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Evaluation of the Compressibility and Thermal Expansivity of Gold–Nickel Alloys

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The compressibility and the thermal expansivity of gold–nickel alloys can be estimated in the complete concentration range through the Varotsos and Alexopoulos model, provided that density data are available and the compressibility (or the expansivity) is experimentally known for a single concentration. The results are discussed in relation to the defect compressibility obtained from the elastic properties of each of the end components.

1. Introduction

The determination of the compressibility or thermal expansivity of an alloy for a given concentration is usually attained by fitting a reasonable equation to the available experimental data. A large amount of experimental points are needed in order to achieve high accuracy. During the last decade Varotsos and Alexopoulos developed a thermodynamical model [1] (hereafter called V-A model) which explains the elastic properties of mixed ionic crystals [1 to 4] and metal alloys [5 to 12] and nonelectronic transport phenomena as a function of the composition in mixed ionic crystals [13 to 15]. The starting point of the V-A model is the variation of the volume of a host crystal when one impurity atom is added. Subsequently the compressibility and thermal expansivity of the “defect volume” v^d can be defined using fundamental thermodynamical relations. Simple equations can determine the compressibility (or expansivity) of the alloy for any concentration by using density data and compressibility data for at least a single concentration and for the host material.

From another viewpoint the formation of a defect (i.e. a vacancy) in a solid will change the volume of the bulk material by v^f where v^f is the formation volume. The compressibility κ^f of the formation volume is defined. The same authors (Varotsos and Alexopoulos) have also established [1] the so-called $cB\Omega$ model that interconnects the point defect parameters of a material with its bulk properties. Within this frame, the compressibility of the afore-mentioned defect volume v^d is determined from the elastic properties of the host crystal. This aspect is limited to lightly doped materials.

The system under examination consists of two metals with elastic properties close together and therefore, whichever we label as “host” material, the defect compressibility for the limiting case of a dilute alloy ($cB\Omega$ model) will be almost the same. A comparison with the value of the defect compressibility obtained from the whole (available) concentration range (V-A model) is desirable.

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2. Theory

We briefly present the V-A model: Assume [1] that an impurity atom is introduced into a pure material with atomic volume Ω_0 . Then the initial volume will increase by $\Omega_0 + v^d$ where v^d is the variation of the host volume V_0 ($V_0 = N\Omega_0$) when one impurity atom replaces one host atom. So, when n foreign atoms get into a host material containing N atoms (N can be set equal to Avogadro's number), then an alloy is formed containing $n + N$ atoms and its volume will be

$$V_{n+N} = N\Omega_0 + n(\Omega_0 + v^d).$$

This can be written as

$$V_{n+N} = V_0 + \frac{n}{N} (V_0 + Nv^d). \quad (1)$$

For reasons of simplicity we identify V_{n+N} with V . We stress that no assumption is made about the value of v^d . It might be equal to the difference between the mean atomic volumes of the two constituents or not. In general, it is experimentally derived as follows: The volume V of the alloy is readily extracted from density measurements recalling that

$$V = \left(m_0 + \frac{n}{N} m_1\right) \varrho^{-1}, \quad (2)$$

where m_0 , m_1 are the g-atoms of the host and impurity material, respectively, while ϱ is the density of the alloy. In a V versus n/N diagram, the slope of the curve permits the direct evaluation of v^d by means of (1). We notice that the molar fraction χ is connected with the ratio n/N by

$$\frac{n}{N} = \frac{\chi}{1 - \chi}. \quad (3)$$

Differentiating (1) with respect to the pressure we get

$$\kappa V = \kappa_0 V_0 + \frac{n}{N} (\kappa^d N v^d + \kappa_0 V_0), \quad (4)$$

where κ_0 is the compressibility of the host material, κ the compressibility of the mixed system, and κ^d is the defect compressibility defined as follows:

$$\kappa^d = -\frac{1}{v^d} \left(\frac{dv^d}{dP}\right)_T. \quad (5)$$

We note that (4) holds either for isothermal or adiabatic compressibility [1].

