The Cd-Se (Cadmium-Selenium) System

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Equilibrium Diagram

The Cd-Se system has a congruently melting intermediate phase,αCdSe, at 50 at.% Se. A liquid miscibility gap exists in the αCdSe-Se region of the phase diagram, resulting in a monotectic reaction, and two eutectics exist, close to pure Cd and pure Se, respectively. The assessed Cd-Se phase diagram given in Fig. 1 is based on our modeling and calculations. Table 1 summarizes the literature data for the invariant equilibria and presents the assessed values.

Liquidus

The melting points of pure Cd and pure Se are 321.108 and 221 °C, respectively. The liquidus in the Cd-Se system was determined by [62Rei]. The data are shown in Fig. 1, together with the assessed phase boundaries. Table 2 lists the assessed liquidus temperatures for selected compositions.

Solid Solubilities

The mutual solid solubilities of Cd and Se have not been experimentally determined and probably are negligible.

αCdSe

αCdSe forms at 50 at.% Se and melts congruently. The deviation from stoichiometric composition is negligible [62Rei], [67Bur]. The congruent melting point of αCdSe as determined by different investigators is given in Table 3, together with the assessed value.

Phase Equilibria Calculations

The assessed Cd-Se phase diagram is based on calculations performed using the thermodynamic data described below.

High-Pressure Equilibria

The αCdSe phase (wurtzite structure) transforms to βCdSe phase (NaCl structure) at high pressures (~25 kb at room temperature) [61Edw, 63Mar, 63Roo1, 63Jay, 69Ono]. [63Jay] determined the melting equilibria of αCdSe and βCdSe as a function of pressure and [69Ono] determined the αCdSe to βCdSe transition pressure as a function of temperature, up to 700 °C. Figure 2 gives the *P-T* phase diagram for CdSe based on these data. [63Jay] reported the L-αCdSe-βCdSe triple point as ~13 kb and ~1252 °C.

Crystal Structures and Lattice Parameters

Tables 4 and 5 summarize the crystal structure and lattice parameter data for the Cd-Se system.

Thermodynamics

Pure Components

The enthalpies of melting given by [Hultgren,E] are used to obtain the Gibbs energy functions for the melting of pure Cd and Se as:

$$\Delta_{fus}G^0(\text{Cd}) = 6190 - 10.417\,T \text{ J/mol} \quad \text{(Eq 1)}$$

and

$$\Delta_{fus}G^0(\text{Se}) = 6694.4 - 13.551\,T \text{ J/mol} \quad \text{(Eq 2)}$$

Liquid Phase

[65Shi] determined the partial pressures of Cd(g) and Se_2(g) along the liquidus in the Cd-Se system. These data may be converted into the activities of Cd and Se in the liquid at the liquidus compositions. There are no other data available on the thermodynamic properties of the liquid phase.

The present evaluators have used an associated solution model to describe the thermodynamic properties of the liquid phase. According to this model, the liquid phase consists of 'Cd,' 'Se,' and 'CdSe' species governed by the equilibrium equation:

$$\text{'Cd'(L)} + \text{'Se'(L)} \leftrightarrow \text{'CdSe'(L)} \quad \text{(Eq 3)}$$

with an equilibrium constant, K, given by:

$$K = \frac{f_3 y_3}{(f_1 y_1)(f_2 y_2)} \quad \text{(Eq 4)}$$

Table 1 Invariant Equilibria in the Cd-Se System

Reaction	Compositions of the respective phases, at.% Se			Temperature, °C	Reference
$L_1 \leftrightarrow$ (Cd) + αCdSe	~0	~0	50	~321	Assessed
$L_1 \leftrightarrow$ αCdSe + L_2	67.5 to 70	50	~99	991	[62Rei]
	67.5	50	99	991	Assessed
$L_2 \leftrightarrow$ αCdSe + (Se)	~100	50	~100	~221	Assessed

where f_1, f_2, and f_3 are activity coefficients and y_1, y_2, and y_3 are the mole fractions of 'Cd,' 'Se,' and 'CdSe,' respectively, in the liquid. The mole fractions, y_i's, are related to the actual mole fractions, x_{Cd} and x_{Se}, of Cd and Se, respectively, by the following mass balance equations:

