The Determination of Thermodynamic Properties of melts from the Cu-Si-System by Mass Spectrometry

G. Riekert, P. Lamparter, and S. Steeb
Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaften, Stuttgart

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The Knudsen effusion technique combined with mass spectrometry has been applied to determine thermodynamic activities and excess Gibbs energies for the liquid Cu-Si System. The system shows a tendency for segregation over the entire composition range. Special features in the partial and integral properties could be interpreted by means of two models.

1. Introduction

Thermodynamic properties of a mixture can be described by the activities a_i of the components i and their dependence on temperature:

$$a_i = p_i/p_i^0\,, \tag{1}$$

where

p_i^0 pressure of the pure component i and

p_i partial pressure of the component i above the mixture.

a_i is related to the mole fraction x_i by Eq. (2)

$$a_i = \gamma_i x_i\,, \tag{2}$$

where γ_i = activity coefficient.

To determine the partial pressure p_i by mass spectrometry the molecular beam effusing the Knudsen cell is ionized and separated spectroscopically. Then the intensities I_i of the different ions are measured by an ion counter. The partial pressure p_i is derived from this measured value by Eq. (3) (see Ref. [1]):

$$p_i = I_i^+ \, T\, K/(\sigma_i h_i^k \gamma_i)\,, \tag{3}$$

where

I_i measured intensity of the isotope k,

T temperature inside the Knudsen cell,

K geometric factor,

σ_i ionization cross section dependend on electron energy,

h_i^k relative abundance of the isotope k,

γ_i relative sensitivity of the multiplier.

Two independent experiments are required to determine activities due to Eq. (1) to obtain the pressures above the alloy and the pure substance. However the change of the factor K caused by the change of the sample produces a large error.

To reduce these difficulties some methods have been developed by Berkowitz and Chupka [2] (Monomer-Dimer-Method) and by Belton and Fruehan [3], [4], [5] (Integration method). By measuring the ratio of two ion currents above the mixture the factor K can be eliminated and the ratio of the partial pressures can be obtained:

$$\frac{p_1}{p_2} = \frac{I_1^+\,\sigma_2 h_2^l \gamma_2}{I_2^+\,\sigma_1 h_1^k \gamma_1}\,. \tag{4}$$

2. Integration Method

The method suggested by Belton and Fruehan was used in the present investigation starting from the Gibbs-Duhem-equation:

$$\sum_i x_i \,\mathrm{d}\ln a_i = 0\,. \tag{5}$$

This equation relates the activities of the different components in the alloy to each other. Considering a binary system of the components 1 and 2 we obtain a relation for the activity coefficients using Eqs. (1, 3, 5):

$$\ln \gamma_1 = -\int_{x_1=1}^{x_1} x_2 \,\mathrm{d}\ln\left(\frac{I_2^+\, x_1}{I_1^+\, x_2}\right). \tag{6}$$

The partial heat of mixing ΔH_1 follows using the Clausius-Clapeyron equation:

$$\Delta H_1 = -R\int_{x_1=1}^{x_1} x_2 \,\mathrm{d}\left\{\frac{\mathrm{d}\ln(I_2^+/I_1^+)}{\mathrm{d}(1/T)}\right\}. \tag{7}$$

Reprint requests to Prof. Dr. S. Steeb, Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaften, Seestraße 92, D-7000 Stuttgart.

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3. Experimental

A double focussing mass-spectrometer (MS 702, AEI, Manchester) was used to carry out the experiments. To reach temperatures up to more than 2000 °C, the heating and Knudsen cell assembly had to be reconstructed [6]. The heating element consisted of tungsten wire (1.5 mm diameter). It was coiled in an inert atmosphere and fixed in two watercooled blocks of copper. The current supplies and the Knudsen cell support (tantalum tube) were also cooled by water. The best fixation of the Knudsen cell was obtained by a thread connection between cell and support. With this arrangement (Fig. 1) it was possible to reach temperatures up to 2300 °C.

