On the Vibrational Spectrum and the Vibrational Specific Heat of a Binary Superlattice Alloy

On the Vibrational Spectrum and the Vibrational Specific Heat of a Binary Superlattice Alloy*

Yoshio SHIBUYA, Yoshiichi FUKUDA** and Tadao FUKUROI

The Research Institute for Iron, Steel and Other Metals

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Synopsis

The change in the vibrational modes of a binary superlattice alloy due to the change in its own degree of order has previously been discussed. It was then expected that the vibrational specific heat of the superlattice alloy would change in response to the change in its own degree of order. Using the result obtained formerly, we have applied, in the present paper, Houston's approximate method of finding the frequency distribution function $N(\nu)$ to the calculation of the vibrational specific heat of β-brass in the state of any specified degree of order. It is shown that the vibrational specific heat of the disordered alloy is generally larger than that of the ordered one at oridnary temperatures. If two kinds of atoms which are the components of alloy are nearly equal in mass, the vibrational specific heat of the ordered alloy becomes larger than that of the disordered one at low temperatures.

I. Introduction

The vibrational spectra of monoatomic substances and ionic crystals[1] have been calculated theoretically by many investigators. No theoretical consideration, however, on the vibrational spectra of superlattice alloys in the state of any specified degree of order has been done until now. In the previous paper,[2] the vibrational modes of β-brass in the state of any specified degree of order were investigated in accordance with the method of Born and von Kármán. As a result of the calculation, it is expected that the vibrational spectrum of a superlattice alloy would change in accordance with the change in its own degree of order. In the present paper we have made a calculation on the vibrational spectrum and the vibrational specific heat of β-brass. The theory of superlattice which takes the lattice vibrations into account may be set up, too, but we will reserve it for future investigation.

II. The vibrational spectrum and the vibrational specific heat of β-brass

It is assumed in the present paper that the degree of order once specified for the superlattice alloy is quenched throughout the temperature range from

(1) Paper I references (3)–(12).
(2) Y. Shibuya, Y. Fukuda and T. Fukuroi, Sci. Rep. RITU 3 (1951), 1, which will be referred to as Paper I in this paper.

$0°K$ up to the melting point, so that there is no atomic interchange at any temperature. We compared the temperature variation of the vibrational specific heat of β-brass in the ordered state with that in the disordered one. As was already stated in Paper I, we can get by no means a β-brass alloy in the disordered state owing to its very short time of relaxation. Therefore, β-brass may be inadequate as the model used for the direct comparison of the results of theoretical calculation with the experiment. Characteristic properties of each component atom are, however, manifested by its mass and force constants in the calculation. Consequently by taking them as parameters and by changing their values, we can find the general behaviour of the change in the temperature variation of the vibrational specific heat of a binary superlattice in accordance with the change in its own degree of order.

We made use of the approximate method[3] proposed by Houston for the calculation of the frequency distribution function $N(\nu)$. Considering the assumptions made and the approximations used in the calculation*, it may properly be said that the results obtained are rather qualitative. In Houston's approximation three "Kubic Harmonics" of lowest order are required. Because some errors** existed in the Kubic Harmonics used by Houston in his paper, we used the three functions which had directly been obtained from van der Lage and Bethe's paper.[4] They are

$$K_0 = \frac{1}{(4\pi)^{\frac{1}{2}}} P_0(\cos \theta) ,$$

$$K_1 = \frac{1}{(4\pi)^{\frac{1}{2}}} \frac{(21)^{\frac{1}{2}}}{2} \left\{ P_4(\cos \theta) + \frac{1}{168} P_4{}^4(\cos\theta)\cos\varphi \right\} ,$$

and

$$K_2 = \frac{1}{(4\pi)^{\frac{1}{2}}} \frac{(26)^{\frac{1}{2}}}{4} \left\{ P_6(\cos\theta) - \frac{1}{360} P_6^4(\cos\theta)\cos4\varphi \right\} ,$$

where the $P_m^n(\cos\theta)$ are the associated Legendre polynomials.

