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Measurement of Equilibrium Vacancy Concentrations in Dilute Aluminum-Magnesium Alloys*

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Precise measurements were made of the differential length expansion ($\Delta L'/L'-\Delta L^0/L^0$) and differential x-ray lattice-parameter expansions ($\Delta a'/a'-\Delta a^0/a^0$), between specimens of pure aluminum and aluminum-base alloys containing 0.56 and 1.11 at.% magnesium, during slow reversible heating and cooling between the solidus and 185°C. The differential-expansion data are used to determine absolute differences between the equilibrium vacancy concentrations C_v in the dilute alloys and the pure metal from the relation

$$\Delta C_v=C_v'-C_v^0=3(\Delta L'/L'-\Delta L^0/L^0)-3(\Delta a'/a'-\Delta a^0/a^0).$$

Here $\Delta L/L$ and $\Delta a/a$ are length and lattice-parameter expansions, and the prime and zero superscripts refer to the alloy and pure aluminum, respectively. Since C_v^0 is known from previous measurements, the vacancy concentrations in each alloy C_v' are then determined. The differential length and lattice-parameter measurements were carried out using the same technique previously employed in the determination of equilibrium vacancy concentrations in dilute aluminum-silver alloys. The technique allows the measurement of concentration differences as small as $\pm 4\times 10^{-5}$. The addition of magnesium caused only exceedingly small changes in the equilibrium vacancy concentrations. The changes did not exceed a few percent of the concentrations in pure aluminum. The results are compared at 650°C to the simple first-order vacancy–solute-atom-binding model of Lidiard and others. It is concluded that the vacancy–magnesium-atom binding free energy was $G_{v,\mathrm{Mg}}^b(650°\mathrm{C})\lesssim 0.01$ eV. Possible values of binding energies and entropies consistent with these results are discussed. The results are compared to the previous measurements for dilute aluminum-silver alloys where larger (but still small) solute-induced vacancy increments were found, and where $G_{v,\mathrm{Ag}}^b(650°\mathrm{C})\approx 0.08$ eV.

I. INTRODUCTION

EQUILIBRIUM vacancy concentrations in dilute aluminum alloys containing 0.52 and 0.94 at.% silver have been determined at elevated temperatures near the melting point.[1] In this work precise measurements were made of the differential length expansions and differential x-ray lattice parameter expansions between specimens of pure aluminum and the alloys during slow reversible heating and cooling between the solidus and the solubility temperature limit. The difference between the vacancy concentration in the alloy, $C_v'(T)$, and in the pure material, $C_v^0(T)$, was obtained from the relations

$$[C_v'(T)-C_v^0(T)]-[C_v'(T_r)-C_v^0(T_r)] =\Delta C_v(T)-\Delta C_v(T_r)=3(\sigma-\rho)\,, \quad (1a)$$

where

$$\sigma=\Delta L'/L'(T_r)-\Delta L^0/L^0(T_r)\,, \quad (1b)$$

and

$$\rho=\Delta a'/a'(T_r)-\Delta a^0/a^0(T_r)\,. \quad (1c)$$

The quantities σ and ρ were measured directly as a function of temperature. Here, σ is the differential length expansion, ρ is the differential lattice parameter expansion, and the prime and zero superscripts refer to the alloy and pure aluminum, respectively. The (T_r) refers to values at fixed low reference temperature. The quantity $[C_v'(T)-C_v^0(T)]$ is a rapidly increasing function of temperature, and when T_r is taken sufficiently low $[C_v'(T_r)-C_v^0(T_r)]$ becomes smaller than experimental error and therefore may be neglected in Eq. (1a). Values of $[C_v'(T)-C_v^0(T)]$ at elevated temperatures may then be determined absolutely from measurements of σ and ρ. Equilibrium vacancy concentrations in the alloy, $C_v'(T)$, may then be determined, since values of $C_v^0(T)$ are known from previous measurements of the equilibrium vacancy concentrations in pure aluminum.[2] This method has the advantage that absolute equilibrium concentrations are obtained and that detailed information regarding the physical properties of the vacancies, some of which may be bound to solute atoms, is not required. Further discussion of Eq. (1) has been given previously.[1]

In the previous aluminum-silver system the vacancy concentration differences were small and amounted to less than 23% of the vacancy concentration in pure aluminum at the solidus temperatures. These small positive vacancy increments indicated the existence of some type of small positive free energy of binding

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[1] D. R. Beaman, R. W. Balluffi, and R. O. Simmons, Phys. Rev. **134**, A532 (1964).

[2] R. O. Simmons and R. W. Balluffi, Phys. Rev. **117**, 52 (1960).

TABLE I. Summary of some data from quenching experiments since 1961 indicating interaction between vacancies and magnesium atoms in aluminum base alloys.