$$y_1 = x_{Cd} - x_{Se}y_3 \quad \text{(Eq 5)}$$

and

$$y_2 = x_{Se} - x_{Cd}y_3 \quad \text{(Eq 6)}$$

The activity coefficients, f_i's, are described by Margules type equations as:

$$\ln f_i = \sum_{j=1}^{3}\left[\left(w_{ij}+w_{ji}\right)/2 + \left(w_{ij}-w_{ji}\right)\left(y_j/2 - y_i\right) - 8v_{ij}x_ix_j\right]x_j$$

$$- \sum_{j=1}^{3}\sum_{p=1}^{3}\left[w_{jp}/2 + \left(w_{jp}-w_{pj}\right)y_p - 6v_{jp}x_jx_p\right]x_jx_p \quad \text{(Eq 7)}$$

where i, j, and p refer to 'Cd,' 'Se,' and 'CdSe,' respectively; w_{ij}, v_{ij}, etc., are the interaction parameters of the solution; and $w_{ii} = w_{jj} = 0$, $v_{ii} = v_{jj} = 0$, and $v_{ij} = v_{ji}$ [84Chu]. The interaction parameters are represented as:

$$w_{ij} = A_{ij}/T + B_{ij} \quad \text{(Eq 8)}$$

and

$$v_{ij} = C_{ij}/T + D_{ij} \quad \text{(Eq 9)}$$

where A_{ij}, B_{ij}, C_{ij}, and D_{ij}, etc., are constants.

The activities of the 'Cd' and 'Se' species, therefore, are:

$$a_1 = f_1y_1 \quad \text{(Eq 10)}$$

and

$$a_2 = f_2y_2 \quad \text{(Eq 11)}$$

with Cd(L) and Se(L) as the standard states. Because the activities of the 'Cd' and 'Se' species are the same as those of the Cd and Se components [65Pri]:

$$a_1 = f_1y_1 = a_{Cd} = \gamma_{Cd}x_{Cd} \quad \text{(Eq 12)}$$

and

$$a_2 = f_2y_2 = a_{Se} = \gamma_{Se}x_{Se} \quad \text{(Eq 13)}$$

where γ_{Cd} and γ_{Se} are the activity coefficients of Cd and Se that differ from f_1 and f_2.

The optimum values of the liquid phase solution parameters have been obtained using the available thermodynamic and phase equilibria data for the Cd-Se system and are given in Table 6.

The calculated activities of Cd and Se along the liquidus are converted to the equilibrium partial pressures, p_{Cd} and p_{Se_2}, of Cd(g) and Se_2(g) using the following relations:

Table 2 Assessed Cd-Se Liquidus Data

Composition, at.% Se	Temperature, °C
0	321.108
0.1	670
1	834
10	1037
20	1100
30	1135
40	1171
50	1264
60	1125
67.5	991
99	991
99.5	884
99.9	676
100	221

Table 3 αCdSe Melting Temperature

Reference	Melting temperature, °C
[17Chi]	1350
[61Mas]	1258 ± 1
[62Rei]	1239
[67Sys]	1264 ± 10
Assessed	1264 ± 10

Table 4 Cd-Se Crystal Structure Data

Phase	Composition, at.% Se	Pearson symbol	Space group	Strukturbericht, designation	Prototype
(Cd)	0	*hP2*	$P6_3/mmc$	*A3*	Mg
αCdSe	50	*hP4*	$P6_3mc$	*B4*	ZnS
βCdSe(HP)	50	*cF8*	$Fm\bar{3}m$	*B1*	NaCl
(Se)	100	*hP3*	$P3_121$	*A8*	Se

Note: From [Pearson2]. HP refers to high-pressure phase.