Differentiating (1) with respect to temperature we get a formula similar to that given by (4),

$$\beta V_{n+N} = \beta_0 V_0 + \frac{n}{N} (\beta^d N v^d + \beta_0 V_0), \quad (6)$$

where β_0 is the host material expansivity and β^d the expansivity of the defect volume defined as follows:

$$\beta^d = \frac{1}{v^d} \left(\frac{dv^d}{dT}\right)_P. \quad (7)$$

If $V = V(n/N)$ is a straight line we conclude that the defect volume v^d is constant and independent of the concentration. In this case ($v^d = \text{const}$), if additionally κ^d is also constant, the relation $\kappa V = \kappa V(n/N)$ is linear. Similarly, if v^d and β^d are constant then $\beta V = \beta V(n/N)$ is a straight line.

The above model proves to be a simple and useful tool: if the available experimental density data indicate that the defect volume v^d is constant and provided that κ^d is also constant then κV versus n/N is expected to be a straight line. This straight line can be easily drawn provided that κ is known for a single concentration and for the host material or, equivalently, for two different compositions. Then by means of (4) the alloy compressibility can be predicted at any concentration. The same method can be applied in order to predict the thermal expansivity β at any composition.

For lightly doped materials, and within the frame of the $cB\Omega$ model (also formulated by Varotsos and Alexopoulos) which interconnects the point defect parameters with the bulk elastic properties of the host crystal, the compressibility κ^d of the defect volume is given by the following equation [1, 16]:

$$\kappa^d = \kappa_0 - \left(\frac{\frac{d^2 B_0}{dP^2}}{\frac{dB_0}{dP} - 1} \right), \quad (8)$$

where $B_0 = 1/\kappa_0$ is the bulk modulus of the pure material. We point out that κ^d is determined only from the properties of the bulk crystal and, consequently, must be constant throughout the composition range. A similar equation holds for the thermal expansion coefficient β^d of the defect volume [1, 16],

$$\beta^d = \beta_0 - \left(\frac{\frac{d^2 B_0}{dP^2}}{\frac{dB_0}{dP} - 1} \right). \quad (9)$$

The defect thermal expansivity is a function of the host crystal properties and therefore independent of the concentration.

3. Application to the Au–Ni Alloys

Golding et al. [17] have reported density, adiabatic compressibility, and linear expansion data of Au single crystals and for various concentrations of Au–Ni alloys (from 0 to 42.42% Ni) at 296.5 K, which we are going to use in the following paragraphs.

By introducing the density data into (2) we plot the V versus n/N diagram (Fig. 1). A least squares fit indicates that it is a straight line with correlation factor $cf = 1.000$. We conclude that v^d is constant. From the slope of the line we find that $Nv^d = -3.32 \text{ cm}^3$. Its negative value suggests the inward relaxation of the Au lattice around Ni. Additionally, the intercept is found to be equal to $10.22 \text{ cm}^3/\text{mol}$ and close to the molar volume of pure gold $V_{\text{Au}} = 10.21 \text{ cm}^3/\text{mol}$. Notice that the value of Nv^d differs from the value $N(\Omega_{\text{Ni}} - \Omega_{\text{Au}}) = -3.62 \text{ cm}^3/\text{mol}$.

In Fig. 2 we have drawn the compressibility κ versus n/N which is obviously non-linear. On the contrary, the $\kappa V = \kappa V(n/N)$ plot is linear with correlation factor $cf = 1.000$. According to (4) we can evaluate the defect compressibility from its slope.