Solute concentration (at.%)	Assumed binding entropy, $S_{v,\mathrm{Mg}}^b$	Estimated binding energy, $E_{v,\mathrm{Mg}}^b$ (eV)	Method	Reference
Mg(0.05 to 0.5)	0	0.18	Electrical resistivity	4
Mg(11.2)	?	very small[a]	Electrical resistivity	5
Mg(0 to 0.1)+Zn(4.3)	?	<0.09	Electrical resistivity and hardness	6
Mg(0.1)+Zn(4.3)	0	0.54	Electrical resistivity annealing kinetics	7
Mg(7.7,10.2)	?	0.3–0.4	Density change	8
Mg(0.1,0.5)	0	0.20	Electrical resistivity	9
Mg(0.008,0.093)	?	>0	Isothermal annealing of electrical resistivity	10
Mg(5)	0	0.1–0.4	Dislocation density and growth rate by electron microscopy	11
Mg(0.02 to 0.05)+Cu(1.7)	0	0.45	Hardness	12
Mg(1.2,3.5,7.3)	0	$\lesssim 0.1$	Dislocation density by electron microscopy	13
Mg(5)	?	>0	Internal friction	14

[a] Analysis of these data using the technique of Ref. 9 yields $G_{v,\mathrm{Mg}}^b=0.016\pm0.004$ eV.

between vacancies and silver atoms which did not exceed kT at the melting point. The results could be fitted within the possible uncertainty of the data to the simple first-order model of Lidiard and others,[3] in which there is a binding free energy between nearest-neighbor vacancies and solute atoms. Assuming the presence of only isolated monovacancies, isolated solute atoms, and simple vacancy-solute pairs, this model yields the relation

$$C_v'=C_v^0[1-12C_s+12C_s\exp(-S_{vs}^b/k)\times\exp(E_{vs}^b/kT)], \quad (2)$$

where C_s is the total solute concentration, E_{vs}^b is the vacancy-solute binding energy, and S_{vs}^b is the binding vibrational entropy. Vacancy-vacancy and solute-solute clustering are neglected. Comparison of the data to Eq. (2) yielded $E_{v,\mathrm{Ag}}^b=0.08\pm0.03$ eV for $S_{v,\mathrm{Ag}}^b=0\pm\frac{1}{2}k$, and $E_{v,\mathrm{Ag}}^b=0.08\pm0.07$ eV for $S_{v,\mathrm{Ag}}^b=0\pm k$. Unfortunately, the data were not sufficiently accurate to determine the unknown entropy $S_{v,\mathrm{Ag}}^b$ although its value is probably in the range indicated above. It was emphasized that the apparent crude agreement of the aluminum-silver alloy data with Eq. (2) did not serve to validate the simple-binding model for this system, and that further work would be required to produce a detailed picture of the equilibrium point-defect structure.

The system aluminum-magnesium was chosen for study in the present work, since this system has been studied rather intensively, and there was some indication of a strong binding between vacancies and magnesium atoms. The presence of strong binding would, of course, produce large vacancy increments and hopefully allow a more quantitative study of possible binding models. A summary of some previous work[4–14] is given in Table I. It is noted that there is considerable disagreement regarding the magnitude of the binding energy. Both large and small binding energies are claimed, and there is a spread of about an order of magnitude in the estimated values. These investigations were all carried out in quenched systems near room temperature where extensive clustering of the dense point-defect system would be expected. The considerable disagreement regarding the binding is not surprising in view of the complex defect structures expected in many cases and the oversimplified *ad hoc* nature of many of the analyses which have led to the estimates in Table I.

In the present equilibrium experiments near the melting point the degree of clustering is minimized, and the binding between small low-order vacancy-solute clusters is investigated directly. The major objective of the present work was, therefore, to obtain as much information as possible regarding the equilibrium point defect structure at elevated temperatures in this system and to attempt to settle the question of

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[3] A. B. Lidiard, Phil. Mag. **5**, 1171 (1960); W. M. Lomer, in *Vacancies and Other Point Defects in Metals* (The Institute of Metals, London, 1958), p. 79; F. Seitz, Acta Cryst. **3**, 355 (1950).

[4] J. Takamura, *Proceedings of the International Conference on Lattice Defects in Quenched Metals, 1964* (Academic Press, Inc., New York, to be published 1965). We want to thank Professor Takamura for a copy of his paper prior to its publication.

[5] K. Detert and L. Thomas, Acta Met. **12**, 431 (1964).

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[7] C. Panseri and T. Federighi, Acta Met. **11**, 575 (1963).

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[9] J. Takamura, K. Okazaki, and I. G. Greenfield, J. Phys. Soc. Japan **18**, Suppl. III, 78 (1963).

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[12] K. M. Entwistle, J. H. Fell, and K. I. Koo, J. Inst. Metals **91**, 84 (1962–1963).

[13] K. H. Westmacott, R. S. Barnes, D. Hull, and R. E. Smallman, Phil. Mag. **6**, 929 (1961).

[14] W. G. Nilson, Can. J. Phys. **39**, 119 (1961).

the magnitude of the binding energy between monovacancies and magnesium atoms in an aluminum matrix.

