

Thermodynamic Assessment of the Sn-Co Lead-Free Solder System

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The Sn-Co-Cu eutectic alloy can be a less expensive alternative for the Sn-Ag-Cu alloy. In order to find the eutectic solder composition of the Sn-Co-Cu system, the Sn-Co binary system has been thoroughly assessed with the calculation of phase diagram (CALPHAD) method. The liquid phase, the FCC and HCP Co-rich solid solution, and the BCT Sn-rich solid solution have been described by the Redlich–Kister model. The Hillert–Jarl–Inden model has been used to describe the magnetic contributions to Gibbs energy in FCC and HCP. The CoSn_2 , CoSn , Co_3Sn_2 , β , and α phases have been treated as stoichiometric phases. A series of thermodynamic parameters have been obtained. The calculated phase diagram and thermodynamic properties are in good agreement with the experimental data. The obtained thermodynamic data was used to extrapolate the ternary Sn-Co-Cu phase diagram. The composition of the Sn-rich eutectic point of the Sn-Co-Cu system was found to be 224°C, 0.4% Co, and 0.7% Cu.

Key words: Lead-free solder, tin cobalt system, thermodynamic calculation, phase diagram

INTRODUCTION

During the last decade, the development of Pb-free solders has become an important issue regarding electronic interconnection materials in the packaging of electronic devices because of the health and environmental safety problems posed by lead usage. The development of lead-free solders has happened despite the favorable properties of conventional Sn-Pb solders, such as good wetting, low-melting temperature, attractive price, and well-established technology. Phase diagrams have played an important role in the development of new lead-free alloys. On the basis of thorough analysis of binary phase diagrams of Sn-X (X representing other elements) systems and element properties of X, the eutectic Sn-Co-Cu alloy can be a less expensive alternative to the Sn-Ag-Cu eutectic solder.¹ Although many properties, such as wetting behavior, mechanical behavior, etc., of the eutectic Sn-Co-Cu alloy should be characterized before it can be used in electronic packaging, finding

the eutectic composition is the first step of these works. Concerning the three binary systems, Sn-Cu, Sn-Co, and Co-Cu, the Sn-Cu binary system has been thoroughly assessed by Shim et al.,² and the Co-Cu system has been assessed by Chen.³ In order to extrapolate the thermodynamic functions of the constituent binary systems and to find the eutectic composition of the Sn-Co-Cu system, the Sn-Co binary system needed to be assessed in the present work.

EXPERIMENTAL DATA

Available data for the Sn-Co system was compiled and evaluated earlier by Ishida and Nishizawa⁴ and Okamoto.⁵ The liquidus temperatures have been determined by thermal analysis in the Co-rich region by Hashimoto,⁶ 0–60% Sn by Comert and Pratt,⁷ and over the whole system by Lewkonja⁸ and Zemczuzny and Belynsky.⁹ Darby and Jugle¹⁰ determined the solubility of Co in liquid Sn by means of a “wet” chemical methodology, analyzing the composition of the quenched liquid in equilibrium with the CoSn intermetallic phase after heating at different temperatures. The agreement of these liquidus data

was acceptable, and they were used in the present optimization procedure. In agreement with Ishida and Nishizawa⁴ and Okamoto,⁵ the data by Hashimoto⁶ and Comert and Pratt⁷ was given high priority. However, and in disagreement with Ishida and Nishizawa⁴ and Okamoto,⁵ the data obtained by Darby and Jugle¹⁰ was given a low priority because it was found to be contradictory to the phase diagram data of the Co-rich side and the activity data obtained by Comert and Pratt.¹¹ When analyzing the experimental procedure by Darby and Jugle,¹⁰ one can presume that the error might be caused by the wet chemical analysis. The result of this method is more dependent on the experience of the analyzer than the equipment itself. The invariant reaction temperatures have been selected according to Ishida and Nishizawa,⁴ but the melting point of $\text{Co}_3\text{Sn}_2\beta$ and the polymorphic transformation temperature between $\text{Co}_3\text{Sn}_2\beta$ and $\text{Co}_3\text{Sn}_2\alpha$ were selected according to Okamoto.⁵

