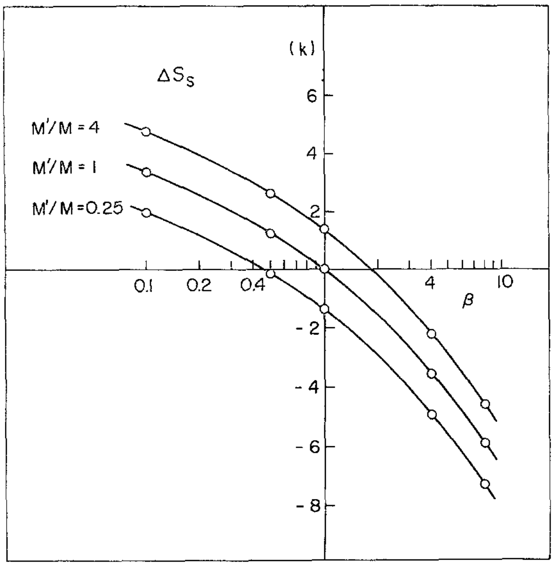

Figure 19 The entropy of substitution by a solute atom in the square lattice. The curves are completely fitted with each other by shifting parallel to the ordinate.

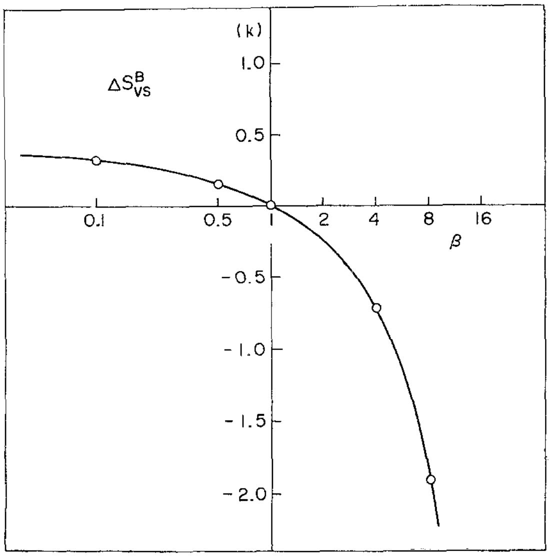

Figure 20 The entropy of binding between a vacancy and a solute atom in the square lattice, being independent of the solute mass.

solute atom, ΔS_{S}, is expressed by the sum of two terms, i.e. a mass dependent term and a force constant dependent term (Equations 17 and 21). The mass dependent term has the form $(n/2)\, k \ln(M'/M)$ where $n = 1$ or 2 for one- or two-dimensional lattices, respectively. The force constant dependent term is a descending function of force constant ratio β, and changes its sign from $+$ to $-$ at $\beta = 1$ when β increases (Figs. 16 and 19).

The binding entropy between a vacancy and a solute atom, $\Delta S_{\mathrm{VS}}{}^{\mathrm{B}}$, is independent of the solute mass, but depends on the force constant around a solute and a vacancy before and after binding (Figs. 18 and 20). Consequently, the binding entropy $\Delta S_{\mathrm{VS}}{}^{\mathrm{B}}$ becomes zero in such a case when only the solute mass is varied without the change in the force constant, i.e. when the solute is isotopic.

All the tendencies stated above may presumably hold also for three-dimensional lattices. In fact, this expectation is proved to be true, as will be published elsewhere.

Useful information on the vibrational properties has been obtained from the frequency spectra as well as the displacement amplitudes. It is particularly interesting that new localized or resonance modes are observed when isolated solutes are bound to vacancies (Figs. 6, 10 and 11) at which the displacement amplitude of solutes is extremely large in the specific modes (Figs. 14 and 15). This may give an important implication to the problem of the solute diffusion which is governed by the vacancy mechanism, as described in the following. The diffusion rate is proportional to the jump frequency j in unit time as $j \propto \nu \exp(-G^{\mathrm{D}}/kT)$, where ν is the vibrational frequency of solute atoms and G^{D} the activation free energy for the solute diffusion. As the value of ν through which solutes diffuse via vacancies, the vibrational frequency of solutes bound with vacancies should be taken instead of that of isolated solutes. In this respect, the localized or resonance mode frequency arisen from solute-vacancy pairs becomes important for the solute diffusion, particularly because of the largeness of the displacement amplitude of solutes in these modes.

In the present calculations, the atomic relaxation around defects was not considered. Even if the relaxation is taken into account, the equation of motion remains unaltered as long as the change in the atomic interaction is mostly confined within the first nearest neighbours, and therefore the above results are still valid. However, when the relaxation causes a substantial change in the force constant beyond the first nearest neighbours, more parameters are needed but the trend may not be far from the present results.

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Received 5 June and accepted 11 September 1972.