Prediction of Ternary Liquidus Temperatures by Statistical Modeling of Binary and Ternary Ag–Al–Sn–Zn Systems

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ABSTRACT: The relationship of liquidus temperatures among six binary and four ternary phases in a Ag–Al–Sn–Zn system was analyzed by means of statistical modeling. Four statistical models to predict changes in the liquidus temperatures in Ag–Al–Sn–Zn were proposed on the basis of different hypotheses derived from macroscopic and microscopic standpoints. The results of interpolation tests to evaluate the prediction accuracies of the ternary liquidus temperatures suggested that the multivariate regression model based on binary liquidus temperatures, interactive binary liquidus temperatures, and products of atomic ratios was found to be the most effective among the four models. It was numerically shown that the prediction accuracies of the liquidus temperatures in local ternary systems of Ag–Al–Sn–Zn can be improved further by using the models identified in their neighboring systems. Finally, the possibility to extract the general trend and the abnormal combination of elements for the prediction of liquidus temperatures was discussed on the basis of the statistical framework we considered.

1. INTRODUCTION

Recent advances in alloys and intermetallic compounds have attracted much attention not only in metallurgy but also in chemistry and material science. For example, nanoparticles of intermetallic compounds and alloys have been intensively studied for their optical, magnetic, and catalytic properties.1,2 Alloys with low melting points, fusible alloys, are widely used in solders, coolants, fluxes, etc. For instance, Gá–In–Sn and related alloys are liquids around room temperature and they are studied for cathode contacts for a light-emitting device,3 sonoluminescence,4 and H2 production sources.5 Thus, exploring new alloys with low melting points is highly demanded. Liquidus temperatures, above which a material is completely liquid, have been widely known in binary systems. These data are summarized as databases of phase diagrams, which exhibit various phase transitions in terms of temperature and atomic ratios mostly under ambient pressure.6 However, in ternary systems, there is only a limited number of phase diagrams.7 In more complex systems, there are much less studies involved.8 The most established approach for the prediction of a phase diagram is based on macroscopic approaches using thermodynamic parameters.9–11 Thermodynamic parameters include enthalpy, entropy, and heat capacity for each phase and the free energy calculated by these parameters should be minimized to reach a thermodynamic equilibrium condition. Thermodynamic software packages have been developed on the basis of these thermodynamic data.12–14 Nonetheless, such predictions are not simple issues and experimental data is still necessary for the prediction. Experimental studies need much efforts in terms of time and cost.

The other approach to understand liquidus temperatures is based on microscopic approaches, including atomic vibration and electronic interaction of atomic orbitals. More than a century ago, Lindemann estimated melting points of metals and compounds on the basis of atomic vibration (Lindemann criterion), although the quantitative estimation of the melting point is difficult.15 Statistical approaches are also utilized to know what factors affect the melting points of metals and compounds. Chelikowsky and Anderson analyzed the relationship between melting points of alloys and other factors: electron count, atomic number, orbital radius, electronic negativity, lattice parameter, etc.16 They found that melting points of binary compounds with normal metals were moderately related to the change in their volumes. Atsuto et al. statistically analyzed the melting points of single metals and binary compounds and various factors calculated by density functional theory: volume, bulk module, etc.17 Nonetheless, these studies are limited to simple substances and stoichiometric binary compounds and not alloys with various atomic ratios. Although statistical approaches have attracted great attention, there is still a limit in predicting melting points.
Predicting melting points by microscopic and macroscopic approaches, the prediction of melting points of ternary or a higher system is still challenging. Considering the recent attention to data analysis, including machine learning, and to high-throughput and statistical analyses for exploring new materials, data analyses must be useful for predicting melting points and have the potential for mining clues for finding undiscovered correlations, including microscopic and macroscopic views. In this work, we statistically analyzed liquidus temperatures of ternary phase diagrams using that of the binary phase diagram in the Ag–Al–Sn–Zn system. Ag–Al–Sn–Zn systems have been intensively studied to develop lead-free solder, and all of the four ternary and six binary phase diagrams are thus available. The accuracy of the prediction of ternary liquidus temperatures was improved by the linear regression model, including both the interaction of two binary liquidus temperatures and atomic interactions. Further improvement was achieved by the hierarchical model, which included extended ternary liquidus temperatures.