Korber and Oelsen¹² determined the enthalpies of liquid-liquid mixing at 1,773 K from differences in heat content, and Esin et al.¹³ obtained their enthalpies of liquid-liquid mixing at 1,850 K with calorimetric measurements. The first result showed positive deviations from the ideal solution model in the Sn-rich solution and negative deviations in Co-rich solutions. On the contrary, the second result showed negative deviations from the ideal in the Sn-rich solution and positive deviations from the ideal in the Co-rich solution. In disagreement with Ishida and Nishizawa⁴ and Heuzey and Pelton,¹⁴ it was found that it was impossible to fit the data by Korber and Oelsen¹² with the phase diagram data. The data by Esin et al.¹³ was accepted in the present optimization. Because lower Gibbs energy indicates higher liquid stability, resulting in the Sn-rich liquid in the Sn-Co system being more stable than Sn-Fe and the Sn-Ni system, it seems more reasonable to assume that Esin's data are correct. Eremenko et al.¹⁵ measured activities of Sn in liquid with Knudsen effusion at 1,573 K. The results were used in the present assessment. The enthalpy for formation of solid alloys was determined by a calorimetric method by Korber and Oelsen¹² and Predel and Vogelbein,¹⁶ by a solid electrolyte galvanic-cell technique by Comert and Pratt,^{7,11} and estimated by Miedema et al.¹⁷ The results are unfortunately quite scattered. The experimental results of CoSn and $\text{Co}_3\text{Sn}_2\alpha$ by Predel and Vogelbein¹⁶ and the experimental results of CoSn_2 by Korber and Oelsen¹² were used in the present assessment. The other data was used for comparison. During optimization, it was found that the calculated formation enthalpy of $\text{Co}_3\text{Sn}_2\alpha$ was actually closer to the data by Korber and Oelsen.¹² According to the Miedema model, $\text{Co}_3\text{Sn}_2\alpha$ should have the highest formation enthalpy, so it was assumed that the data obtained by Predel and Vogelbein¹⁶ was too low. The activity of Sn at 1,073 K and 1,273 K was measured by a solid electrolyte galvanic-cell technique method by Comert and Pratt.^{7,11} It was, however, difficult

to fit their activity data for solid-solid equilibrium, and therefore, only their activity data for liquid-solid equilibrium was used for this optimization.

The composition range of $\text{Co}_3\text{Sn}_2\beta$ is very narrow, and it has only been interpreted by Comert and Pratt^{7,11} from the solid electrolyte galvanic-cell data. Because no direct measured data has been found, this composition range was not considered in the present assessment.

THERMODYNAMIC MODEL

The pure solid elements in their stable state at 298.15 K were chosen as a reference state for the system, stable element reference. The Gibbs energies as a function of temperature for stable and metastable states of pure Co and Sn were taken from the Scientific Group Thermodata Europe databank.¹⁹ Both nonmagnetic and magnetic contributions were taken in to account for FCC_Co and HCP_Co; however, only nonmagnetic contributions were taken into account for the liquid and BCT_Sn.

An ordinary substitutional solution model was applied to the liquid, nonmagnetic contribution of the Co-rich FCC and HCP terminal solution and the Sn-rich terminal solid solution. The mole Gibbs energy of a phase Φ can be represented as a sum of the Gibbs energy for the formation of the pure components, the ideal entropy term describing a random mixing of the components, and the excess Gibbs energy describing the degree of deviation from ideal mixing. The expression is as follows:

$$G_m^\Phi = \sum x_i {}^0G_i^\Phi + RT \sum x_i \ln(x_i) + {}^E G_m^\Phi + {}^{mo} G_m^\Phi \quad (1)$$

where G_m^Φ is the molar Gibbs energy of phase Φ , ${}^0G_i^\Phi$ is the Gibbs energy of pure element I, x_i is the mole fraction of component I, R is the gas constant, T is temperature, and ${}^E G_m^\Phi$ is the excess Gibbs energy. For the ordinary substitutional solution, the excess Gibbs energy of phase Φ can be written in the form of a Redlich-Kister polynomial²⁰ as follows:

$${}^E G_m^\Phi = x_{\text{Sn}} x_{\text{Co}} \sum_{i=0}^n {}^i L_{\text{Co,Sn}}^\Phi (x_{\text{Co}} - x_{\text{Sn}})^i \quad (2)$$

No ${}^E G_m^\Phi$ was used for the Sn-rich terminal solid solution with $n = 0$ for the HCP Co-rich terminal solid solution and FCC Co-rich terminal solution, and $n = 2$ for the liquid phase.

