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High-pressure phase transitions in $Cu_xAg_{1-x}I$ mixed crystals

D. C. Gupta and R. K. Singh
School of Physics, Barkatullah University, Bhopal 462 026, India

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The high-pressure phase transitions in $Cu_xAg_{1-x}I$ mixed crystals have been investigated theoretically by means of a three-body-potential model, which takes proper account of the Cauchy discrepancy and the charge-transfer effects in terms of three-body interactions. We have found that the values of the transition pressures (P_t) increase slowly up to the concentrations $x \leq 0.5$ and remain close to the values of P_t for AgI, while there is a rapid increase in P_t at $x > 0.5$. The slow increase of P_t at $x \leq 0.5$ shows the dominance of the zinc-blende phase of AgI over that of CuI, indicating the persistence of a polytype structure in $Cu_xAg_{1-x}I$ mixed crystals at these concentrations.

I. INTRODUCTION

Silver and copper iodides (AgI and CuI) have attracted the attention of many experimental[1-10] and theoretical[11-14] investigators because of the presence of *d* electrons in their cations, the peculiar nature of their chemical bonding, and high ionicity. The physical properties of these crystals are significantly different as compared to those of the simple ionic crystals and semiconductors. This is probably because they occupy the borderline positions between ionic and covalent materials. Both have their Phillips ionicity[12] around 0.78 and possess a zinc-blende (ZB) structure at ambient conditions. These materials undergo a number of structural phase transitions under pressure as observed by several workers.[1-10] At high pressures, they finally transform to a more dense sixfold-coordinated rocksalt (RS) phase.[1,2,5,13] They have potential applications as photographic materials and ionic conductors.[1] At elevated temperatures, they behave as superionic conductors, whose vibrational, elastic, anharmonic, dielectric, and phase-transition properties have been investigated by many experimental[1-10] and theoretical[11-14] workers. However, such investigations for their mixed-crystal counterparts ($Cu_xAg_{1-x}I$) were lacking until recently, when Livescu and Brafman[1] measured the phase-transition pressures in them up to 9.0 kbar using the Raman-scattering technique. Some of the observed transitions[1-3,5,15] in AgI and CuI are similar in phases but they occur at widely different pressures. This is obvious from the fact that AgI transforms from the ZB ($B3$) to the RS ($B1$) phase at very low pressures (about 4.0 kbar), while the same in CuI takes place at relatively high pressure[11] ranging from 75.0 to 150.0 kbar.

Currently, we have studied the high-pressure phase transition and anharmonic properties of Cu and Ag halides by means of a three-body-potential (TBP) model. We have achieved better agreements than those obtained by Chelikowsky[13] using an *ab initio* pseudopotential total energy method. This TBP model has also been found successful in the cases of III-V and II-VI semiconductors[16] and some alkali halides.[17] Motivated from these successes[11,16,17] and the necessity posed by Chelikowsky[13] and Hanson and co-workers[7] to include the charge-transfer (or many-body interaction) effects for better predictions of the phase transitions, we thought it pertinent to employ the same TBP model[11] incorporated with the zero-point-energy effects to reveal the phase-transition pressures, the equation of state, and the volume collapses in $Cu_xAg_{1-x}I$ mixed crystals. We have obtained reasonably good predictions on these properties.

A brief description of the theory and computed results is given in Sec. II. The results have been discussed in Sec. III.