2. DATA SETS AND CONSTRUCTION OF MODELS

2.1. Data. The data of atomic ratios and liquidus temperatures of binary and ternary phase diagrams in the Ag–Al–Sn–Zn system were extracted from the database books\(^{26\text{-}27}\) and a publication\(^{26}\) by using WebPlotDigitizer software.\(^{27}\) Thus, the data sets were composed of atomic ratios and liquidus temperature on contour lines, at every 50 or 100 °C.

2.2. Construction and Evaluation of Regression Models for Explaining the Change in Liquidus Temperatures. In this subsection, we consider statistical approaches to predict liquidus temperatures in ternary systems from atomic ratios and liquidus temperatures in binary and ternary phase diagrams. Let \(C_A, C_B\), and \(C_C\) be the atomic ratios of \(A, B,\) and \(C\) in the ternary system \((0 < C_A < 1, 0 < C_B < 1, 0 < C_C < 1, C_A + C_B + C_C = 1)\), respectively. Moreover, melting points of \(A, B,\) and \(C\) are represented as \(T_A, T_B,\) and \(T_C\) respectively. Liquidus temperatures in the \(A–B\) binary system are written as \(T_{A-B}(C_A/(C_A + C_B))\), and so on. At atomic ratios in a ternary \(A–B–C\) system, ternary liquidus temperatures are denoted as \(T_{A-B-C}(C_A, C_B, C_C)\). Here, we proposed four statistical models, (i)–(iv), to estimate ternary liquidus temperatures, \(T_{A-B-C}(C_A, C_B, C_C)\), on the basis of different assumptions.

(i) Multivariate regression model based on binary liquidus temperatures:

We assume that liquidus temperatures in a ternary phase diagram, \(T_{A-B-C}(C_A, C_B, C_C)\), are influenced by binary liquidus temperatures, \(T_{A-B}(C_A/(C_A + C_B)))\), \(T_{B-C}(C_B/(C_B + C_C))\), and \(T_{C-A}(C_C/(C_C + C_A))\). By settling the degrees of the affection from binary liquidus temperatures as parameters, the following model is proposed

\[
T_{A-B-C}(C_A, C_B, C_C) = a_0 + a_1 T_{A-B}(C_A/(C_A + C_B)) + a_2 T_{B-C}(C_B/(C_B + C_C)) + a_3 T_{C-A}(C_C/(C_C + C_A)) + \epsilon
\]

where \(a_0, a_1, a_2, a_3\) are unknown coefficients and \(\epsilon\) is the disturbance term associated with a normal distribution. The unit of measure of \(a_0\) is in °C and others are unitless. A maximum likelihood estimation based on the data sets of \(T_{A-B-C}(C_A, C_B, C_C)\), \(T_{A-B}(C_A/(C_A + C_B)))\), \(T_{B-C}(C_B/(C_B + C_C))\), and \(T_{C-A}(C_C/(C_C + C_A))\) gives the estimated values of \(a_i\). Then, the predictor for \(T_{A-B-C}(C_A, C_B, C_C)\) using these three binary liquidus temperatures can be constructed.

(ii) Multivariate regression model based on interactive binary liquidus temperatures:

The model (i) represents the independent effect of three binary liquidus temperatures on ternary liquidus temperatures. However, we cannot deny the possibility of interactive effects between two binary liquidus temperatures. We therefore represented such interactive effects as the products of two binary liquidus temperatures: \(T_{A-B-C}(C_A/(C_A + C_B)) T_{B-C}(C_B/(C_B + C_C))\). The regression model with interactive effects is proposed as below

\[
T_{A-B-C}(C_A, C_B, C_C) = b_1 T_{A-B}(C_A/(C_A + C_B)) T_{B-C}(C_B/(C_B + C_C)) + b_2 T_{B-C}(C_B/(C_B + C_C)) T_{C-A}(C_C/(C_C + C_A)) + b_3 T_{C-A}(C_C/(C_C + C_A)) T_{A-B}(C_A/(C_A + C_B)) + \epsilon
\]

where parameters \(b_1, b_2, b_3\) are unknown coefficient parameters. The units of \(b_1, b_2, b_3\) are in °C and \(a_1, a_2, a_3\) are unitless.