The term ${}^i L_{\text{Co,Sn}}^\Phi$ is an interaction parameter and can be expressed as temperature dependent as follows:

$$(3)$$

where a_i , b_i , and c_i are model parameters, which have been optimized in this paper.

The term ${}^{mo} G_m^\Phi$ represents the magnetic contributions to the Gibbs energy. The magnetic contributions were only considered for the FCC and HCP Co-terminal solid solution.

$${}^{mo} G_m^\Phi = RT \ln(\beta^\Phi + 1) f(\tau) \quad (4)$$

The term β^Φ is a composition-dependent parameter related to the total magnetic entropy, and τ is defined as $\tau = T/T_c^\Phi$, where T_c^Φ is the critical temperature of magnetic ordering. Function $f(\tau)$ takes the polynomial form proposed by Hillert and Jarl.²¹

The intermetallic phases have been treated as stoichiometric phases Co_pSn_q . Their Gibbs energy of phase Co_pSn_q can be described as

$$G_{Co_pSn_q} = \frac{p}{p+q} \times {}^0G_{Co}^{HCP,nmg} + \frac{q}{p+q} \times {}^0G_{Sn}^{BCT} + A + B \times T \quad (5)$$

where ${}^0G_{Co}^{HCP,nmg}$ and ${}^0G_{Sn}^{BCT}$ are the nonmagnetic part of the Gibbs energy of pure HCP Co and the Gibbs energy of pure Sn, respectively. The A and B are the adjusted parameters, which have been optimized in the present work.

OPTIMIZATION AND RESULT

The optimization of the parameters was achieved using the Parrot modules in the Thermo_Calc program developed by Sundman et al.²² At first, the thermodynamic data of liquid was taken into account to optimize simultaneously the binary interaction parameters of liquid. The parameters of various solid phases were then optimized by fitting the phase diagram data and formation enthalpy. Finally, the activity data was used for further refining the thermodynamic description in the whole system. All the parameters obtained in the present assessment are listed in Table I. Table II compares the calculated invariant reactions and the invariant reactions compiled by Ishida and Nishizawa⁴ and Okamoto.⁵ The agreement is acceptable. The calculated phase dia-

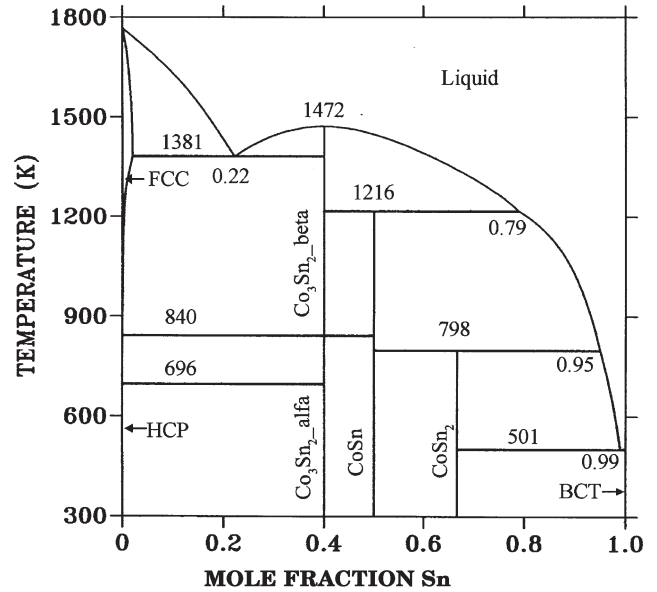


Fig. 1. Calculated phase diagram of the Co-Sn system.

gram is depicted in Fig. 1. Figure 2 compares the experimental and calculated liquidus and solidus. Except for the data by Darby and Jugle,¹⁰ the agreement is quite good. As discussed previously, the disagreement might be caused by the error in the chemical analysis done by Darby and Jugle.¹⁰ Further experiments on the liquidus composition of liquid and CoSn two-phase equilibrium are recommended. The agreement between experimental and calculated activity of liquid/solid equilibria is acceptable; however, the agreement between experimental and

Table I. Summary of the Thermodynamic Parameters of the Sn-Co System (J/mol)