II. THEORY AND COMPUTED RESULTS

The pressure causes a decrease in the volume and consequently it leads to an increase in the overlapping of electron shells of the adjacent ions in crystals. This overlapping gives rise to the charge-transfer effects (or many-body interactions, whose three-body components are most dominant). The effects of these three-body interactions (TBI) and zero-point-energy effects have been included in the Gibbs free energy by expressing it as a function of pressure (P) and charge transfer (i.e., TBI). This Gibbs free energy is expressed as

$$G = U + PV - TS \ , \tag{1}$$

with U as the internal energy of the system equivalent to the lattice energy at temperatures near zero. Here, S is the vibrational entropy at absolute temperature T and V is the volume of the unit cell at pressure P. The Gibbs free energies at $T=0$ for the two phases, ZB ($B3$) and RS ($B1$), are given by

$$G_{B3}(r) = U_{B3}(r) + PV_{B3} \ , \tag{2}$$

$$G_{B1}(r') = U_{B1}(r') + PV_{B1} \ , \tag{3}$$

with V_{B3} ($=3.08r^3$) and V_{B1} ($=2.00r'^3$) as the unit-cell volumes for $B3$ and $B1$ phases, respectively. The lattice energies $U_{B3}(r)$ and $U_{B1}(r')$ corresponding to the TBP model[11] are given as

$$U_{B3}(r) = -\alpha_M e^2 Z[Z+2nf(r)]r^{-1} - Cr^{-6} - Dr^{-8} + b\sum_{i,j}\beta_{ij}\exp[(r_i+r_j-r_{ij})/\rho] + 0.5\hbar\langle\omega^2\rangle_{B3}^{1/2} \ , \tag{4}$$

$$U_{B1}(r')=-\alpha'_M e^2 Z[Z+2n'f(r')]r'^{-1}-C'r'^{-6}-D'r'^{-8}+b\sum_{i,j}\beta_{ij}\exp[(r_i+r_j-r'_{ij})/\rho]+0.5\hbar\langle\omega^2\rangle_{B1}^{1/2}\ . \tag{5}$$

The first term in the above Eqs. (4) and (5) is the long-range Coulomb energy modified with three-body interactions corresponding to the nearest-neighbor separations $r(r')$. α_M (α'_M) are the Madelung constants for ZB (RS) phases. Ze is the ionic charge. $f(r)$ [$f(r')$] are the TBI parameters for ZB (RS) phases and they are dependent on the overlap integrals and expressed as (Singh and Gupta[11])

$$f(r)=f_0\exp(r_{ij}/\rho)\ . \tag{6}$$

The second and third terms in Eqs. (4) and (5) are the van der Waals attraction energy due to the dipole-dipole and dipole-quadrupole interactions with C (C') and D (D') as their overall coefficients estimated from the Slater-Kirkwood variational method[11] for the host and dopant materials. Their values for the mixed crystals have been estimated by applying the Vegard's law as

$$C_{\text{mix}}=xC_{\text{CuI}}+(1-x)C_{\text{AgI}}\ , \tag{7}$$

$$D_{\text{mix}}=xD_{\text{CuI}}+(1-x)D_{\text{AgI}}\ , \tag{8}$$

where x is the composition of dopant CuI. The fourth term in Eqs. (4) and (5) is the Hafemeister-Flygare-type overlap repulsion extended up to the second-neighbor ions with b and ρ as the hardness and range parameters. β_{ij} are the Pauling coefficients and $r_i(r_j)$ are cation (anion) radii. The values of ionic radii for mixed crystals have been calculated by applying Vegard's law as

$$r_{\text{mix}}=xr_{\text{CuI}}+(1-x)r_{\text{AgI}}\ . \tag{9}$$

The last term is the contribution from the zero-point-energy effect with $\hbar$ as the Planck constant and $\langle\omega^2\rangle^{1/2}$ as the mean-square frequency related to the Debye temperature (Θ_D) as

$$\langle\omega^2\rangle^{1/2}=k\Theta_D/\hbar\ , \tag{10}$$

with k as the Boltzmann constant. Here, Θ_D can be expressed as a parameter dependent on the short-range repulsive force constant (R_0) and reduced mass (μ) as

$$\Theta_D=h(R_0/4\pi^2k^2\mu)^{1/2}\ . \tag{11}$$

In the above expression R_0 may be written as a sum of the first- and second-order space derivatives of the short-range repulsive energy as

$$R_0=\{[U''^{\text{SR}}_{(r)}+0.5U'^{\text{SR}}(r)r^{-1}]_{r=r_0}\}/3\ . \tag{12}$$