II. EXPERIMENTAL

The technique used was identical to the one used in the aluminum-silver work.[1] Since σ and ρ as defined by Eq. (1) are slowly varying functions of temperature, they may be safely determined in individual experiments. The estimated error introduced by temperature-measuring problems and most other factors in this procedure is about 1% of ΔC_v. This differential technique, for which a complete error analysis is presented in Appendix B of Ref. 1, has the advantage that small differential effects are measured directly and therefore can be determined with relatively good precision.

A. Specimen Chemistry

The choice of magnesium as a solute was advantageous in one respect since it exhibits extensive solubility in aluminum down to room temperature.[15] However, magnesium is highly volatile and easily oxidized, and a severe problem was anticipated in maintaining the required specimen surface condition and constant composition during extended heating near the solidus temperature. It is known that a continuous loss of magnesium occurs when aluminum-magnesium alloys are heated to elevated temperatures in air, argon,[16] or prepurified nitrogen. However, Hine and Guminski[16] found that the oxidation of aluminum-magnesium alloys was drastically reduced when they were heated in dry carbon dioxide at 510°C, presumably due to the formation of a protective film consisting primarily of magnesium carbonate. In order to ascertain the type of oxidation behavior that would be encountered in the present experiment, a series of test runs was carried out. Strips of material containing 0.55, 1.10, and 2.20 at.% Mg were heated at elevated temperatures in carbon dioxide for periods of up to 210 h, and weight gains were determined. The oxidation kinetics (weight gain *versus* time at oxidation temperature) observed were as follows: (a) linear at 635°C for 0.55 at.% Mg; (b) parabolic at 610°C for 0.55 at.% Mg; (c) linear at 610°C for 1.10 at.% Mg; and (d) parabolic at 585°C for 2.20 at.% Mg. Having these data, and knowing the total high-temperature exposure of the specimens during the subsequent vacancy-measuring runs, we estimate that the uniform oxide thickness which could have developed constituted less than 0.6% of the expected x-ray penetration depth. In addition, the surface appearance was found to be a sensitive measure of the amount and uniformity of oxidation. The surface discoloration observed after the completion of the vacancy-measuring runs indicated only a slight and quite uniform oxidation. Furthermore, fine surface detail, as observed in the 60× telescopes, during the length measurements remained distinct during several heating and cooling runs, and no observable changes occurred in the appearance of the reference indentations.

No magnesium loss was detected in chemical analysis of the oxidized strips. In addition, the x-ray measurements of lattice parameter changes were capable of detecting any magnesium loss in the x-ray volume greater than about 0.001%. Since no systematic irreversibility in the x-ray data curves was noted, and since the x-ray intensity as a function of temperature was reproducible over several heating and cooling runs, it is concluded that no appreciable magnesium loss occurred.

As indicated in the aluminum-silver experiment,[1] specimen homogeneity was an extremely important consideration, since the x-ray volume constituted only an extremely small portion of the total specimen volume. Homogeneous alloy bars approximately 1.9×1.9×56 cm in length were produced[17] using a double-induction melting technique. The starting materials, consisting of 99.999% pure aluminum and 99.995% pure magnesium, were induction-melted in a graphite crucible under one atmosphere of argon prior to vertical casting and gradient freezing. This material was then vacuum-induction melted (10^{-2} mm Hg) and gradient solidified within 10 min. Four bars, two of each composition, were produced. One bar of each composition was then used for extensive destructive chemical analysis. The remaining two bars, i.e., those to be used in the experiment, were cold-rolled, and then surface chemical testing was performed along their entire length using an Applied Research Laboratories Quantometer. The analyses revealed compositions of 0.56 ± 0.01 at.% magnesium (maximum deviation of 0.02 at.% magnesium) and 1.11 ± 0.02 at.% magnesium (maximum deviation of 0.03 at.% magnesium). Spectrographic analysis revealed approximately 10 ppm of other impurities consisting mainly of Cu, Fe, and Si.

The pure aluminum specimens were the same as those used in the previous experiments.[1,2]

The average grain sizes in the specimens at the completion of the experiment were 17, 5, and 3 mm in the 0.00, 0.56, and 1.11 at.% magnesium alloys, respectively.

B. Length Measurements

The length expansion parameter σ was determined by measuring the variable β, where

$$\beta(T)=L'(T)-L^0(T), \tag{3}$$

which is simply the difference in length between the alloy bar and the pure aluminum bar. Substitution of

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[15] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958), p. 105.

[16] R. A. Hine and R. D. Guminski, J. Inst. Metals **89**, 417 (1960–1961).

[17] The alloy material was supplied by Cominco Products, Inc. of Spokane, Washington.

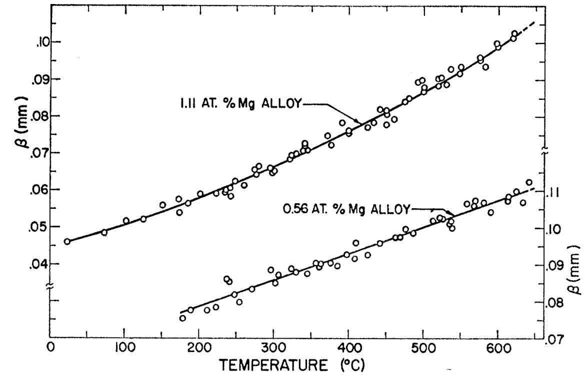

FIG. 1. Measured length differences, $\beta(T)=L'(T)-L^0(T)$, versus temperature for the 0.56 and 1.11 at.% magnesium alloys. Since heating and cooling measurements occurred reversibly, the data points for individual heating and cooling runs are not distinguished.