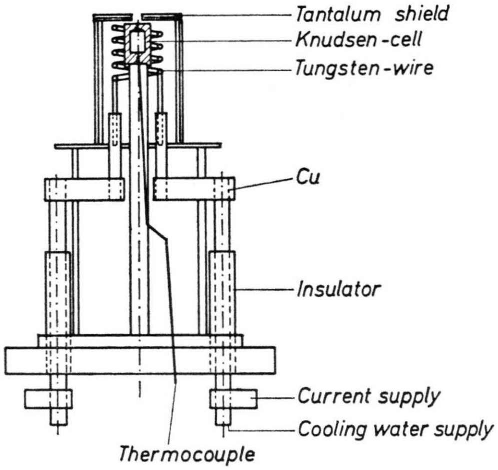

Fig. 1. Knudsen cell and heating assembly.

The temperature was measured by a thermocouple (W-Re 3%—W-Re 25%, Heraeus) which was fixed in the bottom of the Knudsen cell. The heating current was controlled via this thermocouple by means of a temperature control (EUROTHERM).

The molecular beam enters the ionization region through a movable shutter by which Knudsen cell and ion source could be separated. In this way the species effusing the Knudsen cell could be identified.

In order to measure very small intensities an ion counting system consisting of a secondary electron multiplier and a multichannel analyzer (MCA) was used. By scanning simultaneously the electrostatic field of the mass spectrometer and the 4096 channels of the MCA a reproducible registration of the part of the spectrum of interest, e.g. the profile of a single mass line could be obtained.

A computer (PDP 11/03) connected to the MCA was used to write the data down on floppy disc. To investigate the Cu-Si melts Knudsen cells consisting of high density graphite were used which had been coated with SiC as follows:

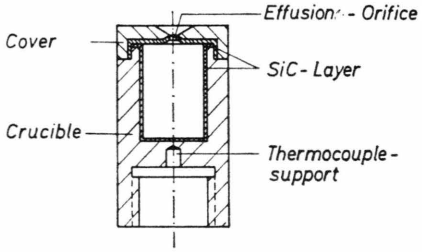

Fig. 3. Section of a graphite Knudsen cell coated with SiC.

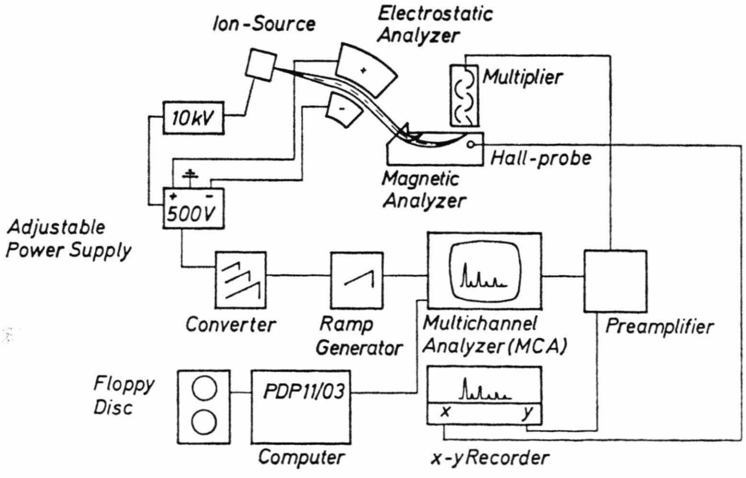

Fig. 2. Schematic presentation of the ion counting system.

Pure silicon was annealed 4 hours inside the graphite cell at 1500 °C and a layer of 0.8 to 0.9 mm was generated. Further annealing did not change this layer any more. Figure 3 shows schematically the Knudsen cell used.

4. Experimental Procedure

The values of $I^+_{\mathrm{Si}}/I^+_{\mathrm{Cu}}$, T and x_{Cu} resp. x_{Si} had to be measured to determine thermodynamic properties according to equations (3) and (6). The parameters σ, h and γ had to be kept constant during the complete set of runs.

The electron energy was chosen as $E = 18$ eV for any investigated concentration. The energy scale was calibrated by means of the appearance potential of Ag^+ ($\mathrm{AP\,Ag}^+) = 7.59$ eV) [7] by linear extrapolation [8].

The ratio of isotopic abundances h was kept constant as only ^{28}Si- and ^{63}Cu-isotopes were measured and evaluated.

The temperature was measured by a thermocouple as described, which was calibrated by means of the known melting point of Ag (960 °C) [9] and Cu (1083 °C) [9].