(iii) Multivariate regression model based on atomic interactions:

Assuming a homogeneous distribution of mixed elements with the same geometric size, the ratio of interactive bonds between \(A\) and \(B\) can be described as \(C_A^2\). Similarly, the ratios of the bonds between \(A\) and \(C\) can be described as \(C_A^2\). Considering that all of the atomic interactions affect the liquidus temperature in the ternary system, the following model is proposed

\[
T_{A-B-C}(C_A, C_B, C_C) = c_1 C_A^2 + c_2 C_B^2 + c_3 C_C^2 + c_4 C_A C_B C_C + \epsilon
\]

where \(c_1, c_2, \ldots, c_6\) were unknown coefficients. The units of \(c_1, c_2, \ldots, c_6\) are in °C.

(iv) Multivariate regression model based on interactive binary liquidus temperatures and ratio of atomic interactions:

In the model (iii), we assumed atomic interactions occur in a homogeneous distribution of mixed elements with the same geometric size. It would be more likely, however, that they occur in an inhomogeneous distribution in different geometric sizes in a ternary liquid. In other words, the model (iii) may be too simplified considering atomic orbitals and their interactions. Therefore, we also propose the regression model taking into account both interactive binary liquidus temperatures and atomic interactions by linear combination of the models (ii) and (iii). In this model (iv), we may consider that an inhomogeneous distribution with different atomic orbitals are represented by binary liquidus temperatures.

\[
T_{A-B-C}(C_A, C_B, C_C) = d_1 C_A^2 + d_2 C_B^2 + d_3 C_C^2 + d_4 C_A C_B C_C + d_5 C_B C_C + d_6 C_C C_A + d_7 T_{A-B}(C_A/(C_A + C_B)) + d_8 T_{B-C}(C_B/(C_B + C_C)) + d_9 T_{C-A}(C_C/(C_C + C_A)) + d_{10} T_{A-B}(C_A/(C_A + C_B)) T_{B-C}(C_B/(C_B + C_C)) + d_{11} T_{B-C}(C_B/(C_B + C_C)) T_{C-A}(C_C/(C_C + C_A)) + d_{12} T_{C-A}(C_C/(C_C + C_A)) T_{A-B}(C_A/(C_A + C_B)) + \epsilon
\]
where \(d_1 - d_{12}\) are unknown coefficient parameters. The units for \(d_1 - d_6\) are in \(^\circ\)C, whereas the units for \(d_7 - d_{12}\) are in \(^\circ\)C\(^{-1}\).

It is difficult to theoretically show which model is the most reasonable because these statistical models are proposed on the basis of different hypotheses. To evaluate the effectiveness of the four models, we introduce Akaike Information Criterion (AIC),\(^{28}\) given by

\[
\text{AIC} = -2 \times \text{logarithmic likelihood} + 2 \times \text{number of parameters}
\]

The first term is log likelihood of the fitted model and decreases as the number of parameters increases. The second term is a penalty one and monotonously increases with increasing the number of parameters included in a model. We therefore select the model providing a minimum value of AIC as the best one.

3. RESULTS

Statistic models were evaluated by three steps. First, we predicted liquidus temperatures on the basis of four statistic models to find which model was most effective (Section 3.1). Second, we further evaluated the most effective model by interpolation tests (Section 3.2). Finally, we predicted the ternary liquidus temperature in more practical situations, such as prediction from limited initial data sets and expanded ternary liquidus temperatures (Section 3.3).

3.1. Fitting the Regression Models. Figure 1 shows the contour map of experimental liquidus temperatures and predicted liquidus temperatures of Al–Ag–Zn ternary phase on the basis of the models (i)–(iv). The prediction of the model (i) is poor especially in Al- and Ag-rich regions. The predicted liquidus temperatures in the Al-rich region by the model (ii) improve from those of the model (i). The prediction of the liquidus temperatures by the model (iii) further improves in the Al- and Ag-rich region. The model (iv) is the most predictable. The prediction accuracy near the kink at the composition at \(\text{Al}_{0.57}\text{Ag}_{0.36}\text{Zn}_{0.07}\) is also improved by using model (iv) when compared with that predicted by other models. The maximum error of the model (iv) in this region is approximately 30 \(^{\circ}\)C.

Further improvement of the model remains a challenge, which may be achieved by using nonlinear regression models.

Table 1 shows the number of data \((N)\), the values of AIC, and the adjusted coefficients of determination (Adj-\(R^2\)) for each ternary system. The values of Adj-\(R^2\) suggest that the models (ii), (iii), and (iv) are fitted better than the model (i). AIC values are different depending on the models but have the tendency regardless of individual systems. AIC values tend to decrease from the model (i) to (iv). The above results suggest that the model (iv) can be evaluated as the most effective structure for the Al–Ag–Zn ternary system.
explaining the change in liquidus temperatures in the proposed four models.