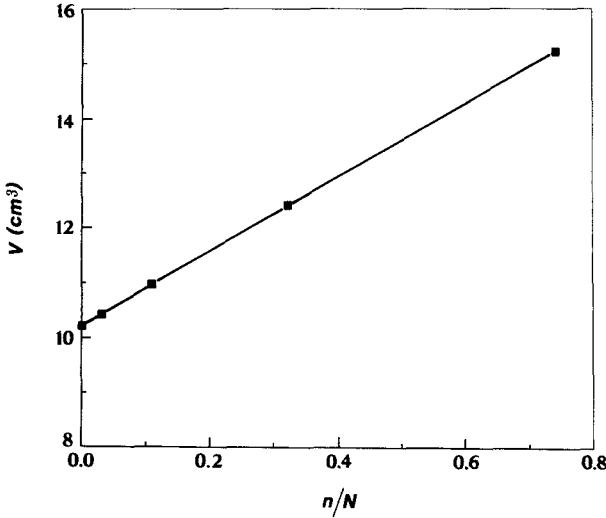


Fig. 1. The volume V vs. the ratio n/N . The linearity indicates that the defect volume is independent of concentration

We find $\kappa^d = 5.331 \times 10^{-8} \text{ cm}^2/\text{N}$ and $\kappa^d/\kappa_0 = 0.92$, i.e., the defect compressibility (which was experimentally determined) is almost equal to the bulk compressibility.

Golding et al. [17] provided a list of the linear expansion coefficients α for different compositions. In Fig. 3 we plot the thermal expansivity $\beta = 3\alpha$ versus n/N which is nonlinear. A $\beta V = \beta V(n/N)$ plot reveals its linearity with correlation factor $cf = 0.999$. As (6) indicates, the thermal expansivity of the defect volume is readily evaluated from its slope: $\beta^d = 0.612 \times 10^{-4} \text{ K}^{-1}$. The thermal expansivity of the defect volume is about 50% larger than the bulk one, since $\beta^d/\beta_0 = 1.45$.

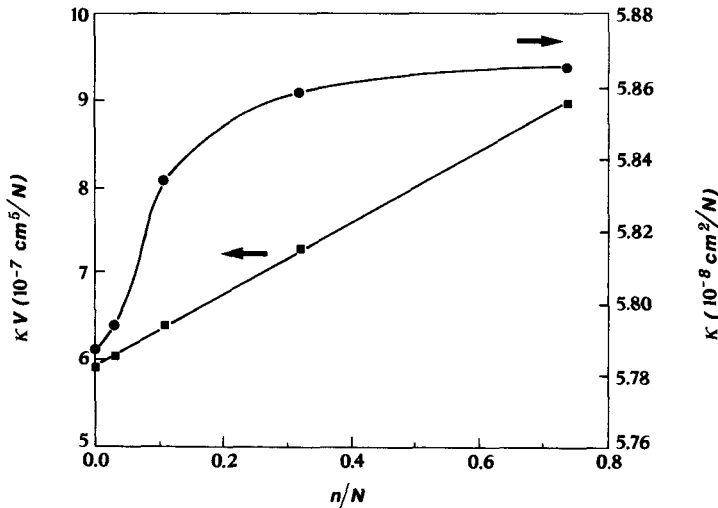


Fig. 2. The compressibility κ vs. n/N (circles) and the product κV as a function of n/N (squares). It is worthwhile to notice that κV depends linearly upon n/N while κ does not