The specimens were prepared from the pure components Cu and Si (purity 99.99%) which were melted in an induction furnace and casted. The composition change caused by vaporization losses during the experiment was determined. From the weight loss of the sample according to Ref. [10] the sample-composition could be obtained. The arithmetic mean between initial and final composition was taken for the evaluation.

About 0.5 to 1.5 g of the sample were put into the coated graphite Knudsen cell. Heating was started when the vacuum pressure of the ion source had reached a value of about $2 \cdot 10^{-8}$ torr. The measurements were carried out in a region of temperature of about 1250 K to 1700 K (Cu-rich samples) and 1650 K to 1800 K (Si-rich samples).

Using an acceleration voltage of 5 kV, an ionization voltage of 18 V, and an electron trap current of 10 μA, the mass spectrometer was adjusted on the mass line of $^{28}\mathrm{Si}^+$ and $^{63}\mathrm{Cu}^+$, respectively. This was done by the variation of the magnetic field measured by a Hall probe, which had been calibrated by a standard spectrum.

The ion intensities were measured by scanning the electric field and registrating with the MCA the profile of the respective mass line. The movable shutter and the isotopic distribution were used to identify the various species. It was also possible to separate signal and noise by means of the shutter.

The spectrometer's resolution was adjusted to obtain a good separation of the $^{28}\mathrm{Si}^+$-peak and the $^{28}\mathrm{N}_2$-peak (mass (^{28}Si): 27.976929 [11]; mass ($^{28}\mathrm{N}_2$): $28.006146 \Rightarrow M/\Delta M = 960$).

5. Evaluation and Results

Table 1 shows the logarithms of the ratios of intensities $\ln I^+_{\mathrm{Cu}}/I^+_{\mathrm{Si}}$ dependend on temperature and concentration. According to [12] the ionization cross sections for 18 eV electrons are

$$\sigma_{\mathrm{Cu}} = 3.29\ \text{Å}^2\,, \quad \sigma_{\mathrm{Si}} = 4.18\ \text{Å}^2\,,$$

and the relative abundances [13]:

$$h(^{63}\mathrm{Cu}) = 69.09\%\,, \quad h(^{28}\mathrm{Si}) = 92.21\%\,.$$

A plot of $\ln I^+_{\mathrm{Cu}}/I^+_{\mathrm{Si}}$ vs. temperature for the various compositions is shown by Figure 4. The straight lines of the form

$$\ln(I^+_{\mathrm{Cu}}/I^+_{\mathrm{Si}}) = A\,(10^4/T) + B\,,$$

were evaluated by least squares analysis. Table 2 shows the results.

As indicated in Fig. 4 an intersection was applied to these lines at a temperature of 1700 K and the values obtained were used for the integration plot $[\ln(I^+_{\mathrm{Cu}}x_{\mathrm{Si}})/(I^+_{\mathrm{Si}}x_{\mathrm{Cu}})$ vs. $x_{\mathrm{Si}}]$ which is necessary for the evaluation of activities (see Figure 5).

Table 1. Experimental values of the ratios of ion currents.

x_{Cu}							
0.098	T [K]	1694	1721	1748	1776		
	$\ln I^+_{\mathrm{Cu}}/I^+_{\mathrm{Si}}$	0.57	0.33	0.02	−0.05		
0.282	T [K]	1694	1710	1748	1776		
	$\ln I^+_{\mathrm{Cu}}/I^+_{\mathrm{Si}}$	1.53	1.24	1.17	0.90		
0.484	T [K]	1532	1559	1586	1613	1639	1666
	$\ln I^+_{\mathrm{Cu}}/I^+_{\mathrm{Si}}$	3.19	2.80	2.67	2.23	2.21	1.95
0.590	T [K]	1614	1641	1668	1695	1722	
	$\ln I^+_{\mathrm{Cu}}/I^+_{\mathrm{Si}}$	2.32	2.25	1.79	1.68	1.48	
0.700	T [K]	1561	1582	1587	1614	1641	1668
	$\ln I^+_{\mathrm{Cu}}/I^+_{\mathrm{Si}}$	1.55	2.15	1.70	1.57	2.00	1.43
0.800	T [K]	1587	1614	1641	1668		
	$\ln I^+_{\mathrm{Cu}}/I^+_{\mathrm{Si}}$	3.42	3.16	2.73	2.62		
0.885	T [K]	1534	1561	1603	1614	1641	1695
	$\ln I^+_{\mathrm{Cu}}/I^+_{\mathrm{Si}}$	4.56	4.09	3.77	3.81	3.61	3.04