Eq. (3) in Eq. (1b) yields

$$\sigma=\frac{L^0(T)+\beta(T)}{L^0(T_r)+\beta(T_r)}-\frac{L^0(T)}{L^0(T_r)}, \tag{4}$$

where σ is given as a function of β and the length of the pure aluminum bar [$L^0(20°\text{C})=494.78$ mm and 494.33 mm for the 0.56 and 1.11 at.% Mg alloys, respectively]. Two bars, one alloy and the pure aluminum, after being precisely machined and stress relieved, were fitted together in a closely interlocking assembly,[18] and placed in a precisely controlled furnace. The parameter σ was then determined by measuring β as a function of temperature during slow step heating between room temperature and the solidus temperature of the alloy. Further details may be found in Ref. 1.

The values of β for the two alloys are shown in Fig. 1. Since no systematic lack of reversibility during several heating and cooling runs was observed, the individual heating and cooling points are not distinguished. For the 0.56 at.% alloy the mean absolute deviation from the smooth curve of the 46 points obtained in two heating and three cooling runs was $\pm 1.3\,\mu$. For the 1.11 at.% alloy the mean absolute deviation of 63 points obtained in five heating and six cooling runs was $\pm 1.1\,\mu$. (See Appendix B in Ref. 1 for errors caused by these deviations.)

C. X-Ray Lattice Parameter Measurements

The x-ray expansion parameter ρ was determined by measuring the spacing (X) between the diffracted lines from the alloy and the pure aluminum. The computation involved in reducing X data to ρ values is outlined in the appendix. This method differed from that employed in the aluminum-silver experiment[1] because the lattice parameters of dilute aluminum-magnesium alloys are substantially different from those of pure aluminum.

After an x-ray sample of the proper orientation [(442) planes parallel to the x-ray specimen front surface] was cut from each length bar using an electrical discharge cutting machine, the three samples were inserted in a spectroscopically pure graphite holder which was placed in the precisely controlled furnace. Each specimen was x rayed by an oscillating camera using Ni $K\alpha_1$ radiation (1.65784 Å) at a series of selected equilibrium-holding temperatures, and the three diffraction peaks at each temperature recorded on a single x-ray film. The separation between these peaks (X) was then measured by means of a coordinate comparator. A more detailed description of the procedure used is presented in Ref. 1 Measurements were carried out between 185 and 644°C, and the maximum temperature drift during each three exposures was maintained at less than 0.1°C.

The values of X are shown in Fig. 2. Since no systematic lack of reversibility during four heating and two cooling runs was observed, the individual heating and

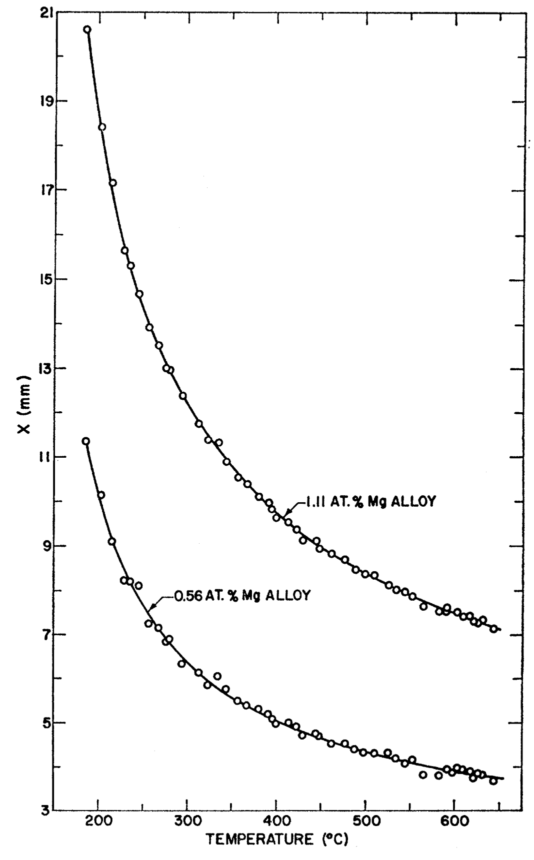

FIG. 2. Measured diffraction line separations $X(T)$ versus temperature for the 0.56 and 1.11 at.% magnesium alloys. The distance X is the separation on the film between the pure aluminum and the alloy Laue-Bragg diffraction lines (see Fig. 6).

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[18] The accurate machining required was performed by the American Machine and Foundry Company of Chicago, Illinois.