Of the four ternary systems Table 2 shows the estimated values of the parameters. The top and bottom of each table shows estimated values and the t-value; the t-value is a test statistic and asterisks indicate that parameters are significantly different from zero at a 5% level. All of the variables, except the parameter of binary liquidus temperature in the Ag-Zn-Al system, are in accordance with our assumption about the model; ternary liquidus temperature can be expressed by interactive binary liquidus temperatures and the ratio of interacting bonds.

### 3.2. Prediction Accuracy of Liquidus Temperature by Interpolation Test

In the following subsection, we evaluated the prediction accuracy of ternary liquidus temperatures by using the models presented in the previous subsection. For this purpose, we carried out the statistical interpolation test, described as below. First, we identified the models (i)–(iv) using the data of binary and ternary liquidus temperatures. Then, the prediction accuracy of ternary liquidus temperatures by using the models was evaluated by the difference between actual data and the estimated values.

Figures 2–5 show the results of the prediction of liquidus temperatures in four ternary systems with the models (i)–(iv). The distribution diagrams shown in the left side exhibit that the estimated values close to the broken line represent the ideal estimation. The accuracy of the estimation tends to improve from the results by using the models (i), (ii), and (iii). Histograms in the right side show the distribution of prediction errors: the difference between the actual and estimated temperatures. Table 3 shows the number of data used for the interpolation test (N), the average of the estimated error (\( \hat{\mu} \)), standard deviation (\( \hat{\sigma} \)), and root mean square errors (RMSEs).

Table 3 shows that \( \hat{\sigma} \) and RMSE of the statistical models improve from the models (i)/(ii) to the model (iii) and further to the model (iv). The comparison between the models (i) and (ii) suggests that the interactions of binary liquidus temperatures are effective for the prediction except in the Sn–Ag–Zn system. The model (iii) is further improved by considering only atomic interactions using the products of atomic ratios. Thus, the model with atomic interactions would be more effective for the prediction than the model with binary liquidus temperature. The model (iv), a linear combination of the models (ii) and (iii), lowers standard deviations and RMSE of the model (iii) by ca. 10, giving the best prediction accuracy among the four models. These accuracies indicate that the model (iv) is practically useful for describing ternary liquidus temperatures.

### 3.3. Application of the Model to the Prediction of Ternary Liquidus Temperatures in Some Practical Aspect

In this section, we investigate whether the model (iv) is also available for prediction of ternary liquidus temperatures in a more practical situation. We examined the prediction of ternary liquidus temperatures using the statistical model (iv) proposed in the previous section. The prediction was performed by a partial data set of \( T_{A-B-C}(C_A, C_B, C_C) \) and used to evaluate the remaining data set.

**3.3.1. Predicting Ternary Liquidus Temperature from Specific Situations.** In this subsection, we consider whether the model (iv) has the predictability of ternary liquidus temperatures under the condition that experimental data are obtained in a specific situation. As an example, we investigate the prediction accuracy in the situation that all of the data of ternary composition are close to that of binary composition.

The prediction test is carried out in the following way. First, we define the values of the ratios, \( R_0 \) and \( R_1 \), satisfying \( 0 < R_0 \leq R_1 < 1 \). Then, we prepare the two data sets on the atomic ratios, \( C_A, C_B, \) and \( C_C \) which satisfies the following conditions:

\[
\begin{align*}
& (a) \ C_A < R_0 \text{ or } C_B < R_0 \text{ or } C_C < R_0 \\
& (b) \ C_A > R_1 \text{ and } C_B > R_1 \text{ and } C_C > R_1
\end{align*}
\]

The data set satisfying (a) is used for model identification and the other one satisfying (b) is used for the prediction test for \( T_{A-B-C}(C_A, C_B, C_C) \). The prediction accuracy can be statistically evaluated by a similar experiment as presented in Section 3.2.2.