Liquid phase (Co,Sn)	${}^0L_{Co,Sn}^{Liq} = 17,852.99 - 233.03 * T + 29.68 * T * \ln(T)$
	${}^1L_{Co,Sn}^{Liq} = 9,855.59 - 12.61 * T$
	${}^2L_{Co,Sn}^{Liq} = -35,947.6 + 27.76 * T$
FCC phase (Co,Sn)	${}^0L_{Co,Sn}^{FCC} = 11,649.47$
	p is 0.28 for fcc_A1
	${}^0Tc_{Co,Sn}^{FCC} = -2,975.98$
HCP phase (Co,Sn)	${}^0L_{Co,Sn}^{HCP} = 50,000$
CoSn ₂	${}^0G_{CoSn_2} - 0.333 * {}^0G_{Co}^{HCP} - 0.667 * {}^0G_{Sn}^{BCT} = -12,796.22 + 0.3292 * T$
CoSn	${}^0G_{CoSn} - 0.5 * {}^0G_{Co}^{HCP} - 0.5 * {}^0G_{Sn}^{BCT} = -20,529.81 + 5.0229 * T$
Co ₃ Sn ₂ _beta	${}^0G_{Co_3Sn_2_Beta} - 0.6 * {}^0G_{Co}^{HCP} - 0.4 * {}^0G_{Sn}^{BCT} = -17,069.19 + 1.8315 * T$
Co ₃ Sn ₂ _alfa	${}^0G_{Co_3Sn_2_Beta} - 0.6 * {}^0G_{Co}^{HCP} - 0.4 * {}^0G_{Sn}^{BCT} = -17,489.19 + 2.3315 * T$

Table II. Comparison Calculated and Compiled Invariant Reactions

Reaction	Temperature (°C)			Liquid Composition (At.% Sn)		
	This Work	Ref. 4	Ref. 5	This Work	Ref. 4	Ref. 5
L → CoSn ₂ + (Sn)	229	229	229	0.99	0.99	—
L + CoSn → CoSn ₂	525	525	525	0.95	0.97	0.97
L + Co ₃ Sn ₂ _beta → CoSn	943	936	936	0.79	0.78	0.78
L → Co ₃ Sn ₂ _beta	1,199	1,170	1,200	—	—	—
L → Co ₃ Sn ₂ _beta + FCC	1,108	1,112	1,125	0.22	0.205	—
Co ₃ Sn ₂ _beta → Co ₃ Sn ₂ _alfa	567	500	567	—	—	—

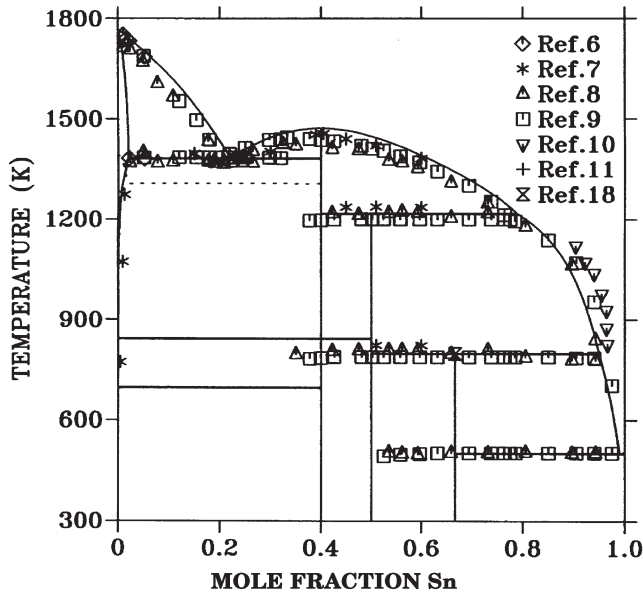


Fig. 2. Comparison of the calculated phase diagram with the experimental data.