$$a_{Cd} = p_{Cd}/p^0_{Cd} \qquad \text{(Eq 14)}$$

and

$$a_{Se} = \left(p_{Se_2}/p^0_{Se_2}\right)^{1/2} \qquad \text{(Eq 15)}$$

where p^0_{Cd} and $p^0_{Se_2}$ are the equilibrium pressures of Cd(g) and Se_2(g) over pure Cd(L) and Se(L), respectively, reported by [74Mil], [Hultgren,E], and [74Jel] as:

$$\log p^0_{Cd}(\text{bar}) = -\frac{5317}{T} + 5.123 \qquad \text{(Eq 16)}$$

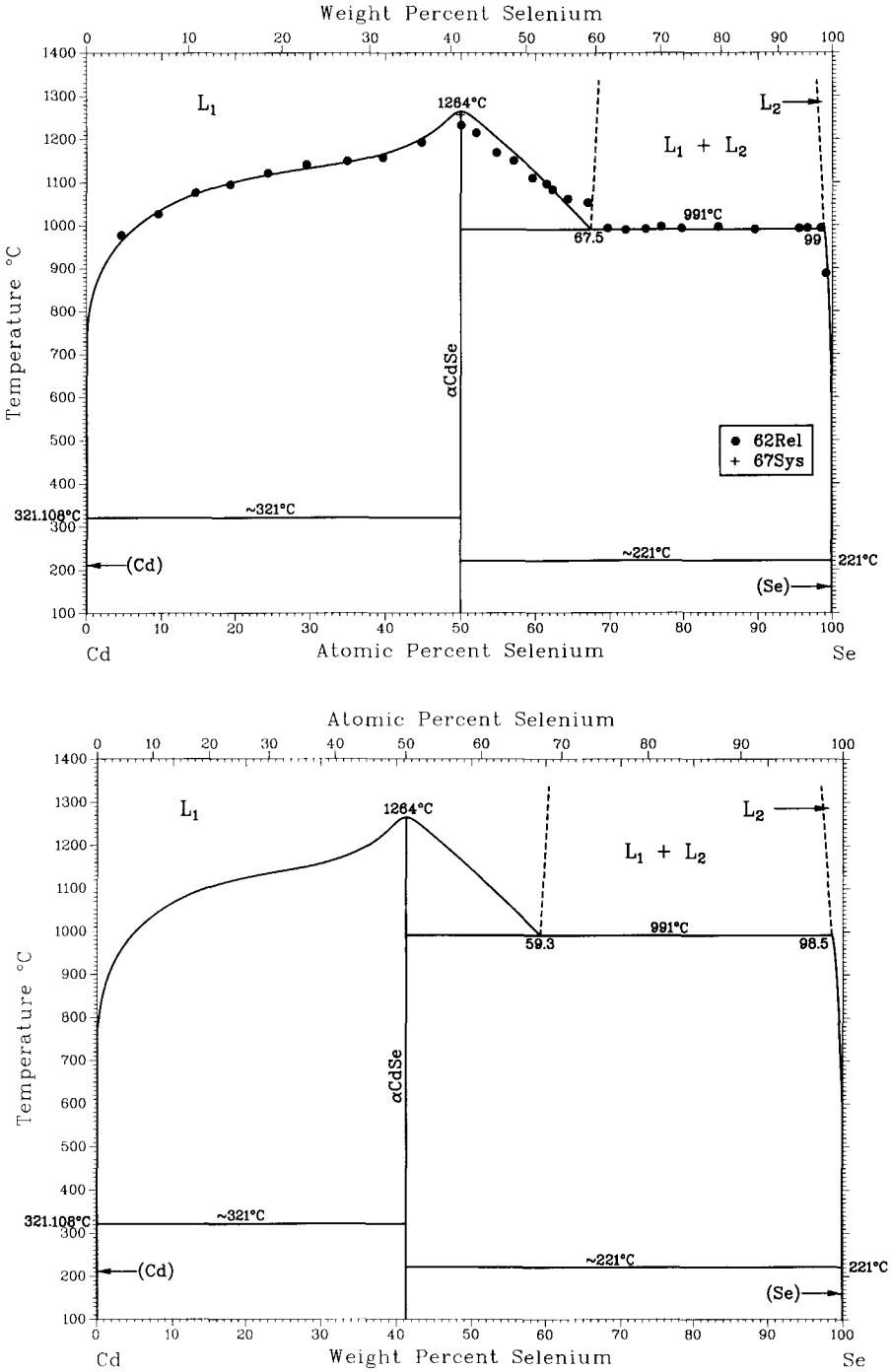

Fig. 1 Assessed (calculated) Cd-Se phase diagram.