The TBP model contains only three parameters (b, ρ, and f_0) whose values have been evaluated using the expressions of the equilibrium condition

$$\left[\frac{dU}{dr}\right]_{r=r_0}=0 \tag{13}$$

and the second-order elastic constants.[11] The strategy for parameter determination is the same as that adopted by us earlier.[11] In the present calculations, we have taken the values of ρ directly from Ref. 11 for AgI and CuI. The novelty in our calculations lies in the fact that we have not used any of those pressure dependent properties whose predictions are intended. The values of the input data along with the model parameters are listed in Table I.

We have calculated the phase-transition pressures (P_t) by minimizing the Gibbs free energy at different pressures (P) and thus obtained the equilibrium lattice separations r (r') of ZB (RS) phases of $\text{Cu}_x\text{Ag}_{1-x}\text{I}$. The values of these lattice separations and corresponding lattice energies at $P=0$ have been reported in Table II and compared with their available experimental data.[11,18]

We have plotted the Gibbs-free-energy differences, ΔG [$=G_{B1}(r')-G_{B3}(r)$], against the pressure (P) in Fig. 1. The pressure at which ΔG approaches zero is the phase-transition pressure (P_t) as marked by arrows. The values of these transition pressures are collected in Table I along with their measured[1-10] and other theoretical[13] results. Besides, we have plotted the variation of transition pressures with composition (x) in Fig. 2 and compared with the available experimental data.[1]

The calculated values of relative volumes $V(P)/V(0)$ have been depicted in Fig. 3 against pressure (P) to ob-

TABLE I. Input data and model parameters for $\text{Cu}_x\text{Ag}_{1-x}\text{I}$ mixed crystals.

	Input data[a]			Model parameters		
Crystals	r (Å)	B_T (10^{12} dyn cm^{-2})	C_{44} (10^{12} dyn cm^{-2})	b (10^{-12} erg)	f_0	ρ (Å)
AgI	2.803[b]	0.24[b]	0.817[b]	0.134	−1165.76	0.283
$\text{Cu}_{0.2}\text{Ag}_{0.8}\text{I}$	2.766	0.263	0.690	0.189	−1062.93	0.289
$\text{Cu}_{0.4}\text{Ag}_{0.6}\text{I}$	2.731	0.286	0.563	0.248	−885.58	0.295
$\text{Cu}_{0.5}\text{Ag}_{0.5}\text{I}$	2.712	0.298	0.500	0.301	−797.62	0.298
$\text{Cu}_{0.6}\text{Ag}_{0.4}\text{I}$	2.693	0.309	0.436	0.379	−654.89	0.309
$\text{Cu}_{0.8}\text{Ag}_{0.2}\text{I}$	2.657	0.332	0.309	0.463	−396.95	0.332
CuI	2.620[b]	0.355[b]	0.182[b]	0.539	−146.64	0.355

[a] The values for mixed crystal counterparts of $\text{Cu}_x\text{Ag}_{1-x}\text{I}$ have been obtained by applying Vegard's law to the two end crystals.
[b] Reference 11.