**3.3.2. Validity of the Statistical Model.** Figure 6 shows the liquidus temperature derived by the exploration test. The predicted data shown in the middle are similar to experimental data, showing that prediction accuracies are practically allowable. Figure 7 shows the distribution of prediction errors on liquidus temperature in four ternary systems under \( R_0 = R_1 = 0.1 \). Table 4 summarizes the numbers of data for the estimation (\( N_0 \)) and the prediction test (\( N_1 \)), the average prediction error (\( \hat{\mu} \)), the standard deviation of the prediction errors (\( \hat{\sigma} \)), and RMSE.
under $R_0 = 0.1$ and $R_1 = 0.1, 0.2,$ and 0.25. It is important to note that the value of the statistical criteria (i.e., $\hat{\mu}$, RMSE) tends to be unstable as $R_1$ becomes larger because $N_1$ decreases. The result shows that RMSE of the predicted values are distributed in the range of $10^{-30}^\circ C$, whose accuracies are practically allowable. It is concluded that the statistic model (iv) is effective for prediction.

3.3.3. Improvement of the Predictability Based on Extended Ternary Systems.

In this subsection, we are interested in whether the predictive accuracy of ternary liquidus temperatures can be improved by considering extended ternary systems. We examine this point by considering a statistical model with a hierarchical structure. Suppose that we estimate the liquidus temperatures in the $A-B-C$ system on the basis of the three adjusted systems, $A-B-X$, $B-C-Y$, and $A-C-Z$. First, we write the model to express $T_{A-B-C}(C_A, C_B, C_C)$ in the $A-B-C$ system.

$$T_{A-B-C}(C_A, C_B, C_C) = a_1 C_A^2 + a_2 C_B^2 + a_3 C_C^2 + a_4 C_A C_B$$
$$+ b_1 T_{A-B-X}^* + b_2 T_{B-C-Y}^* + b_3 T_{C-A-Z}^* + \varepsilon$$

where $(a_j, b_j)$ $(j = 1-6)$ are unknown coefficients, $T_{A-B-X}^*(C_A, C_B)$, $T_{B-C-Y}^*(C_B, C_C)$, and $T_{C-A-Z}^*(C_C, C_A)$, respectively, stand for liquidus temperatures of the statistical modes in $A-B-X$, $B-C-Y$, and $C-A-Z$ systems, and $\varepsilon$ means the disturbance term following normal distribution. Because $T_{A-B-X}^*$, $T_{B-C-Y}^*$ and $T_{C-A-Z}^*$ are unknown, it is necessary to estimate these values in $A-B-X$, $B-C-Y$, and $A-C-Z$ systems.

Here, we assume that ternary liquidus temperatures follow the statistic model (iv) presented in the previous system. In the $A-B-X$ system, for example, the model can be written by

$$T_{A-B-X}(C_A, C_B) = a_{1A} C_A^2 + a_{2A} C_B^2 + a_{3A} C_A C_B + b_{1A} T_{A-B-X}^* + \varepsilon_{A-B-X}$$

Figure 2. Prediction of liquidus temperatures in a Ag–Zn–Al ternary system with the models (i)–(iv).
Where \((p_j, q_j)\) \((j = 1−6)\) are unknown parameters. To estimate the value of \(T_{A−B−X}(C_A, C_B, C_X)\), for example, it is necessary to know the situation of \(\Delta H_{A−B−X}(C_A, C_B, C_X)\) on the basis of the model (II). Under \(C_X = 0\), the following relationship holds

\[
T_{A−B−X}(C_A, C_B, C_X) = T^*_{A−B−X}(C_A, C_B) + q_1 T_{A−B}(C_A/C_B) + \ldots + q_6 T_{A−B}(C_A/C_B) + \varepsilon
\]

where \(T_A\) and \(T_B\) represent melting points of A and B. Therefore, the model (II) in this situation can be rewritten as

\[
T^*_{A−B−X}(C_A, C_B) = p_1 C_A^2 + p_2 C_B^2 + \ldots + p_6 C_A C_B + q_1 T_{A−B}(C_A/C_B) + \ldots + q_6 T_{A−B}(C_A/C_B) + \varepsilon
\]

It is possible to estimate the values of the parameters \((p_j, q_j)\) by using the data obtained in the A−B−X system, and therefore the estimation value of \(T^*_{A−B−X}(C_A, C_B)\) can also be obtained by using the fitted model. The values of \(T^*_{B−C−Y}\) and \(T^*_{A−C−Z}\) can be estimated in the same way by using the data obtained in B−C−Y and C−A−Z systems, respectively. The model (I) can be identified by the following two steps. First, we estimate the values of \(T^*_{A−B−X}\), \(T^*_{B−C−Y}\) and \(T^*_{A−C−Z}\) by fitting the model (III). Then, the coefficient parameters \((a_j, b_j)\) in the model (I) are estimated.
estimated. The predicted values of $T_{A-B-X}(C_A, C_B, C_X)$ can be obtained by using the fitted model of (I).