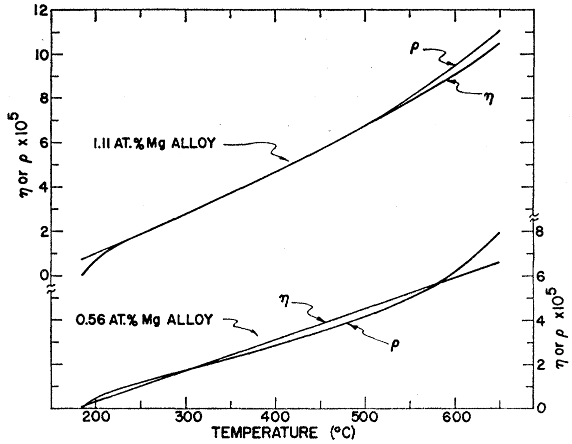

FIG. 3. η and ρ versus temperature for the 0.56 and 1.11 at.% magnesium alloys. The values of η and ρ are obtained from the smooth β and X curves drawn in Figs. 1 and 2. The values of $\frac{1}{3}\Delta C_v(T_r)$ are 0.1×10^{-5} and 0.7×10^{-5} for the 0.56 and 1.11 at.% magnesium alloys, respectively (see text Sec. III).

cooling points are not differentiated. In the case of the 0.56 at.% alloy, 46 points show a mean absolute deviation in X of ±0.05 mm in the temperature range of 340 to 650°C and ±0.11 mm in the temperature range of 185 to 340°C. For the 1.11 at.% alloy 46 points show a mean absolute deviation in X of ±0.04 mm in the temperature range of 340 to 650°C and ±0.06 mm in the temperature range of 185 to 340°C.

III. RESULTS

Having the β and X curves giving the best fits in Figs. 1 and 2, we calculated corresponding values of σ and ρ using a reference temperature of $T_r=185°\text{C}$ which corresponded to the lowest temperature of the lattice parameter data. These values therefore served to determine the quantity $[\Delta C_v(T)-\Delta C_v(T_r)]$ from Eq. (1). The problem at this point was to pick a small suitable value of $\Delta C_v(T_r)$ so that $\Delta C_v(T)$ averaged out to near zero in the low temperature range near T_r. This procedure was based on the fact that these quantities must be exceedingly small at low temperatures in the vicinity of T_r. We therefore followed our previous procedure[1] and defined a new parameter η by

$$3\eta=3\sigma+\Delta C_v(T_r)\,, \tag{5}$$

so that

$$\Delta C_v(T)=3(\eta-\rho)\,. \tag{6}$$

Best results were obtained by using values of $\frac{1}{3}\Delta C_v$ (185°C) of 0.1×10^{-5} and 0.7×10^{-5} for the 0.56% and 1.11% alloys, respectively. The resulting η and ρ curves are shown in Fig. 3. It is seen immediately that any excess vacancy concentrations near the solidus temperature were exceedingly small in these alloys. For purposes of comparison we have included the corresponding "best fit" data obtained previously (but not given explicitly in Ref. 1) for the aluminum-silver alloys in Fig. 4. The vacancy increments at elevated temperatures were considerably larger in the aluminum-silver system.

TABLE II. Values of ΔC_v (in units of 10^{-5}) at 650°C for present aluminum-magnesium alloys and previously measured aluminum-silver alloys. $C_v^0(650°\text{C})=81\times10^{-5}$.

	0.56 at.% Mg	1.11 at.% Mg	0.52 at.% Ag	0.94 at.% Ag
Average "best fit"	−4	−1	12	13[a]
Maximum	+1	+3	17	18[a]
Minimum	−8	−5	8	7[a]

[a] Value at 643°C.

Since the differential effects in the present work were so small, it was necessary to devote considerable attention to the probable magnitude of the experimental uncertainties. Essentially the same methods as those used previously were employed. It was again assumed that the uncertainty in the β and X values was given by the mean absolute deviation of the data points from the best smooth curve drawn through the data. Thus, the possible β values for the 0.56 at.% magnesium alloy lay in a β error band 2.6 μ wide (±1.3 μ) centered on the curve in Fig. 1. The corresponding band for the 1.11 at.% alloy was 2.2 μ wide (±1.1 μ). The X error bands were wider at low temperatures (high Bragg angles θ) because of $\tan\theta$ line broadening. In the temperature range 185 to 340°C the bandwidths were 0.22 mm (±0.11 mm) and 0.12 mm (±0.06 mm) for the 0.56 at.% and 1.11 at.% alloys, respectively. In the range 340 to 650°C, the corresponding widths were 0.10 mm (±0.05 mm) and 0.08 mm (±0.04 mm). We note that the magnitudes of these mean deviations are quite similar to those obtained in the previous work.[1]