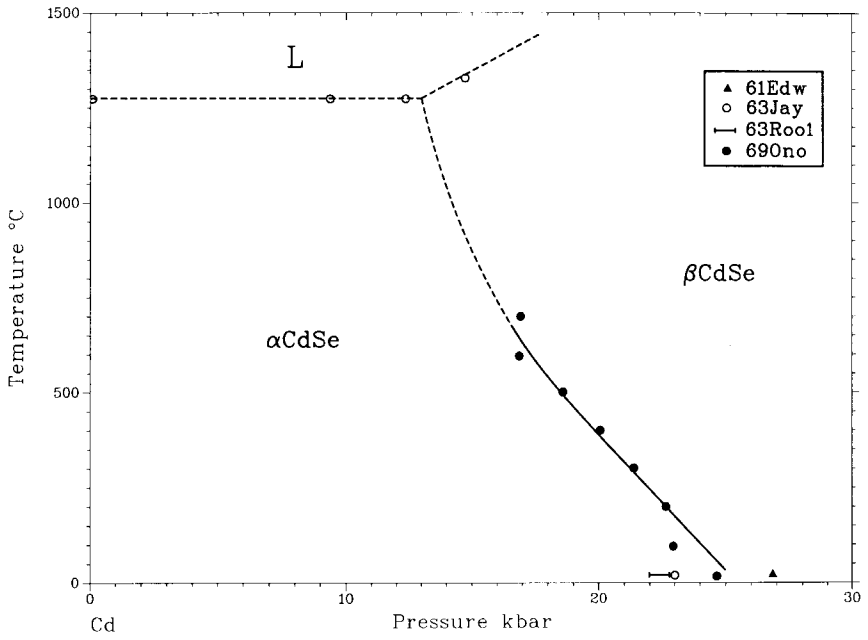

Fig. 2 CdSe *P-T* phase diagram.

Table 5 Cd-Se Lattice Parameter Data

Phase	Composition, at.% Se	Lattice parameters, nm *a*	*c*	Reference
(Cd)	0	0.29788	0.56167	[Pearson2]
αCdSe	50	0.430	0.701	[63Mar]
		0.42999	0.70109	[76Ree]
βCdSe(HP)	50 (32 kb)	0.549	...	[63Mar]
	(22 kb)	0.554	...	[63Roo2]
(Se)	100	0.43656	0.49590	[Pearson2]

Note: HP refers to high-pressure phase.

and

$$\log p^0_{Se_2}(\text{bar}) = -\frac{7712}{T} + 19.346 - 1.7055 \ln T \qquad \text{(Eq 17)}$$

Figures 3 and 4, respectively, compare the calculated equilibrium partial pressures of Cd(g) and Se_2(g) along the liquidus with the experimental data, and the agreement is reasonably good.

αCdSe

The Gibbs energy of formation of αCdSe was determined by [64Ter] using the emf method and by [61Wos], [64Gol], [64Pas], [65Shi], [69Boe], and [69Flo] using dissociation pressure measurements. [69Dem1], [69Dem2], and [69Sha] measured the low-temperature specific heat of αCdSe. These data were assessed by [74Mil] to give:

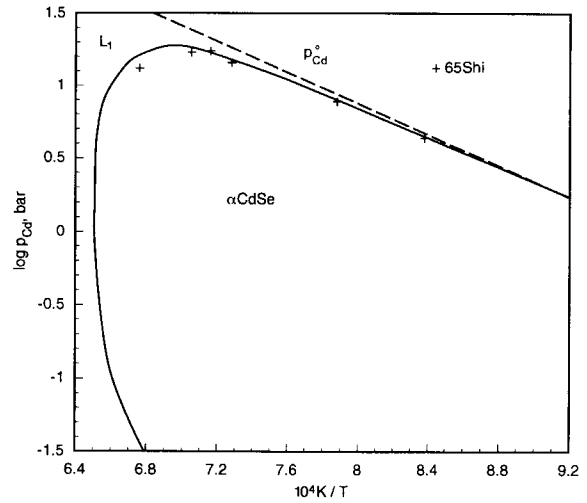

Fig. 3 Partial pressure of Cd(g), p_{Cd}. Along the liquidus.