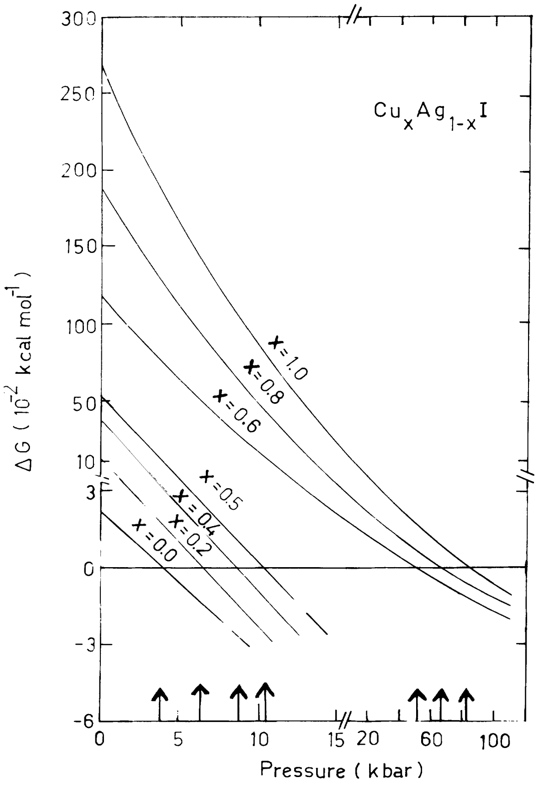

FIG. 1. The variation of Gibbs-free-energy differences (ΔG in kcal mol^{-1}) for $Cu_xAg_{1-x}I$ mixed crystals.

tain the equation of state and the volume collapses $\Delta V(P_t)/V(0)$ associated with these transitions. The values of $\Delta V(P_t)/V(0)$ and $V(P_t)/V(0)$ at P_t have also been reported in Table III and compared with the measured data available only for pure AgI and CuI crystals.[5,11,15] A discussion on these results has been conducted below.

III. DISCUSSION AND CONCLUSION

It is seen from Table I that the values of the TBI parameter (f_0) are negative in all the cases and hence the present model is capable of explaining the proper sign of the observed Cauchy discrepancy ($C_{12}-C_{44}$), which is positive in the system under consideration.

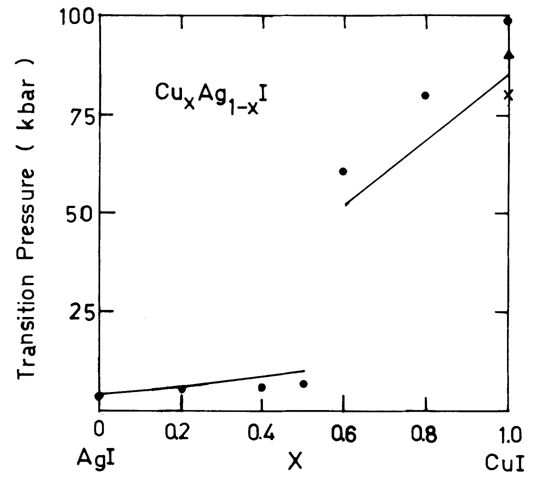

FIG. 2. Variation of transition pressures (P_t in kbar) with composition (x) for $Cu_xAg_{1-x}I$ mixed crystals. (●) Experimental points from Ref. 1, × from Ref. 11, ▲ Experimental from Ref. 10, and —— present.

Also, it is clear from Table II that the present TBP model correctly predicts the relative stability of both the competitive phases, as the values of ΔG at $P=0$ are positive, which is the required criterion.[19] This prediction from TBP model has the same success as has been found in the cases of perfect crystals, i.e., Cu and Ag halides.[11] The values of the equilibrium separations (r) obtained from the minimization technique are closer to their experimental data[11] available for the parent and dopant materials. Here, it may be mentioned that although there is a substantial disagreement between the observed and our calculated values of G for AgI and presumably AgI-rich solutions, as is seen from Table II, but the Gibbs-free-energy differences (ΔG) are derived accurately as is obvious from the following discussions.

In Fig. 1, we have depicted the pressure variations of ΔG for $Cu_xAg_{1-x}I$ at different concentrations to obtain the phase-transition pressures (P_t). The values of P_t obtained from these variations have been compared with the measured[1-10,15] and other theoretical[13] values in Table III. It is seen from this table that our values of P_t

TABLE II. The values of equilibrium lattice separations, cohesive energies and their differences for $Cu_xAg_{1-x}I$ mixed crystals at $P=0$. The values within the parentheses are experimental values taken from Refs. 11 and 18.