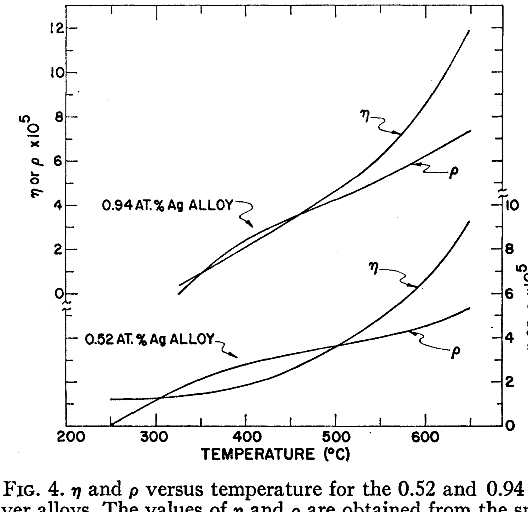

FIG. 4. η and ρ versus temperature for the 0.52 and 0.94 at.% silver alloys. The values of η and ρ are obtained from the smooth β and X curves presented in Figs. 2 and 3 of Ref. 1. The values of $\frac{1}{3}\Delta C_v(T_r)$ are 1.2×10^{-5} and 0.3×10^{-5} for the 0.52 and 0.94 at.% silver alloys, respectively.

Smooth curves of maximum and minimum slope were then drawn within these bands, and the results were combined appropriately to obtain maximum and minimum values of $(\eta-\rho)$. The results at the highest temperature of 650°C, multiplied by 3 to convert them to values of ΔC_v, are shown in Table II. The "best fit" values are seen to be slightly negative. However, the maximum and minimum values fall on either side of a zero effect, and we must conclude that the definite establishment of any effects of alloying on the equilibrium vacancy concentration was below the resolution of the present experiment. The equilibrium vacancy concentration in pure aluminum at 650°C is $C_v{}^0 = 81\times10^{-5}$,[2] and therefore any alloying effects were no larger than a few percent. In contrast to this, the effects in the aluminum-silver system, which are also given in Table II, were substantially larger.

As a final test of the general procedure, a check was made of the sensitivity of the results to the choice of reference temperature. Sensibly the same results were obtained for reference temperatures between 185 and 325°C.

IV. MODELS AND DISCUSSION

It is interesting to compare the present data to the simple first-order binding model represented by Eq. (2). As pointed out previously, the data for the aluminum-silver alloys were not inconsistent with the model within the experimental uncertainty of the data.[1] Arguments were given there that vacancy-vacancy clustering and silver atom-silver atom clustering were probably not sufficiently important near the solidus temperature to invalidate the simple model. For example, it was concluded from the available experimental data that $E_{\mathrm{Ag,Ag}}{}^b$ was less than kT near the solidus. This conclusion was also consistent with the small magnitude of the attractive chemical interaction predicted by Blandin *et al.*[19] Despite these conclusions, however, it must be stressed that the results previously obtained for the aluminum-silver did not serve to validate uniquely the simple nearest neighbor model.

In the case of the aluminum-magnesium system it appears that similar conclusions should hold near the solidus regarding the possible perturbing effects of clustering. The type of phase diagram exhibited by this system, and the fact that zone formation is observed at low temperatures, indicates that at least some degree of clustering of magnesium atoms indeed occurs at all temperatures. However, there is no reason to suspect from the phase diagram that clustering is much more severe than in the aluminum-silver system. The free energies of mixing at elevated temperatures in the dilute fcc phases of the aluminum-magnesium and aluminum-silver systems are of the same order.[20] (Unfortunately, however, heats of mixing for the aluminum-magnesium system are unavailable.) Finally, Blandin *et al.*[19] predict a chemical attractive interaction between magnesium atoms of only ~0.01 eV.

Since the excess vacancy increments were so small and therefore known with low precision, we calculate the free energy of binding,

$$G_{vs}{}^b = E_{vs}{}^b - TS_{vs}{}^b, \tag{7}$$

only at the highest temperature of 650°C using Eq. (2). Comparing the data for the individual alloys to Eq. (2), we find for the 0.56 at.% alloy at 650°C: $G_{v,\mathrm{Mg}}{}^b$(best fit) $= -0.11$ eV; $G_{v,\mathrm{Mg}}{}^b(\max) = 0.01$ eV; and $G_{v,\mathrm{Mg}}{}^b(\min) = -\infty$. For the 1.11 at.% alloy; $G_{v,\mathrm{Mg}}$(best fit) $= -0.01$ eV; $G_{v,\mathrm{Mg}}{}^b(\max) = 0.02$ eV; and $G_{v,\mathrm{Mg}}{}^b(\min) = -0.05$ eV. Seeking a common free energy for both alloys, we conclude that the maximum possible *attractive* free energy of binding is about 0.01 eV.

The data by themselves do not preclude a negative binding energy (nearest neighbor repulsion). However, no realistic estimates of possible limits to this possibility can be made in view of the accuracy of the differential data. The large calculated negative free energies are misleading in this nearest neighbor model, since very large repulsive interactions are required to produce even extremely small values of (ΔC_v) in this model. For example, in the limit, an infinite repulsion (i.e., $G_{vs}{}^b = -\infty$) is only capable of clearing out the equilibrium vacancy concentration in the 12 sites adjacent to each solute atom. This concentration increment is only $(\Delta C_v) = 12C_v{}^0C_s \simeq 10\times10^{-5}$ at 650°C. Experiments of the present type therefore do not allow the quantitative investigation of possible repulsive interactions using this model.