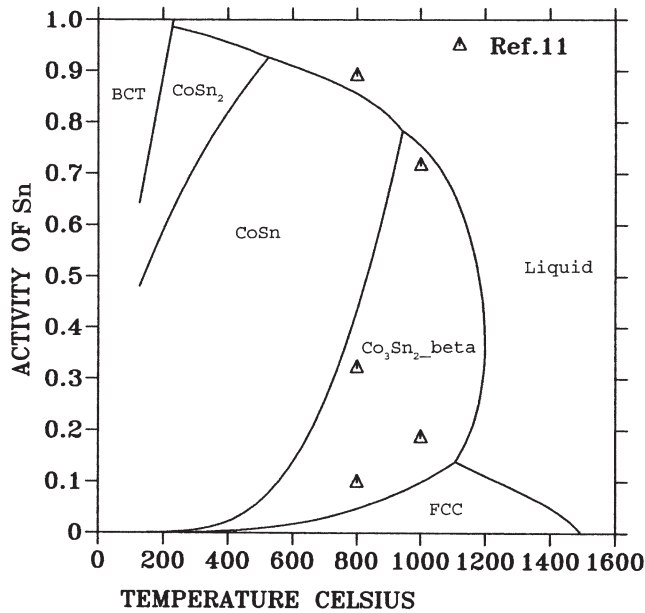


Fig. 3. Experimental and calculated activity of Sn at 800°C and 1,000°C.

calculated activity of solid/solid equilibria is poor (Fig. 3). This is caused by the slow equilibrium procedure during the activity test. The calculated formation enthalpies of $\text{Co}_3\text{Sn}_2_\alpha$, CoSn , and CoSn_2 are comparable to the experimental data and the data estimated by the Miedma model¹⁷ (Fig. 4). The calculated enthalpy of mixing of liquid is in agreement with the experimental data by Esin et al.¹³ (Fig. 5), except for the highest value that was shifted to the Co-rich side. It is reasonable if we consider that the $\text{Co}_3\text{Sn}_2_\beta$ has the highest melting point in this system. It was impossible to fit the enthalpy of mixing data by Korber and Oelsen¹² in the optimization, even when we did not consider its contradiction with

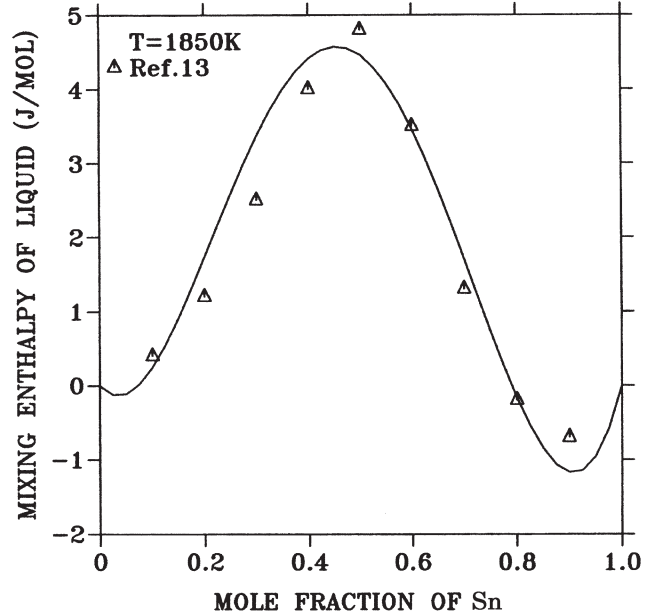


Fig. 4. Experimental and calculated formation enthalpy for the intermetallics in the Co-Sn system.

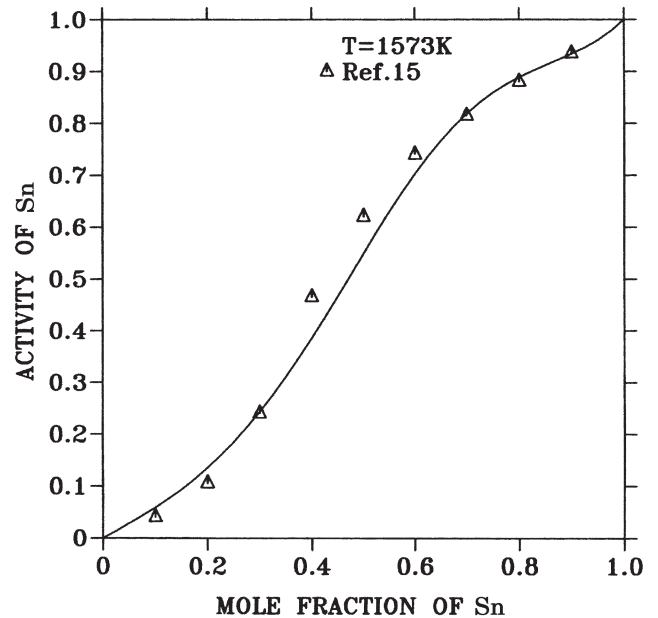


Fig. 5. Experimental and calculated enthalpy of mixing of liquid at 1,850 K.

