TECHNICAL NOTE

PREDICTION OF THE PRESSURE DERIVATIVE OF THE ADIABATIC BULK MODULUS OF AgBr:AgCl

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Abstract—The pressure derivative of the adiabatic bulk modulus of AgBr:AgCl mixed crystals as a function of concentration is evaluated from the elastic and molar volume data of the end members in terms of a macroscopic model previously formulated by Varotsos and Alexopoulos. Our results are close to the experimental data.

1. INTRODUCTION

Varotsos and Alexopoulos [1–3] have developed a macroscopic model considering an alloy as a defect crystal. This model has been successfully applied to mixed ionic crystals [4–9] and metal alloys [10–14].

A brief presentation of this model is as follows [2]. When we add n foreign atoms into a host crystal having N atoms with a mean atomic volume u_1, the total volume V_{n+N} of the material containing $N + n$ atoms will be:

$$V_{n+N} = Nu_1 + n(u_1 + u^d),$$

where u^d is the defect volume defined as the variation of the host material volume $V_1 = Nu_1$ when one impurity atom replaces one host atom [1] (N can be set equal to Avogadro's number).

The last relation can be written as:

$$V_{n+N} = V_1 + \frac{n}{N}(Nu^d + V_1). \qquad (1)$$

We stress that no assumption is made about u^d: it is not necessarily constant or independent of the composition. It can also be either positive or negative [3].

The atomic fraction χ is connected to the ratio n/N by means of:

$$n/N = \chi/(1 - \chi). \qquad (2)$$

In an approximation, we may evaluate the defect volume u^d through the next relation:

$$Nu^d = V_2 - V_1, \qquad (3)$$

where V_1 and V_2 are the molar volumes of the host material and the impurity, respectively. The validity of eqn (3) can readily be checked for V_{n+N} vs n/N is a straight line then u^d is constant and is calculated from the slope of the line. As already mentioned by Varotsos and Alexopoulos [1], the defect volume for AgBr:AgCl derived from density measurements is constant, so from eqn (1) we get $Nu^d = -3.233\,\text{cm}^3$. This value is very close to the value $V_2 - V_1 = -3.265\,\text{cm}^3$, and thus eqn (3) is a good approximation.

For reasons of simplicity we set V_{n+N} identical to V. By differentiating eqn (1) with respect to the pressure we get [3]:

$$\kappa V = \kappa_1 V_1 + n(\kappa^d u^d + \kappa_1 u_1), \qquad (4)$$

where κ, κ_1 and κ^d are the compressibility of the alloy, the host material and the defect volume, respectively. κ^d is defined as follows: $\kappa^d = -(1/u^d)(du^d/dP)$.

Equation (4) can be rewritten:

$$\kappa V = \kappa_1 V_1[1 + (n/N)] + (n/N)\kappa^d(Nu^d). \qquad (5)$$

From eqns (3) and (5) and by recalling that the bulk modulus is given by $B = 1/\kappa$, we get a formula that permits the evaluation of the bulk modulus of the mixed crystal at any concentration from the bulk moduli and the molar volume data of the end components:

$$B = B_1 \frac{1 + \chi[\mu - 1]}{1 + \chi\left[\dfrac{\mu}{\lambda} - 1\right]}, \qquad (6)$$

where $\mu = V_2/V_1$ and $\lambda = B_2/B_1$.

The differentiation of the last relation results in the following eqn [1]:

$$\frac{dB}{dP} = \frac{1 + \chi[\mu - 1]}{1 + \chi[(\mu/\lambda) - 1]}\frac{dB_1}{dP} - \chi\frac{\mu}{\lambda}\frac{(1 - \chi)(1 - \lambda)[1 - (1/\lambda)] + (1 - \chi + \chi\mu)\left[\dfrac{dB_1}{dP} - \dfrac{1}{\lambda}\dfrac{dB_2}{dP}\right]}{[1 - \chi + (\mu/\lambda)]^2}. \qquad (7)$$

Table 1. Input parameters from [15] for the Varotsos
and Alexopoulos model

	AgBr	AgCl
B ($\times 10^{12}$ dyn cm^{-2})	0.406	0.442
V (cm^3 mole^{-1})	28.996	25.731
dB/dP	6.82	6.57

Table 2. Calculated and experiemental values of the adia-
batic bulk modulus pressure derivative in AgBr:AgCl at
295 K

χ	dB/dP		
	Calculated		Experimental
(% AgCl)	Present work	Ref. 16	(Ref. 15)
0	—	5.26	6.82
19.5	6.87	6.20	6.76
39.1	6.91	7.13	6.74
56.6	6.92	6.30	6.65
78.7	6.84	7.55	6.63
100	—	6.86	6.57

The pressure derivative of the bulk modulus of the alloy
at any concentration can be calculated in terms of the molar
volumes V_1, V_2, the bulk moduli B_1, B_2 and the pressure
derivatives dB_1/dP, dB_2/dP of the host material and the
impurity, respectively.