In the following, we examine the prediction accuracy by using the model (I). To investigate whether the model has advantage in the prediction accuracy, we carried out the similar prediction experiments, as stated in Section 3.2 and then compared the accuracy among the following methods:

(M1) The multivariate model based on atomic interaction (i.e., the model (iii) defined in Section 2.2)

(M2) The multivariate model from interactive binary liquidus temperatures and the ratio of interactive bonds (i.e., the model (iv) defined in Section 2.2)

(M3) The method presented above. Note that for the prediction of liquidus temperature in the Ag−Al−Sn system using Ag−Zn−Al, Sn−Ag−Zn, and Zn−Al−Sn systems as extended systems, $X = Y = Z = Zn$.

Figure 8 and Table S(a)−(d) show the results of the prediction experiment on the liquidus temperatures in four systems, which are similar to those carried out in Sections 3.2 and 3.3.2. Specific steps for our test are as follows. First, we listed the liquidus temperatures in accessing order, and numbered the data points of atomics ratios and liquidus temperatures. The odd numbers of the data are used for the estimation of coefficient parameters by a maximum likelihood estimation, and the even number of the data with different $R_i$ values, which are defined in Section 3.3.1, are used for the statistical evaluation of the model on the basis of the error. In the tables, the number of data identification ($N_0$) and prediction test ($N_1$), the mean ($\hat{\mu}$) and standard deviation ($\hat{\sigma}$) of the prediction errors, and RMSE are shown. We see that (M3) tends to give better prediction accuracies than those of (M1) and (M2). This suggests that the extended ternary systems improve the prediction accuracy obtained by using the model considered in the extended ternary systems.

4. DISCUSSION
The results of our analyses in the Ag−Al−Sn−Zn system suggest that atomic ratios and binary liquidus temperatures are effective
factors to predict the distribution of ternary liquidus temperatures. The analyses taking in the product terms on atomic ratios and binary liquidus temperatures further improved the prediction of ternary liquidus temperatures. Assuming a homogeneous distribution of mixed elements with the same geometric size, the products of the atomic ratios can be interpreted as the ratios of interactive bonds in the nearest neighborhood in a microscopic view. All of the coefficients of these products of the atomic ratios are significant and positive, thus interactive bonds in the nearest neighborhood should increase ternary liquidus temperatures. On the other hand, binary liquidus temperatures and their interaction terms can be understood as other microscopic factors to predict ternary liquidus temperatures. Thus, the structure of model (iv), which is the most effective to predict ternary liquidus temperatures, can be understood as the linear combination of microscopic and macroscopic factors.

The statistic model (iv) for the prediction of ternary liquidus temperatures can be interpreted as microscopic atomic interaction modified by macroscopic binary liquidus temper-

Table 3. Results of Interpolation Tests by Applying the Four Statistical Models

| model | Ag−Zn−Al | Sn−Ag−Zn | Zn−Al−Sn | Ag−Al−Sn |
|-------|----------|----------|----------|----------|
|       | \( \hat{\mu} \) | \( \hat{\sigma} \) | RMSE     | \( \hat{\mu} \) | \( \hat{\sigma} \) | RMSE     | \( \hat{\mu} \) | \( \hat{\sigma} \) | RMSE     |
| (i)   | 3332      | 0.28     | 36.84    | 708      | 1.13     | 53.37    | 1571      | 0.08     | 30.24    |
| (ii)  | 3332      | 0        | 20.78    | 708      | 0        | 29.79    | 1571      | 0        | 16.94    |
| (iii) | 3332      | 0        | 12.37    | 708      | 0        | 16.54    | 1571      | 0        | 12.87    |
| (iv)  | 3332      | 0        | 12.37    | 708      | 0        | 18.52    | 1571      | 0        | 12.87    |

Figure 5. Prediction of liquidus temperatures in a Ag−Al−Sn ternary system with the statistical models (i)−(iv).
Figure 6. Data set of the Al–Ag–Zn system used for identification of the model (left) and difference between predicted and experimental temperatures in an extrapolation test with $R_0 = R_1 = 0.1$ (right). Data set without grey region (left) is used for the identification of the model (iv). The color indicator of the prediction error ranges from $-75$ to $+75 ~{^\circ}C$, which is not same for the indicator in Figure 1.