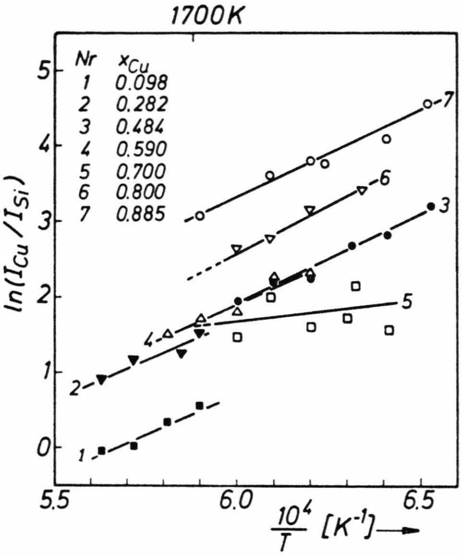

Fig. 4. Cu-Si system: Logarithm of the ratio of the corrected ion intensities I^+_{Cu} and I^+_{Si} versus reciprocal temperature.

Table 2. Coefficients of the straight lines $\ln(I^+_{Cu}/I^+_{Si}) = A \cdot (10^4/T) + B$.

x_{Cu}	A	B
0.098	2.39	− 13.58
0.282	1.98	− 10.23
0.484	2.30	− 11.88
0.590	2.32	− 11.99
0.700	0.37	− 0.51
0.800	2.78	− 14.10
0.885	2.25	− 10.19

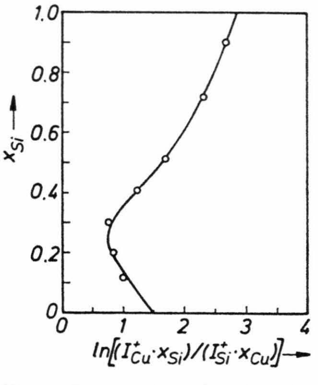

Fig. 5. Integration plot for the determination of activity coefficients for $T = 1700$ K.

The values obtained by numerical integration according to Eq. (6) are listed in Table 3 for the both components copper and silicon.

Figure 6 shows the activities vs. atomic fraction at 1700 K.

Table 3. Activities and activity coefficients of Cu and Si in dependence of the concentration at $T = 1700$ K.

x_{Cu}	$\ln \gamma_{Cu}$	γ_{Cu}	a_{Cu}	x_{Si}	$\ln \gamma_{Si}$	γ_{Si}	a_{Si}
1	0	1	1	0	0.480	1.615	0
0.9	−0.018	0.983	0.88	0.1	0.515	1.673	0.17
0.8	−0.070	0.932	0.75	0.2	0.769	2.158	0.43
0.7	−0.056	0.946	0.66	0.3	0.774	2.167	0.65
0.6	0.064	1.066	0.64	0.4	0.546	1.725	0.69
0.5	0.224	1.251	0.63	0.5	0.353	1.423	0.71
0.4	0.440	1.552	0.62	0.6	0.195	1.215	0.73
0.3	0.647	1.910	0.57	0.7	0.090	1.094	0.77
0.2	0.835	2.304	0.46	0.8	0.035	1.036	0.83
0.1	1.005	2.732	0.27	0.9	0.008	1.008	0.91
0	1.157	3.180	0	1	0	1	1

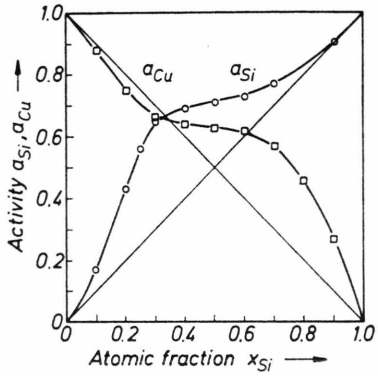

Fig. 6. Cu-Si system: Activities at 1700 K.