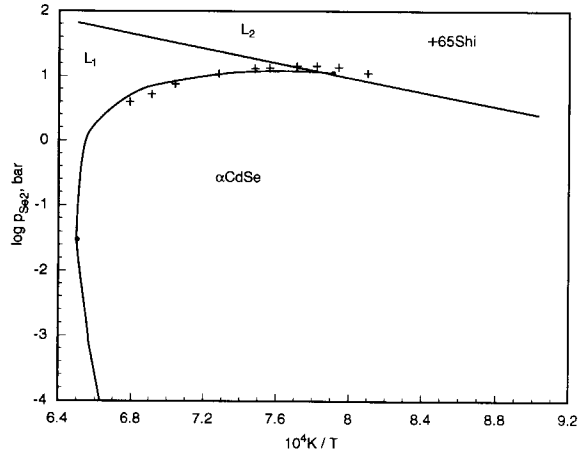

Fig. 4 Partial pressure of Se_2(g), p_{Se_2}. Along the liquidus.

Table 6 Thermodynamic Data for the Cd-Se Liquid Phase

'Cd'(L) + 'Se'(L) ↔ 'CdSe'(L); $K = \frac{f_3 y_3}{(f_1 y_1)(f_2 y_2)}$

$\ln K = -2.03165 + \frac{14\,569.2}{T}$

$w_{13} = \frac{2\,269.5}{T}$

$w_{31} = -4.7610 + \frac{9\,018.2}{T}$

$v_{13} = v_{31} = 0.0$

$w_{23} = \frac{1\,937.3}{T}$

$w_{32} = 1.8972 + \frac{2\,808.1}{T}$

$v_{23} = v_{32} = \frac{1\,938.7}{T}$

$w_{12} = w_{21} = v_{12} = v_{21} = 0.0$

Subscript 1: the 'Cd' species, subscript 2: the 'Se' species, and subscript 3: the 'CdSe' species.

$\Delta_f H^0_{298}$ = 144.8 kJ/mol (αCdSe) (Eq 18)

and

S^0_{298} (αCdSe) = 83.3 J/mol·K (Eq 19)

$\Delta_f H^0_{298}$ assessed by [74Mil] has been used together with the $\left[\frac{G_T - H^0_{298}}{T}\right]$ functions for αCdSe from [74Mil] and for Cd and Se from [Hultgren,E] to calculate the Gibbs energy of formation of αCdSe. A least squares fit through these values gives:

$\Delta_f G^0 = -163\,750 + 44.518\,T$; 500 K < T < 1 500 K (Eq 20)

Table 7 Dissociation Pressure of αCdSe

Investigator	Method	log p(bar) = $-A/T + B$	
		A	*B*
[61Som]	Bourdon gauge	10020	6.926
[61Wos]	Transpiration	11480	7.309
[64Gol]	Knudsen effusion	10976	6.766
[65Shi]	Boiling point	11306	7.102
[69Boe]	Transpiration	10848	6.586
[69Flo]	Transpiration	11088	7.009
Assessed	...	11088	7.009

for the reaction:

Cd(L) + Se(L) ↔ αCdSe(s) (Eq 21)

The αCdSe enthalpy of melting was determined by [63Kul] to be 44 ± 4 kJ/mol. The present optimization of the thermodynamic and phase equilibria data gives the enthalpy of melting as 43.7 kJ/mol (αCdSe), in agreement with the value of [63Kul].

Dissociation Pressure of αCdSe

The dissociation pressures of αCdSe were determined by [61Som], [61Wos], [64Gol], [64Pas], [65Shi], [69Boe], and [69Flo]. These data are presented in Table 7, together with the assessed value [74Mil].

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