

Pseudopotential study of lattice parameter and heat of formation for substitutional alloys

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Abstract. Ashcroft's empty core pseudopotential is applied to the substitutional alloy (K-CS) to calculate the heat of formation and lattice parameter over the entire concentration range. At any concentration the defect crystal is considered to be equivalent to a perfect crystal with a modified lattice parameter and the potential parameter for the defect crystal is calculated by using some suitable interpolation formula. The calculated results agree well with the available experimental results.

Keywords. Ashcroft pseudopotential; substitutional alloy; heat of formation; lattice parameter; Vegard's law.

1. Introduction

The study of pure metals on the basis of pseudopotential theory has made spectacular progress during the past few years. The formalism is so powerful that Cohen (1979) describes it as a 'panacea' in solid state physics. Static properties of alkali metals can reasonably be well reproduced by Ashcroft's model potential. Recently Sen and Sarkar (1980) have made a unified study of alkali metals on the basis of Ashcroft's (1966) model potential and obtained fairly good agreement for most of the static properties.

The above facts led us to investigate how much effective is the pseudopotential method in describing the properties of substitutional alloys. Several attempts (Tanigawa and Doyama 1973; Singh and Young 1972; Zhernov and Solt 1977) have already been made to calculate the heat of formation of metallic alloys. Tanigawa and Doyama (1973) calculated the heat of formation of (K-Rb) and (Rb-CS) alloys using Ashcroft's pseudopotential. They assumed Vegard's (1921) law for the lattice parameter and determined the lone parameter r_c for the alloys from the equilibrium condition. The values of r_c determined in this way is found to vary linearly with concentration and the heat of formation calculated with these values of r_c shows discrepancy upto 300%. Zhernov and Solt attempted a better calculation using local Heine-Abarenkov potential and considering local distortion and change in vibrational energy. They used Harrison's (1966) prescription that the average form factor of an alloy at a particular concentration is given by the weighted average of the form factors of the host and impurity crystals. Though the theoretical basis of their calculation seems to be sound the calculated values of heat of formation for (K-CS) shows a discrepancy no less than 600%.

An important difficulty in these calculations is that the heat of formation is a very small quantity in comparison with the total crystal energy. Hence the calculated values of heat of formation are very sensitive to the parameter of the pseudopotential. Hence, whatever be the model pseudopotential that is used, the most important question remains as to how the values of these parameters are determined. The main reason for the large discrepancies in the calculations mentioned above should be traced to a wrong method of evaluating the parameters. For example in the work of Tanigawa and Doyama (1973), the essential error seems to be the use of Vegard's law for r_s .

Our main purpose in the present paper is to see if a suitable procedure of selecting the value of the potential parameter can be found which will not only reproduce the lattice parameters but also the heat of formation over the entire concentration range. For simplicity we use Ashcroft pseudopotential. The work of Tanigawa and Doyama suggests that the Vegard's law for r_c will not lead to the desired result. We, therefore, suggest an interpolation formula for selecting an r_c value which deviates slightly from the Vegard's law. We show that r_c determined from empirical formula leads to surprisingly good agreement with both the lattice parameters and the heat of formation of the alloy.

2. Theory

Ashcroft's model potential in r -space is given by

$$\begin{aligned} V(r) &= 0, \quad r < r_c, \\ &= -Ze^2/r, \quad r > r_c. \end{aligned} \quad (1)$$

and its Fourier transform is given by

$$V(q) = -\frac{4\pi Ze^2}{q^2 \Omega_0} \cos q r_c. \quad (2)$$

where r_c is the pseudopotential parameter, Z = valency, q = momentum transfer vector, Ω_0 = atomic volume = $\frac{4}{3}\pi Z r_s^3$, and r_s = radius of Wigner-Seitz sphere.

For pure crystals, the lone parameter r_c is determined from the equilibrium condition using harmonic values of the lattice parameter. Harmonic values of r_s used and the calculated r_c values are shown in table 1.

Table 1. Pseudopotential parameters of pure crystals and data used for their evaluation.

Metal	Harmonic value of r_s^\dagger (a.u.)	Parameter r_c (a.u.)
K	4.83726	2.69336
CS	5.60606	3.27036

[†]Simmons and Wang (1971)

For a substitutional alloy of alkali metals the total crystal energy/ion (in units of Rydbergs/ion) is given by

$$\bar{E} = \frac{2.21}{\bar{r}_s^2} - \frac{1.792}{\bar{r}_s} - \frac{0.916}{\bar{r}_s} + (-0.115 + 0.031 \times \ln \bar{r}_s) + \bar{E}_1 + \bar{E}_2. \quad (3)$$