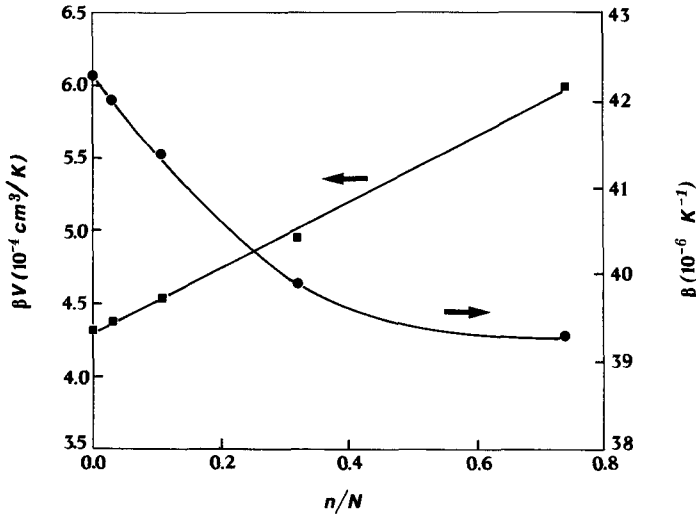


Fig. 3. The thermal expansivity β vs. n/N (circles) and the product βV for varying n/N (squares) which is a straight line in contrast to the β vs. n/N plot

4. Comment on the Defect Compressibility Value

We have repeated the above procedure taking nickel as the host material. The V versus n/N and κV versus n/N plots are straight lines with excellent correlation factors. We found $Nv^d = 3.28 \text{ cm}^3$ and $\kappa^d = 4.891 \times 10^{-8} \text{ cm}^2/\text{N}$. A deviation of about 1% in the defect volume and about 10% in the defect compressibility exists in comparison to the values obtained when we started from Au. This result was expected because different sets of data points participate in the fit: the selection of the one end member as “host”, excludes the other end member from the fitting procedure. We speculate that the aforementioned deviations would be minimal if data from the complete concentration range ($1 > \chi > 0$) were available.

We shall compare the defect compressibility experimentally determined above (V-A model) with the value that can be evaluated from (8) for the low concentration limits ($cB\Omega$ model): Golding et al. [17] have measured at 296.5 K the adiabatic compressibility of Au single crystals $\kappa_0 = 5.7870 \times 10^{-8} \text{ cm}^2/\text{N}$ and the pressure derivative of the adiabatic bulk modulus $dB_0/dP = 6.15$, which practically coincides with the isothermal one [1]. The following equation is valid for metals and provides the second pressure derivative of the bulk modulus [6, 1]:

$$B_0 \frac{d^2 B_0}{dP^2} \approx - \frac{dB_0}{dP} . \tag{10}$$

From (8) and (10) we get

$$\kappa^d \approx \kappa_0 \left(1 + \frac{dB_0/dP}{(dB_0/dP) - 1} \right) . \tag{11}$$

From (11) we get the value $\kappa^d = 12.698 \times 10^{-8} \text{ cm}^2/\text{N}$ or $\kappa^d/\kappa_0 = 2.19$.

The experimental adiabatic compressibility of Ni at 300 K reported in [18] is $\kappa_0 = 5.45553 \times 10^{-8} \text{ cm}^2/\text{N}$. Recalling that the pressure derivative of the adiabatic bulk modulus does not significantly change with temperature [1] we may use the value $dB_0/dP = 6.07$ at 298 K reported in [19]. By using (11) we find $\kappa^d = 12.002 \times 10^{-8} \text{ cm}^2/\text{N}$ and $\kappa^d/\kappa_0 = 2.20$.

We notice that the defect compressibility determined either from the elastic properties of Au or from the elastic properties of Ni is more than two times larger than the defect compressibility obtained from the experimental data of the alloy.

5. Conclusion

We have verified that the Au-Ni alloy is a system for which the V-A model applies well. Therefore, prediction of the compressibility and the thermal expansivity is attainable.

The defect compressibility obtained from the complete concentration range, being the same considering either Au or Ni as the host material, does not coincide with that evaluated from the end member elastic data. This was expected since as the alloy becomes richer in impurity atoms, the environment that surrounds the defect changes drastically. The dilute approximation limit governed by the end member properties can therefore hardly be expanded to the whole concentration range. One cannot ignore the fact that the defect compressibility in a wide composition range (i.e., for concentrations that well characterise the alloy as being heavily doped) is constant for a large number of mixed systems, and might reveal a systematic property.

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