$F(\nu, \theta, \varphi)$ corresponding to the three directions [100], [110], and [111] are as follows:

$$F_1(q, 0, 0) = \frac{1}{(4\pi)^{\frac{1}{2}}} f_0(q) + \frac{(21)^{\frac{1}{2}}}{2(4\pi)^{\frac{1}{2}}} f_1(q) + \frac{(26)^{\frac{1}{2}}}{4(4\pi)^{\frac{1}{2}}} f_2(q) ,$$

$$F_2(q, \frac{\pi}{2}, 0) = \frac{1}{(4\pi)^{\frac{1}{2}}} f_0(q) - \frac{(21)^{\frac{1}{2}}}{8(4\pi)^{\frac{1}{2}}} f_1(q) - \frac{13(26)^{\frac{1}{2}}}{32(4\pi)^{\frac{1}{2}}} f_2(q) ,$$

(3) W. V. Houston, Rev. Mod. Phys., 20 (1948), 161.
* In Paper I we resorted to Bragg-Williams' approximation, assuming that the force between atoms was central, and neglected the contributions from the third neighbours, etc.
** It was first pointed out by T. Nakamura, Butsusei-Ron Kenkyû (in Japanese), No. 24 (1950), 40.
(4) F. C. van der Lage and H. A. Bethe, Phys. Rev., 71 (1947), 612.

$$F_3(q, \cos^{-1}\frac{1}{\sqrt{3}}, \frac{\pi}{4}) = \frac{1}{(4\pi)^{\frac{1}{2}}}f_0(q) - \frac{(21)^{\frac{1}{2}}}{3(4\pi)^{\frac{1}{2}}}f_1(q) + \frac{4(26)^{\frac{1}{2}}}{9(4\pi)^{\frac{1}{2}}}f_2(q) \ .$$

From these it follows that

$$N(\nu) = \int\int F(\nu,\theta,\varphi)\sin\theta\,d\theta\,d\varphi = (4\pi)^{\frac{1}{2}}f_0(\nu)$$

$$= \frac{4\pi}{35}\left\{10F_1(q, o, o) + 16F_2(q, \frac{\pi}{4}, o) + 9F_3(q, \cos^{-1}\frac{1}{\sqrt{3}}, \frac{\pi}{4})\right\} \ .$$

This is plotted as a function of ν in Fig. 1 for the two extreme cases of $S=0$ and $S=1$.

The specific heat at constant volume C_v, can be derived from the frequency distribution shown in Fig. 1 by means of the following equation:
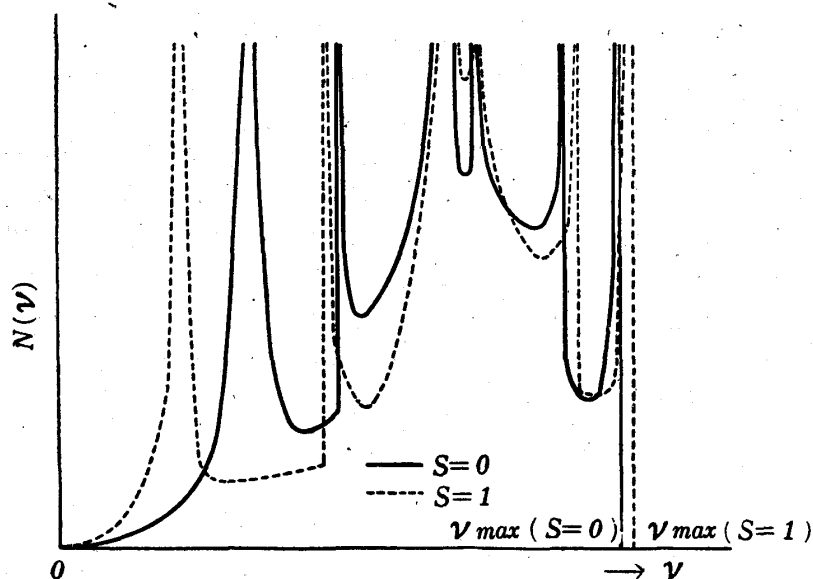
Fig. 1 Frequency distribution functions $N(\nu)$ for the ordered state $(S=1)$ and the disordered one $(S=0)$.

$$C_v = \int_0^{\nu_{max}} k\left(\frac{h\nu}{kT}\right)^2 \frac{\exp\frac{h\nu}{kT}}{(\exp\frac{h\nu}{kT} - 1)^2} N(\nu)d\nu.$$

It is, however, not always necessary to use $N(\nu)$ in the form as shown in Fig. 1. Since $N(\nu)$ is of such a form as $\sum_i A_i \sigma^2 \frac{d\sigma_i}{d\nu}$[*], we may change the independent variable from ν to σ, and may take ν as a function of σ. Then

$$C_v = \int_0^{\nu_{max}} k\left(\frac{h\nu}{kT}\right)^2 \frac{\exp\frac{h\nu}{kT}}{(\exp\frac{h\nu}{kT} - 1)^2}\left(\sum_i A_i \sigma^2 \frac{d\sigma}{d\nu}\right)d\nu$$

$$\rightarrow \sum_i \int k\left(\frac{h\nu_i}{kT}\right)^2 \frac{\exp\frac{h\nu_i}{kT} A_i \sigma^2 d\sigma}{(\exp\frac{h\nu_i}{kT} - 1)^2}$$

Of course, the functional forms of ν_i's with respect to different directions and different branches are different from one another. Although we cannot avoid by all

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[*] It should be noticed that we must use the absoluts value of $\frac{d\sigma_i}{d\nu}$.

means some numerical integration, this procedure relieves us of some difficulties which we encounter at infinite peaks of $N(\nu)$ in the numerical integration. The summation $\sum\limits_i$ should extend over all three principal directions, in each one of which all the branches should be taken into account.

