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Thermal Expansion and Elastic Constants of β′-AgMg. I. The Coefficient of Thermal Expansion from 77° to 800°K

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The linear coefficient of thermal expansion of β′-AgMg has been determined from 77° to 800°K by means of lattice-parameter measurements below room temperature and dilatometric measurements at higher temperatures. At room temperature, the linear coefficient of thermal expansion was found to be 21×10^{-6} per °C. The Grüneisen parameter derived from the coefficient of thermal expansion obtained here and from other thermal data available in the literature is essentially constant ($\gamma\simeq1.8$) above the Debye temperature, but increases at lower temperatures. Using Slater's formula, a value of 2.2 was obtained for the Grüneisen parameter at 0°K.

INTRODUCTION

THE coefficient of thermal expansion is of great utility in the analysis of the elastic constant and specific heat data of solids. Intermetallic compounds such as β′-AgMg with their combination of metallic and ionic bonding are of special interest. AgMg has, at room temperature, an ordered CsCl structure[1] which, as specific heat measurements indicate,[2] remains ordered to at least 800°K. In the present study, the coefficient of thermal expansion of a slightly off-stoichiometric AgMg alloy has been determined over the temperature interval 77°–800°K by means of lattice-parameter and dilatometric measurements. The thermal expansion data are then used together with other available thermal data, to calculate the Grüneisen parameter γ as a function of temperature.

In Part II of this paper the coefficient of thermal expansion is used to evaluate the elastic constants of β′-AgMg.

EXPERIMENTAL PROCEDURE

The silver–magnesium alloy used in the present study was furnished in the form of ingots, containing according to chemical analysis 48.2±0.3 at.% Mg. The ingots were produced by melting and chill-casting high-purity silver and magnesium (both 99.99%) in an induction furnace under a helium atmosphere.

Below room temperature, the thermal expansion was determined by means of lattice-parameter measurements. Alloy filings with a particle size less than 40 μ were annealed in vacuum in a closed quartz vial at 700°K for one day, and cooled to room temperature at a rate of 1°C/min. The lattice-parameter measurements were carried out on a General Electric XRD-5 diffractometer using a commercial low-temperature vacuum attachment (Materials Research Corporation, Orangeburg, New York). The experimental conditions were as follows:

Copper tube, 50 kV, 16 mA
3° target angle, 3° medium-resolution beam slit:
0.2° medium-resolution receiving slit, no filter;
Proportional counter with pulse-height discriminator;
0.2°/min scanning speed.

The temperature was measured by means of a copper–constantan thermocouple. The peak positions of lines above $2\theta=120°$ were evaluated using the following wavelengths:

$$\mathrm{Cu}K\alpha_1=1.54050\ \text{Å},$$

$$\mathrm{Cu}K\alpha_2=1.54433\ \text{Å}.$$

The $\cos^2\theta$-extrapolation function was employed, and no correction for vertical divergence or refraction was applied. The specimen alignment was carried out by mixing the alloy filings with diamond powder.

The thermal expansion above room temperature was measured by means of a Linseis dilatometer in an inert atmosphere at a heating rate of 2.5°C/min. Quartz served as a comparison standard. Specimens of about 4-mm diameter and 50-mm length were machined from the alloy ingots and given the same heat treatment as described above for the filings. The temperature was measured by means of a Pt–Pt-10%Rh thermocouple.

RESULTS AND DISCUSSION

The values of the lattice parameter, "a" for β′-AgMg below room temperature are given in Table I with an average precision of ±0.0002 Å. The linear coefficient of thermal expansion for both the low and high temperature ranges was obtained using the following relationship:

$$\beta=(1/l_{298})(l_{T_2}-l_{T_1})/(T_2-T_1),$$

where β is the linear coefficient of thermal expansion, l_{298} is the reference length at 298°K, and l_{T_2} and l_{T_1}

[1] E. A. Owen and G. D. Preston, Phil. Mag. **2**, 1266 (1926).
[2] P. Schübel, Z. Anorg. Chem. **87**, 81 (1914).

TABLE I. Lattice parameters of AgMg below room temperature.

T (°K)	a (Å)
77	3.2961
143	3.3000
196	3.3035
251	3.3071
295	3.3102

are the lengths at the temperatures T_2 and T_1 (°K). The values of β obtained from the dilatometric data are given in Table II. Figure 1 shows in graphical form the coefficient of thermal expansion as a function of temperature for the combined results of x-ray and dilatometer measurements. The values join smoothly, indicating a satisfactory agreement between the two methods.