Figure 7. Extrapolation test of ternary liquidus temperatures in a Ag–Al–Sn–Zn system applying the model (iv) with $R_0 = R_1 = 0.1$. 
On this basis, the coefficients of atomic interaction can be related to elemental factors. Figure 9 shows the ratios of metallic radii and coefficients of the products of atomic ratios. We observed a positive correlation between the ratios of metallic radii and the coefficients of the products of atomic ratios, with the exception found in the combination between Ag and Sn. The coefficients of the products of atomic ratios are considered as strength factors of atomic interactions because high liquidus temperatures are generally attributed to strong chemical interactions between composed elements. Thus, the statistical analysis of liquidus temperatures suggests that the increase in the ratios of atomic radii strengthen atomic interactions. The coefficients of the combination between Ag and Sn are found to be abnormally low. The Ag−Sn system is a well-known system for lead-free solder. Thus, this statistical approach finds new designing principles by revealing the linear trend between the ratios of atomic radii and the strength of atomic interaction.

The prediction tests of ternary liquidus temperatures from binary liquidus temperatures and the part of ternary liquidus temperatures give allowable accuracy, which are useful for designing materials or synthesis protocols. The proposed structural model can handle not only ternary liquidus temperatures but also extended ternary liquidus temperatures. Although further research is essential to establish general trends of these statistical approaches, this statistical work shows the possibility of the prediction of ternary or higher systems by combining data of binary and ternary systems.

Table 4. Results of the Extrapolation Tests Applying the Model (iv) with Different Data Setsa

| System | N0  | N1  | \( \bar{\mu}_e \) | \( \sigma_\varepsilon \) | RMSE |
|--------|-----|-----|-----------------|----------------|-------|
| Ag−Zn−Al | 1415 | 1676 | 0.30           | 12.23          | 12.23 |
| Sn−Ag−Zn | 412  | 226  | −16.92         | 18.74          | 24.89 |
| Zn−Al−Sn | 614  | 813  | 2.58           | 14.73          | 14.95 |
| Ag−Al−Sn | 851  | 1080 | 1.83           | 27.27          | 27.32 |
|        | \( R_i = 0.2 \) |
| Ag−Zn−Al | 1415 | 524  | 4.36           | 10.50          | 11.36 |
| Sn−Ag−Zn | 412  | 66   | −21.99         | 18.57          | 28.69 |
| Zn−Al−Sn | 614  | 173  | 6.42           | 8.43           | 10.58 |
| Ag−Al−Sn | 851  | 362  | 2.61           | 28.98          | 29.06 |
|        | \( R_i = 0.25 \) |
| Ag−Zn−Al | 1415 | 213  | 10.59          | 9.50           | 14.25 |
| Sn−Ag−Zn | 412  | 28   | −33.06         | 7.79           | 35.88 |
| Zn−Al−Sn | 614  | 102  | 4.80           | 6.30           | 7.90  |
| Ag−Al−Sn | 851  | 118  | −3.68          | 33.01          | 33.07 |

\( a R_0 = 0.1, R_1 = 0.1, 0.2, \) and \( 0.25. \)

Figure 8. Prediction accuracy of the liquidus temperature by using a hierarchical model (\( R_1 = 0.1 \)).
The statistical framework that we have considered throughout this article possibly gives new application to various chemical properties related to atomic interactions, which are not limited to liquidus temperatures. For example, by considering the coefficients of the products of atomic ratios as strengths of atomic interaction, a linear trend between the ratios of atomic radii and the strength of atomic interaction was found and the relationship between the ratio of metallic radii and other properties related to the atomic interactions.

We also found out that the prediction accuracies of the liquidus temperatures in a ternary system of Ag–Al–Sn can be improved further by using the models identified in their neighboring ternary systems. This result implies that this method may have the potential of general prediction on liquidus temperatures.

The statistical framework that we have considered throughout this article possibly gives new application to various chemical properties related to atomic interactions, which are not limited to liquidus temperatures. For example, by considering the coefficients of the products of atomic ratios as strengths of atomic interaction, a linear trend between the ratios of atomic radii and the strength of atomic interaction was found and the normally weak interaction between Ag and Sn was also suggested. The proposed models are potentially applicable to other properties related to the atomic interactions.