The result of calculation is as follows: the disordered alloy has larger specific heat (slighty more than 1 per cent) than the ordered one at ordinary temperatures. However, as is clearly seen from the low frequency part to $N(\nu)$ for the ordered state in Fig. 1, the specific heat of the ordered alloy is larger than that of the disordered one at low temperatures. The crossing of the specific heat vs. temperature curves for the two states occurs at a temperature lower than 50°K. The difference between the specific heat-temperature curve of the ordered alloy and that of the disordered one is so small that we can hardly show it in a small scale diagram. It is shown, however, exaggeratedly in Fig. 2.
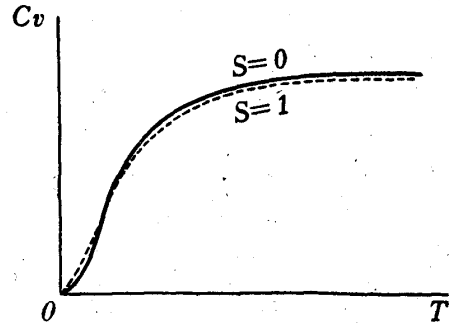

Fig. 2 Specific heat at constant volume C_v as a function of temperature for the ordered state ($S=1$) and the disordered one ($S=0$).

III. Consideration on the results

As mentioned above, the characteristic properties of component atoms of the alloy are indicated by their masses and force constants in the calculation. Next we shall change these values in order to investigate the general behaviour of the change in the specific heats of superlattice alloys in response to the change in their degree of order.

As the first step, let us change the force constants without changing the mass-ratio. Since the change in the value of the ratio $\lambda_{AA} : \lambda_{BB} : \lambda_{AB}$ * does not bring about a remarkable change in the results, we shall change the value of the ratio $c = \lambda_{AA} : \nu_{AA}$. The calculation carried out in Section II corresponds to that performed for the case of this value to be two. The crossing of two specific heat-temperature curves in Fig. 2 shifts towards low temperature side with the increase of c, and towards high temperature side with the decrease of c. Moreover, even in the two extreme cases of $c = \infty$ (the case in which contributions from second neighbours are negligibly small) or $c = 0$ (the case in which those from second neighbours are extremely large), the crossing still stays at a finite temperature lower than ordinary temperatures. Therefore, it is likely that the crossing of two specific heat-temperature curves does occur in case two component atoms of a body-centered cubic superlattice alloy are nearly equal in mass.

Next we assume that masses of two kinds of atoms are considerably different from each other (we assume, for example, they are in the ratio 1:3). In this case

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* For the notations as these, see Paper I.

the disordered alloy generally has larger (about 3 per cent) specific heat than the ordered one at ordinary temperatures. If c is comparatively small $(c \leqq 1.5)$, the ordered alloy has larger specific heat than the disordered one at low temperatures. In case of large c, however, the specific heat of the disordered alloy is larger than that of the ordered one throughout the temperature range defined in Section II. Consequently, if masses of two kinds of atoms are considerably different, it is not always expected that such a crossing of two specific heat-temperature curves as shown in Fig. 2 occurs.

Summary

The result obtained above may be summarized as follows:

(i) If the contributions from the second neighbours to the interatomic forces exerted on an atom is of long range*, the disordered alloy has larger specific heat than the ordered one at high temperatures, but, on the contrary, the latter exceeds the former at low temperatures, so that the crossing of two specific heat-temperature curves occurs at a certain temperature. This is true irrespective of the magnitude of the mass-ratio of two atoms.

(ii) If the contributions from the second neighbours are small, the crossing occurs only when two component atoms are nearly equal in mass.

(iii) These circumstances are mainly due to the fact that whereas the peak to the low frequency side of the vibrational spectrum for the disordered state $(S=0)$ remains unchanged irrespective of the change in c, that for the state of $S \neq 0$ shifts generally towards the high frequency side with the increase of c.

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* In this case the alloy may be regarded as nearly isotropic.