Having determined the coefficient of thermal expansion as a function of temperature, it is possible to calculate the Grüneisen parameter γ according to the following formula:

$$\gamma = 3\beta V/C_p\kappa_s, \tag{1}$$

where V is the atomic volume, C_p the specific heat at constant pressure, and κ_s the adiabatic compressibility. The atomic volume was calculated from the lattice parameter measurements by Ageev and Kuznetzov[3] and Hagel and Westbrook.[4] The data of these authors are in good agreement for the stoichiometric composition, the lattice parameter "a" having a value of 3.3135 Å at room temperature. Values of C_p were determined by Schübel[2] and Schimpff[5] and those of κ_s were measured by Chang, Himmel, and Neumann[6] by means of the ultrasonic pulse-echo technique. The value of γ shown in Fig. 2 as a function of temperature is nearly constant above the Debye temperature of 287°K,[6] but increases at lower temperatures. The

TABLE II. The linear coefficient of thermal expansion of AgMg from dilatometric measurements.

Temperature (°K)	β (10^{-6} per °K)
298–400	21.9
400–500	22.6
500–600	23.7
600–700	24.3
700–800	24.8

[3] N. V. Ageev and V. G. Kuznetzov, Izvest. Akad. Nauk. SSSR 289 (1937).
[4] W. C. Hagel and J. H. Westbrook, Trans. Met. Soc. AIME **221**, 951 (1961).
[5] H. Schimpff, Z. Phys. Chem. **71**, 257 (1910).
[6] Y. A. Chang, L. Himmel, and J. P. Neumann, J. Appl. Phys. **38**, 649 (1967), following article.

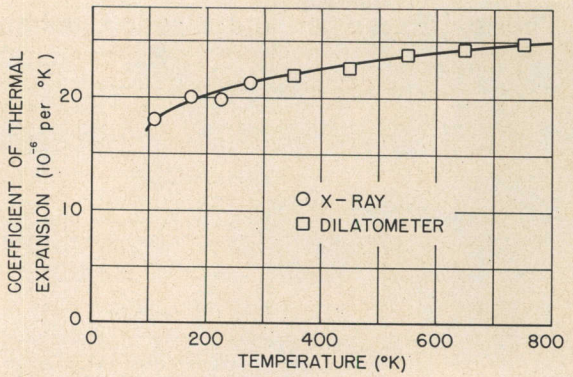

FIG. 1. The linear coefficient of thermal expansion β as a function of temperature.

Grüneisen parameter can also be calculated from a relationship derived by Slater[7] for metallic solids.

$$\gamma = (ar_0/2) + \tfrac{1}{3}, \tag{2}$$

where "r_0" is the interatomic distance at 0°K, and "a" is a parameter in the Morse potential curve. This parameter can be expressed in terms of the heat of sublimation ΔH_v and the bulk modulus B:

$$a = 3(BNcr_0/2\Delta H_v)^{1/2} \tag{3}$$

where "N" is Avogadro's number and "c" is a constant characteristic of the crystal structure. For a body-centered cubic solid, c has a value of 0.77.

From relationship (3) a value of 1.34 Å^{-1} was obtained for "a" resulting in a value of 2.24 for γ according to Eq. (2).

This value of γ is not in exact accord with the one obtained from thermal data alone (Fig. 2), but it shows the general usefulness of the Slater equation even for solids with not purely metallic bonding.

In evaluating Eqs. (2) and (3) the following data were used: The heat of sublimation of β'-AgMg at 0°K

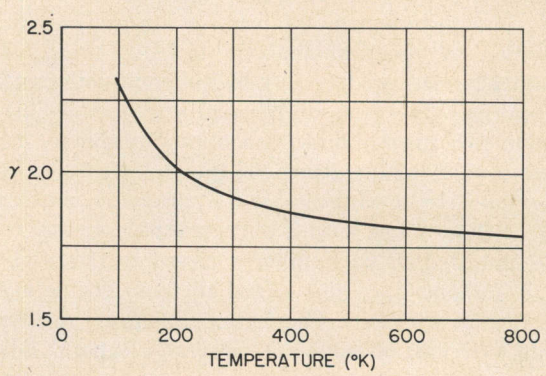

FIG. 2. The Grüneisen parameter γ as a function of temperature.

[7] J. S. Slater, *Introduction to Chemical Physics*, (McGraw-Hill Book Co., New York, 1939).

was obtained from the heats of sublimation of silver and magnesium and the heat of formation of β'-AgMg as follows: $\Delta H_{v,\mathrm{AgMg}}=0.5\Delta H_{v,\mathrm{Ag}}+0.5\Delta H_{v,\mathrm{Mg}}-\Delta H_{f,\mathrm{AgMg}}$. The values of ΔH_v for Ag and Mg were taken from Hultgren, Orr, Anderson, and Kelley,[8] the value of ΔH_f for AgMg from Robinson and Bever,[9] and the bulk modulus of AgMg from Chang, Himmel, and Neumann.[6] A value of 2.856 Å was taken for the interatomic distance at 0°K, based on the lattice parameter of the stoichiometric composition (3.3135 Å) and the coefficient of thermal expansion determined in the present work.

[8] R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, *Selected Values of Thermodynamic Properties of Metals and Alloys* (John Wiley & Sons, New York, 1963).

[9] P. M. Robinson and M. B. Bever, Trans. Met. Soc. AIME **230**, 1487 (1964).

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