2. THE PRESSURE DEPENDENCE OF THE ADIABATIC BULK MODULUS OF AgBr:AgCl

The pressure derivative of the adiabatic bulk modulus
vs concentration at 295 K (the only temperature where
experimental data are available [15]) is predicted inserting
the experimental molar volume and elastic data of the end
components from Table 1 into eqn (7). We consider AgBr
and AgCl as the host material and the impurity, respectively.
In Table 2 our results are listed together with the exper-
imental values of dB/dP reported by Cain [15] and those
calculated by Shanker et al. [16].

The dB/dP dependence upon χ is, according to the
Varotsos and Alexopoulos model, similar to that obtained
using the experimental values as shown in Fig. 1. On the
other hand, our results overestimate the experimental data
by no more than 4%, while the values computed in [16]
scatter around the experimental ones with a maximum
deviation of about 14% for the intermediate composition
range and 23% for pure AgBr. The deviation of the
Varotsos and Alexopoulos model can be attributed to the
fact that the defect volume $Nu^d = -3.233$ cm^3 is slightly
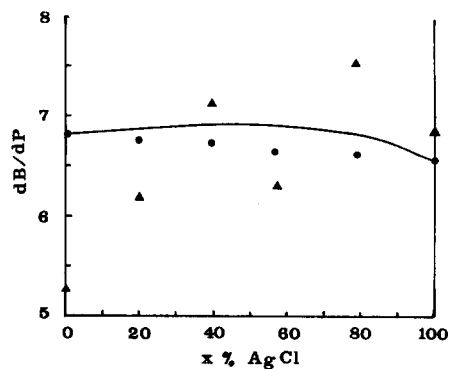different from the difference $V_2 - V_1 = -3.265$ cm^3.

Fig. 1. The pressure derivative of the adiabatic bulk
modulus in AgBr:AgCl as a function of concentration at
$T = 295$ K. ● Experimental points from [15]. —— Cal-
culated from the Varotsos and Alexopoulos model.
▲ Calculated by Shanker et al. [16].

REFERENCES

1. Varotsos P. and Alexopoulos K., *Thermodynamics of Point Defects and their Relation with Bulk Properties* (Edited by Amelinckx S. *et al.*) pp. 325–347. North-Holland, Amsterdam (1986).
2. Varotsos P., *Phys. Stat. Solidi (b)* **99**, K93 (1980).
3. Varotsos P. and Alexopoulos K., *J. Phys. Chem. Solids* **41**, 1291 (1980).
4. Varotsos P. and Alexopoulos K., *Phys. Stat. Solidi (b)* **102**, K67 (1980).
5. Varotsos P., *J. Phys. Chem. Solids* **42**, 405 (1981).
6. Varotsos C. and Lazaridou M., *Phys. Stat. Solidi (b)* **129**, K95 (1985).
7. Lazaridou M. and Varotsos C., *J. Phys. Chem. Solids* **46**, 643 (1985).
8. Grammatikakis J., Lazaridou M. and Eftaxias K., *J. Phys. Chem. Solids* **46**, 1243 (1985).
9. Manoravi P. and Shahi K., *Solid State Ionics* **45**, 83 (1991).
10. Grammatikakis J., Eftaxias K., Patapis S. and Hadjicontis V., *J. Phys. Chem. Solids* **49**, 965 (1988).
11. Grammatikakis J. and Londos C., *J. Phys. Chem. Solids* **49**, 1465 (1988).
12. Hadjicontis V., Varotsos C. and Eftaxias K., *J. Phys. F.* **18**, 1133 (1988).
13. Grammatikakis J. and Katsika V., *J. Phys.: Condens. Matter* **2**, 3903 (1990).
14. Papathanassiou A. N., Grammatikakis J. and Bogris N., *Phys. Stat. Solidi (a)* **125**, 529 (1991).
15. Cain L. S., *J. Phys. Chem. Solids* **38**, 73 (1977).
16. Shanker J., Jain G. D. and Sharma S. K., *Phys. Stat. Solidi (b)* **104**, 75 (1981).