Additionally more partial and integral properties of mixing were calculated using $\ln \gamma_{Cu}$ and $\ln \gamma_{Si}$. Thus the excess Gibbs energy is

$$\Delta G^E = \underbrace{x_{Cu} R T \ln \gamma_{Cu}}_{\mu^E_{Cu}} + \underbrace{x_{Si} R T \ln \gamma_{Si}}_{\mu^E_{Si}} . \quad (8)$$

The excess Gibbs energy ΔG^E vs. atomic fraction at $T = 1700$ K is presented in Fig. 7 as well as the

Table 4. Cu-Si-system: Chemical potentials and excess Gibbs energy in kJ/mol at $T = 1700$ K.

x_{Si}	μ^E_{Cu}	μ^E_{Si}	ΔG^E
0.0	0	6.785	0
0.1	− 0.254	7.279	0.499
0.2	− 0.989	10.869	1.383
0.3	− 0.792	10.940	2.728
0.4	0.905	7.717	3.630
0.5	3.166	4.989	4.078
0.6	6.219	2.756	4.141
0.7	9.145	1.272	3.634
0.8	11.802	0.495	2.756
0.9	14.205	0.113	1.522
1.0	16.354	0	0

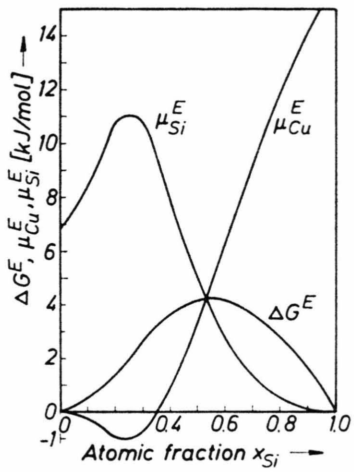

Fig. 7. Cu-Si system: Excess Gibbs energies ΔG^E and excess chemical potentials μ^E_{Cu} and μ^E_{Si}.

excess chemical potentials μ^E_{Cu} and μ^E_{Si}. The numerical values have been calculated from Eq. (8) and listed in Table 4.

6. Discussion

As indicated by Fig. 6 we find that the Cu-Si melts show a significant tendency to self-coordination i.e. segregation because the activity curves mainly exceed the Raoult's lines of ideal mixture. Exceptional behaviour is only shown by the copper-activity between 0 at.% and 35 at.% Si.

The Gibbs energy allows a definite statement about Cu-Si melts over the entire composition range because it combines both acitivitiy coefficients (see Figure 7).

The above mentioned peculiarity of the activity of copper is expressed by the lower values of ΔG^E on the copper-rich side rather than on the silicon-rich side. This ΔG^E-curve is interpreted by the application of two models in the following. The estimated over-all error is about ±5% at a concentration of 50 at.%

6.1. Regular Model

The Regular Model suggested by Hildebrand [14] describes the property of mixing as a quadratic function of concentration:

$$\Delta G^E_R = x_1 x_2 \beta_0 , \tag{9}$$

where the magnitude and sign of the constant β_0 describes the magnitude and nature of the atomic interaction. If β_0 is independent of concentration and positive, a system with segregation tendency must be assumed. To apply the Regular Model, the function $\Delta G^E/x_1 x_2$ vs. x_{Si} is plotted (Fig. 8, upper part).

The values of ΔG^E from Fig. 7 yield the drawn curve. It is obvious, that the Cu-Si melts above 50 at.% Si can be well described by the Regular Model which is indicated by the dashed line. Below 50 at.% Silicon we find the parameter β to be dependent on concentration, thus

$$\Delta G^E_{exp}/x_1 x_2 = \beta(x_1) . \tag{10}$$

This dependence of β on concentration is illustrated in Fig. 8 (lower part) by the value of $d\beta/dx_1$. Regular behaviour is indicated by $d\beta/dx = 0$. The magnitude of $d\beta/dx$ thus describes the magnitude of deviation from the Regular Model and here we find a maximum at about 20 at.% Si. The deviation tends towards a statistical distribution caused by the interaction forces between unlike atoms Cu and Si which are stronger than those required in the Regular Model.

It might be pointed out, that there are several intermetallic compounds in the copper-rich part of the solid system, which support the assumption of an enforcement of interaction between unlike atoms.