We note that the corresponding common fit to the simple model for the two previous aluminum-silver alloys yielded a free energy of binding $G_{v,\mathrm{Ag}}{}^b = 0.08$ eV at 650°C.

At this point we have derived free energies of binding at 650°C by a one-point comparison at high temperature. The incremental data for both the present and previous systems were not accurate enough at the lower temperatures to allow separate determinations of the binding energies and entropies. It is noted that with systems such as the present, where the free energy of binding is exceedingly small, the binding energy may differ appreciably from the binding free energy at high temperatures when the binding entropy is significantly large. This is shown in Fig. 5 which illustrates possible pairs of corresponding $E_{vs}{}^b$ and $S_{vs}{}^b$ values which are consistent with given fixed values of $G_{vs}{}^b$ at 650°C. For example, for $G_{v,\mathrm{Mg}}{}^b(650°\mathrm{C}) = 0.01$ eV, we

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[19] A. Blandin, J. L. Déplanté, and J. Friedel, J. Phys. Soc. Japan, **18**, Suppl. II, 85 (1963).

[20] R. Hultgren, R. L. Orr, P. D. Anderson, K. K. Kelley, *Selected Values of Thermodynamic Properties of Metals and Alloys* (John Wiley & Sons, Inc., New York, 1963), pp. 335 and 419.

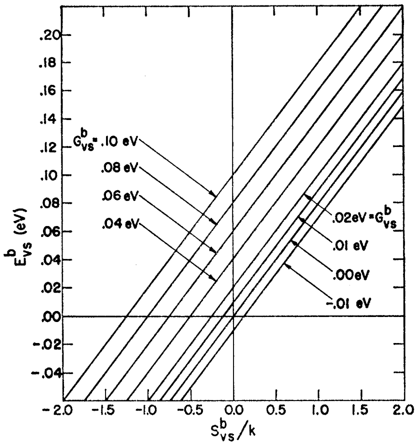

FIG. 5. Possible pairs of corresponding $E_{vs}{}^b$ and $S_{vs}{}^b$ values which are consistent with selected values of $G_{vs}{}^b$ at 650°C according to the relation $G_{vs}{}^b=E_{vs}{}^b-TS_{vs}{}^b$.

have $E_{v,\mathrm{Mg}}{}^b=0.05$ eV if $S_{v,\mathrm{Mg}}{}^b=k/2$. Unfortunately, there is little more that we can say at present about the actual values of $E_{v,s}{}^b$ and $S_{v,s}{}^b$ for either the aluminum-silver or aluminum-magnesium systems. However, since the self entropies are in the range 1–3k,[21] it is probable that the actual values of $S_{vs}{}^b$ are within the range shown in Fig. 5 and therefore that the $E_{vs}{}^b$ does not differ from $G_{vs}{}^b$(650°C) by more than about ±0.1 eV.

We conclude from the above that $E_{v,\mathrm{Mg}}{}^b \lesssim 0.1$ eV and that $E_{v,\mathrm{Ag}}{}^b \lesssim 0.2$ eV but emphasize that these energies may actually be considerably lower than these, if the binding entropies $S_{vs}{}^b$ are small (or negative). In fact, if the binding entropies are essentially zero, then $E_{v,\mathrm{Mg}}{}^b<0.01$ eV, and $E_{v,\mathrm{Ag}}{}^b \simeq 0.08$ eV. These results are not inconsistent with the chemical interaction calculated by Blandin *et al.*,[18] which predicted attractive interactions of the order of a few hundredths of an eV for these systems.

The present results clearly indicate that binding effects between single vacancies and single magnesium atoms are quite small in aluminum. The large binding energies reported by several investigations (see Table I) therefore cannot be correct. In cases where these investigations were carried out in dense clustered systems obtained by quenching, the observed phenomena were most likely controlled by higher order clusters exhibiting apparent strong binding. Our results render questionable the application of simple binding models to complex quenched systems at low temperatures. Additional difficulties in the interpretation of quenching results on alloy systems have been discussed by Bass.[22]

V. SUMMARY

We summarize our results for the aluminum-magnesium and aluminum-silver systems.[1]

(1) Any excess vacancy concentrations at elevated temperatures in the aluminum-magnesium alloys (relative to the concentrations in pure aluminum) were exceedingly small. In fact, when probable experimental error was taken into account, the results straddled a zero effect, and it was concluded that any differential effects were below the well-defined resolution of the measurements. At 650°C any excess vacancy concentrations were no larger than a few percent of the concentrations in pure aluminum.

(2) Excess vacancy concentrations in the aluminum-silver alloys were larger and were measured with fair precision at 650°C.[1] In these alloys the excess concentrations were less than $\frac{1}{4}$ of the concentrations in pure aluminum at 650°C.