the data by Esin et al.¹³ Further experimental work on the mixing enthalpy of liquid is needed. The agreement of experimental and calculated activity of liquid at 1,573 K is fairly good (Fig. 6).

EXTRAPOLATION AND DISCUSSION

The Muggianu extrapolation model²³ was used to extrapolate the binary phase diagram to the Sn-Co-Cu ternary system. No ternary parameters were used. The calculated liquidus projections in the Sn-rich corner are shown in Fig. 7. From this diagram, we can see the eutectic point in the Sn-rich corner is about 224°C, 98.9% Sn, 0.4% Co, and 0.7% Cu.

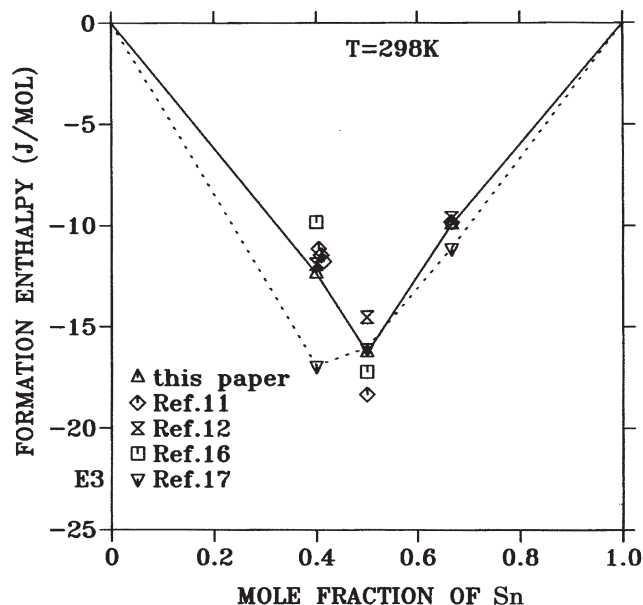


Fig. 6. Experimental and calculated activity of Sn in liquid at 1,573 K.

As mentioned in the introduction, before the eutectic Sn-Co-Cu alloy can be used in electronic packaging, many other properties, such as wetting and mechanical behavior, must be characterized. There may be many other problems with this alloy. For example: What is the effect of the many CoSn intermetallics? How does the Co affect the wetting behavior and oxidation? etc. Finding the eutectic composition is only the starting point for developing a new solder in this system.

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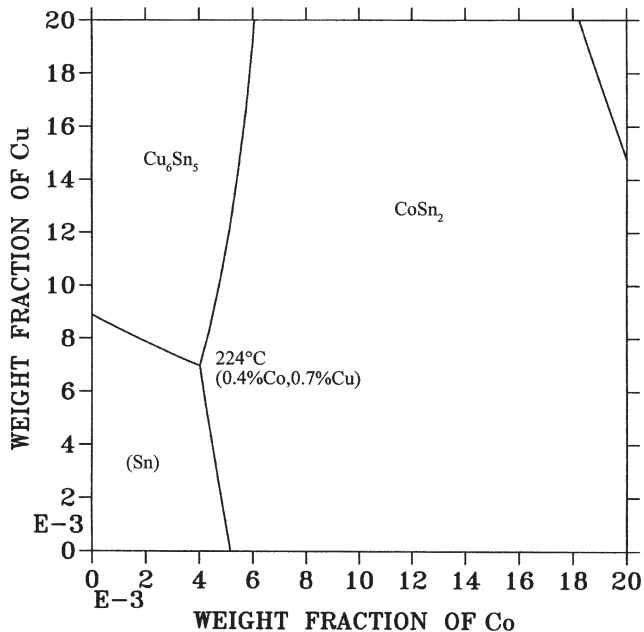


Fig. 7. Calculated eutectic point the Sn-rich corner of the Sn-Co-Cu system.

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