6.2. Schmid and Schürmann's Model [15]

A rather formal description of mixing effects in binary systems is given by the Schmid and Schürmann Model. This model starts from the assumption that when the components A and B are mixed

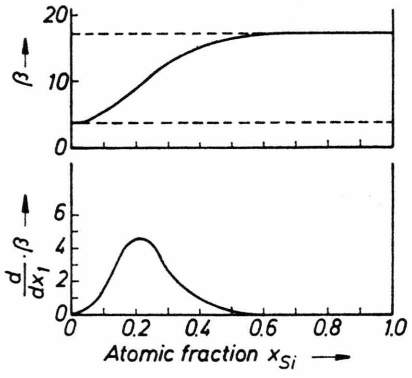

Fig. 8. Regular Model: β and $d\beta/dx_1$ vs. concentration of Si.

each deviation from ideal Raoult's behaviour can be explained by the existence of clusters of certain stoichiometric composition. These clusters shall obey the mass law like chemical compounds.

Principally all kinds of clusters are considered, namely the self-coordinated $A_2, A_3, \ldots, A_n$ and $B_2, B_3, \ldots, B_m$ as well as the coordinated AB, $A_2B, AB_2, \ldots, A_nB_m$.

For the equations of reaction we obtain:

$$nA + mB \rightleftarrows A_nB_m \quad (n, m \geqq 0)\,. \tag{11}$$

The order R of the model is defined by

$$n + m \leqq R\,.$$

For the activities $a_{A_nB_m}$ of the agglomerates the mass laws (12) may be valid:

$$a_{A_nB_m} = K_{nm}\, a_A^n\, a_B^m \quad (1 \leqq n + m \leqq R)\,. \tag{12}$$

The mass law (ML) constants K_{nm} are considered as the parameters of the model. Each deviation from Raoult's Law is described by Eq. (12) and thus the real binary A-B system is replaced by an ideal $(R^2 + 3R)/2$-System.

Interactions of the A and B atoms are described by the ML-constants of the model. One atom appears either as a free particle (no interaction) or as a partner in an agglomerate.

Though this description is a strong simplification of the real conditions, a good approximation of the measured values can be obtained even by the assumption of simple agglomerates. The parameters of these agglomerates (ML-constants) were determined by a computer program [16] which applies least squares analysis.

In the present work the computations were carried out assuming Si_4 and Cu_4Si agglomerates. Correspondent to results from diffraction experiments of Si- and Al-Si-melts the Si_4 seemed to be significant [17]. The reduction of the activity of copper at about 20 at.% Si should be described by Cu_4Si.

To obtain a still better approximation of the segregation tendency, a Cu_4 agglomerate was assumed additionally. This yielded a quite good approximation of the model-line and measured values as Fig. 9 shows.

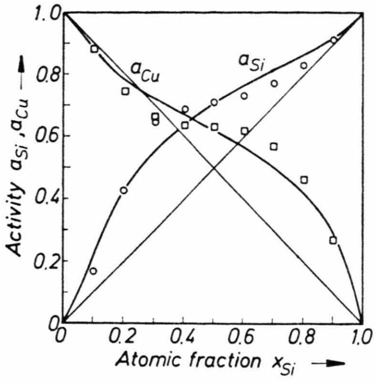

Fig. 9. Cu-Si system: Computed activities according to the model of Schmid and Schürmann with the agglomerates Si_4, Cu_4Si and Cu_4 (○, □) = measured activities.

Especially the computed activity of copper lies under Raoult's line on the copper-rich side just as it was obtained from the experiment.

The ML-constants were as follows:

$$\begin{aligned} 4\,Si &\rightleftarrows Si_4 &&: \ MLC = 18.86\,, \\ 4\,Cu &\rightleftarrows Cu_4 &&: \ MLC = \ \ 1.67\,, \\ 4\,Cu + Si &\rightleftarrows Cu_4Si &&: \ MLC = 10.07\,. \end{aligned}$$

Considering both models and comparing the results with the phase diagram of the Cu-Si system, we find that conditions which cause the formation of Hume-Rothery phases might have consequences on the liquid state: the activities of Cu lie under the values of ideal mixture (around 20 at.% Si).

This had been observed earlier [18] in the Ag-Si system which shows similar behaviour of activities as well as in the Au-Si system.

Acknowledgement

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