### 5. CONCLUSIONS

In this article, we analyzed liquidus temperatures of six binary and four ternary systems in a Ag–Al–Sn–Zn system by means of statistical modeling. We found that products of atomic ratios, binary liquidus temperatures, and their interactions are effective as descriptors for ternary liquidus temperatures. The multivariate regression model based on products of atomic ratios, binary liquidus temperatures, and their interactions was found to be effective from the standpoint of AIC. The prediction accuracy of the extrapolation test was found to be practically allowable, which suggested statistical reasonableness of the model structure. From the chemical standpoint, this model can be interpreted as the microscopic atomic interactions modified by macroscopic binary liquidus temperatures.

Figure 9. Relationship between the ratio of metallic radii and coefficients of products of atomic ratios. A blue broken line represents the linear regression line except the coefficients of Ag–Sn.
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References

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References

(1) Leonard, B. M.; Bhuvanesh, N. S. P.; Schaak, R. E. Low-Temperature PolySynthesis of AuCuSn2 and AuNiSn2: Using Solution Chemistry to Access Ternary Intermetallic Compounds as Nanocrystals. J. Am. Chem. Soc. 2005, 127, 7326–7327.
(2) Miura, A.; Wang, H.; Leonard, B. M.; Abruña, H. C. D.; DiSalvo, F. J. Synthesis of Intermetallic PtZn Nanoparticles by Reaction of Pt Nanoparticles with Zn Vapor and Their Application as Fuel Cell Catalysts. Chem. Mater. 2009, 21, 2661–2667.
(3) Gao, F. G.; Bard, A. J. High-Brightness and Low-Voltage Light-Emitting Devices Based on Trischelated Ruthenium(II) and Tris(2,2′-bipyridine)osmium(II) Emitter Layers and Low Melting Point Alloy Cathode Contacts. Chem. Mater. 2002, 14, 3465–3470.
(4) Plevachuk, Y.; Skyarchuk, V.; Eckert, S.; Gerbeth, G.; Novakovíc, R. Thermophysical Properties of the Liquid Ga–In–Sn Eutectic Alloy. J. Chem. Eng. Data 2014, 59, 757–763.
(5) Zielbarth, J. T.; Woodall, J. M.; Kramer, R. A.; Choi, G. Liquid phase-enabled reaction of Al–Ga and Al–Ga–In–Sn alloys with water. Int. J. Hydrogen Energy 2011, 36, 5271–5279.
(6) Binary Alloy Phase Diagrams, 2nd ed.; Massalski, T. B., Okamoto, H., Subramanian, P. R., Kacprzak, L., Eds.; ASM International: Materials Park, 1990; pp 8, 94, 117, 215, 239, 3416.
(7) Ternary Alloys: A Comprehensive Compendium of Evaluated Constitutional Data and Phase Diagrams; Effgenben, G., Petzov, G., Eds.; VCH publishers: New York, 1989; pp 76, 91, 385.
(8) Liu, Y. Q.; Xu, X. T.; Xie, D.; Li, Z. M. Phase diagram calculations of Al–Cr–Nb–Ti quaternary system. Mater. Res. Innovations 2014, 18, 52–573–578.
(9) Mallik, A. K. Computer calculations of phase diagrams. Bull. Mater. Sci. 1986, 5, 107–121.
(10) Bhansali, A. S.; Mallik, A. K. Calculation of ternary phase diagrams with binary data. Calphad 1987, 11, 105–116.
(11) Chang, X. A.; Chen, S.; Zhang, F.; Yan, X.; Xie, F.; Schmid-Fetzer, R.; Oates, W. A. Phase diagram calculation: past, present and future. Prog. Mater. Sci. 2004, 49, 313–345.
(12) Lukas, H. L.; Weiss, J.; Henig, E. T. Straegies for the calculation of phase diagrams. Calphad 1982, 6, 229–251.
(13) Sundman, B.; Jansson, B.; Andersson, J.-O. The Thermo-Calc databank system. Calphad 1985, 9, 153–190.
(14) Eriksson, G.; Hack, K. ChemSage—A computer program for the calculation of complex chemical equilibria. Metall. Trans. B 1990, 21, 1013–1023.
(15) Lindemann, F. A. The calculation of molecular vibration frequencies. Phys. Z. 1910, 11, 609–612.
(16) Chelikowsky, J. R.; Anderson, K. E. Melting point trends in intermetallic alloys. J. Phys. Chem. Solids 1987, 48, 197–205.
(17) Seko, A.; Maezawa, T.; Tsuda, K.; Tanaka, I. Machine learning with systematic density-functional theory calculations: Application to melting temperatures of single- and binary-component solids. Phys. Rev. B 2014, 89, No. 054303.