In equation (3), the first, second, third and fourth terms are kinetic, electrostatic exchange and correlation energies respectively. \bar{E}_1 and \bar{E}_2 are the first order non-coulomb and the band structure energies respectively. For Ashcroft model

$$\bar{E}_1 = 3 \bar{r}_c^2 / \bar{r}_s^3, \quad (4)$$

and
$$\bar{E}_2 = \frac{1}{\pi \Omega_0} \sum_{\vec{g}}' \frac{\cos^2(2\pi \vec{g} \bar{r}_c)}{g^2} (\epsilon(\Omega_0, \vec{g})^{-1} - 1), \quad (5)$$

where \vec{g} is a reciprocal lattice vector and \bar{r}_c is the pseudopotential parameter for the defect crystal with defect concentration χ . We calculate \bar{r}_c according to the following formula

$$\bar{r}_c = r_c^B + \chi (r_c^A - r_c^B) + m \chi (1 - \chi^n), \quad (6)$$

where r_c^A and r_c^B are the pseudopotential parameters for defect and host crystals respectively. m and n are two parameters, whose values are determined by trial so that the best fit with experimental results is obtained. The values thus obtained are $m = -0.0737$ a.u., $n = 1.2200$. In expression (5), $\epsilon(\Omega_0, \vec{g})$ is the dielectric function. Here we have used Taylor's (1978) dielectric function.

2.1 Heat of formation and lattice parameter of the substitutional alloy

Lattice parameter for the alloy as a function of impurity concentration can be determined from the equilibrium condition of the alloy e.g.

$$\partial \bar{E}(r_s, \chi) / \partial r_s = 0. \quad (7)$$

The heat of formation or the heat of mixing of an alloy is defined as

$$H_{ss}(\chi) = \bar{E} - \chi E_A - (1 - \chi) E_B, \quad (8)$$

where E_A and E_B are crystal energies/ion of impurity and host crystals respectively. χ is the concentration of A -type ions.

3. Discussion

Concentration dependence of the heat of formation and the deviation of the lattice parameter from that given by Vegard's law in (K-CS) substitutional alloy are studied

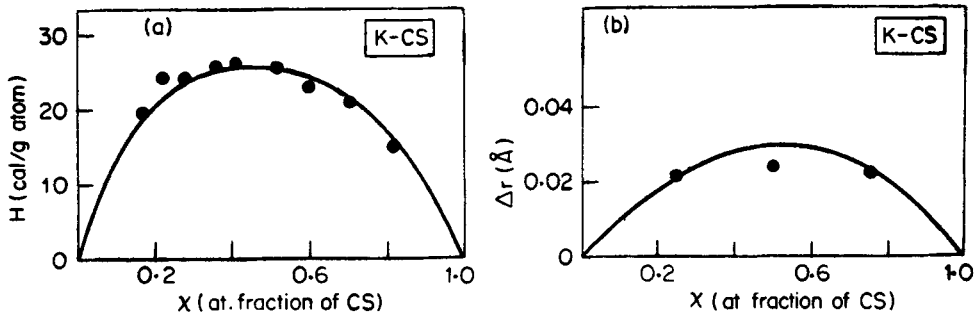


Figure 1. a. Heat of formation (H) as a function of impurity concentration χ . b. Deviation ($\Delta r = r_v - r_{ss}$) of the calculated lattice parameter (r_{ss}) from that given by Vegard's law as a function of impurity concentration χ . The curves represent the theoretical values while the points represent the experimental values of Yokokawa and Kleppa (1964) and Pearson (1958) respectively.

by using (6), (7) and (8). The results are shown graphically in figures 1a and 1b. Experimental values of the heat of formation are taken from Yokokawa and Kleppa (1964). It is found that calculated values agree well within 20%. One important point to be noted here is that the experimental values are those of binary liquid alloys, whereas we have calculated heat of formation of solid substitutional alloy. Comparison between the experimental values and our calculated values is possible only if we assume that the latent heat of liquefaction of pure and mixed solids satisfy Vegard's law. Such an assumption may not be unreasonable.

In figure 1b, we have plotted the deviation ($\Delta r = r_v - r_{ss}$) of the calculated lattice parameter (r_{ss}) of the (K-CS) alloy from that given by Vegard's law (r_v) as a function of the impurity concentration. The agreement between the calculated and experimental values is found to be good. A simpler interpolation formula was also tried with $n=1$ in equation (6). It is seen that even if we determine the parameter m by fitting the heat of formation at 50% concentration, the heats of formation at other concentrations do not at all agree with the experimental values. At concentrations less than 50% the heats of formations are very much less than and those at higher concentrations are very much larger than the experimental values. Moreover the experimental deviation of the lattice parameter from Vegard's law is not at all well reproduced. Thus considering the simplicity, the results of the present calculation seem to be encouraging.

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