(3) Attempts were made to compare the results to the simple single vacancy-single solute atom binding model of Lidiard *et al.*[3] It was concluded that perturbing effects due to the formation of other clusters were probably not sufficiently strong in these systems to seriously invalidate the model at high temperatures. Because of the generally low accuracy of the incremental data, it was reasonable to derive free energies of binding, $G_{vs}{}^b$, only at 650°C. It was concluded that $G_{v,\mathrm{Mg}}{}^b(650)<0.01$ eV and $G_{v,\mathrm{Ag}}{}^b(650) \simeq 0.08$ eV. Our data for the aluminum-magnesium system did not preclude a conceivable repulsive free energy of binding. However, it was pointed out that no reasonable estimate of such a repulsive energy could be made. It was also pointed out that these experimental results did not necessarily tend to validate the simple model.

(4) The above binding free energies allowed a considerable range in possible values of pairs of corresponding binding energies and entropies, obeying the relation $G_{vs}{}^b=E_{vs}{}^b-TS_{vs}{}^b$. Some discussion was given of the range of possibilities.

(5) The present equilibrium results appear to differ considerably from those of several previous investigations of quenched alloy systems. Such studies have generally not independently validated the simple-binding (or other) model, yet many have used such a model in their interpretation. It appears that considerable caution is appropriate in examining such experiments and their interpretation.

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Trevison of Cominco Products, Inc., for his cooperation in supplying the alloy materials.

APPENDIX

Method for Determining ρ from Experimentally Obtained Quantities

In order to determine ρ, consider the geometry of diffraction shown for a given temperature (T) in Fig. 6. $F(T)$ is the distance from the fiducial mark on the film to the peak of the diffraction line for the pure aluminum sample. It can either be measured directly or calculated from known $\Delta a/a$ data for pure aluminum[2] using Bragg's law, since M (specimen-to-film distance at the tangent point$=505.16$ mm), $N(57.90$ mm$)$, $\alpha(7°18'09'')$, $\gamma(6°32'19'')$, and $a^0(20°\mathrm{C})$ (4.04911 Å) are known constants. $F'(T)$ is the distance from the fiducial mark to the peak of the alloy diffraction line and is obtained from the experimental X data by taking $F'(T)=F(T)+X(T)$. The Bragg angle for the alloy material $\theta'(T)$ is determined from the diffraction geometry.

$$\theta'=\tfrac{1}{2}(\pi-\arctan\{[F'(T)-N]/M\}-\alpha-\gamma).$$

Bragg's law then gives $a'(T)$ (lattice parameter of the alloy material), and the knowledge of a' and a^0 as functions of temperature permits the calculation of ρ at any particular temperature using a selected reference temperature (T_r).

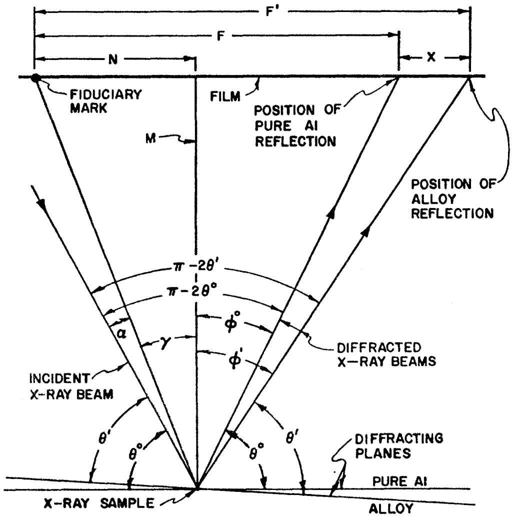

FIG. 6. X-ray diffraction geometry for the pure aluminum and one alloy sample at a fixed temperature. α, γ, M, and N are constants of the camera which oscillates about an axis at the sample face.

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Self-Compensation-Limited Conductivity in Binary Semiconductors. IV. n-$\mathrm{Zn}_x\mathrm{Cd}_{1-x}\mathrm{Te}$*†

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The electrical conductivity of heavily Al-doped $\mathrm{Zn}_x\mathrm{Cd}_{1-x}\mathrm{Te}$ has been studied. The sharp transition expected from theory in the conductivity as a function of x is confirmed at a value of $x=0.69$. Above this value only high-resistivity material is obtainable which becomes high-resistivity p type for x above ≈ 0.75. The fact that the transition from low to high resistivity as a function of x is not nearly so sharp as expected from the theory is attributed to the spread in vacancy sizes and hence energy levels of the compensating vacancies that one expects in such an alloy system; pairing effects may also play a role.

We have described in preceding papers of the present series[1–3] the limitation imposed on the accessible conductivity in binary semiconductors by the process of self-compensation by natural defects. In the course of these studies it has been pointed out that in compounds of intermediate ionicity, specifically the II–VI compounds, the second ionization levels of the natural defects involved, e.g., vacancies, are of critical importance. In order to study these levels experimentally, we have chosen to examine the electrical conductivity of single crystals of solid solutions of II–VI compounds. In particular, we have chosen to study Al-doped solid solutions consisting of ZnTe (in which appreciable n-type conductivity cannot be obtained[2]) with CdTe (in which appreciable n-type conductivity is easily obtained[4]).

As has been suggested, the sizes of the atoms comprising a particular II–VI compound determine the

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