Crystals	r (Å)	r' (Å)	G (kcal mol^{-1})	ΔG (kcal mol^{-1})
AgI	2.800	2.962	−219.68	0.025
	(2.803)		(−208.10)	
$Cu_{0.2}Ag_{0.8}I$	2.766	2.922	−219.99	0.121
$Cu_{0.4}Ag_{0.6}I$	2.730	2.884	−220.74	0.387
$Cu_{0.5}Ag_{0.5}I$	2.712	2.863	−221.83	0.548
$Cu_{0.6}Ag_{0.4}I$	2.690	2.841	−222.79	1.181
$Cu_{0.8}Ag_{0.2}I$	2.657	2.800	−223.46	1.866
CuI	2.620	2.768	−224.19	2.687
	(2.620)		(−225.80)	

TABLE III. The values of phase-transition pressures (P_t), percent of volume collapses [$\Delta V(P_t)/V(0)$], and relative volumes [$V(P_t)/V(0)$] at P_t for $Cu_xAg_{1-x}I$ mixed crystals. The values within parentheses are experimental.

Crystals	P_t (kbar) Present	P_t (kbar) Others[a]	$\Delta V(P_t)/V(0)$ (%)	$V(P_t)/V(0)$
AgI	4.14 (4.0, 3.15)[b,c]	10.2	18.58 (16.23)[c]	0.98 (0.99)[c]
$Cu_{0.2}Ag_{0.8}I$	6.26 (5.8)[b]		18.66	0.97
$Cu_{0.4}Ag_{0.6}I$	8.93 (6.4)[b]		18.75	0.95
$Cu_{0.5}Ag_{0.5}I$	10.26 (6.75)[b]		18.79	0.92
$Cu_{0.6}Ag_{0.4}I$	52.72 (61.00)[d]		18.83	0.90
$Cu_{0.8}Ag_{0.2}I$	68.89 (78.00)[d]		18.92	0.87
CuI	85.10 (75–150)[b,e,f]	25.10	19.00 (15.00)[f], (19±)[g]	0.84

[a] Reference 13.

[b] Reference 1.

[c] Reference 5.

[d] Interpolated from the values of the two end crystals.

[e] Reference 2.

[f] Reference 15.

[g] Reference 12.

(=4.14, 6.26, 8.93, 10.26, and 85.10 kbar) for AgI, $Cu_{0.2}Ag_{0.8}I$, $Cu_{0.4}Ag_{0.6}I$, $Cu_{0.5}Ag_{0.5}I$, and CuI are in good agreement with their corresponding experimental[1] values (4.0, 5.8, 6.4, 6.75, and 75.0–150.0 kbar). Their values for other mixed-crystal counterparts of AgI and CuI could not be compared due to the lack of the measured data.

It is obvious from Fig. 2 that the composition (x) dependence of the transition pressures obtained by us are in closer agreement with their experimental values available only up to $x \leq 0.5$. The values of P_t at higher compositions ($x > 0.5$) have been compared with those obtained from the linear interpolation between the transition pressures of the two end crystals AgI and CuI. The transition pressure increases slowly up to $x \leq 0.5$, while it increases rapidly at $1.0 \leq x > 0.5$. At $x > 0.5$, the rapid increase of P_t seems to be due to the more stable ZB phase of CuI as this material has higher transition pressures as compared to that of AgI and remain in the parent phase within the pressure range (0–12 kbar) at which the crystal with $x \leq 0.5$ transform to a new RS phase. The slow increase of P_t at $x \leq 0.5$ shows that the ZB phase of AgI is more dominant over the ZB phase of CuI, which transforms to a denser phase, i.e., sixfold-coordinated RS structure at lower pressures (~4.0 kbar) as compared to that of CuI (75–150 kbar).

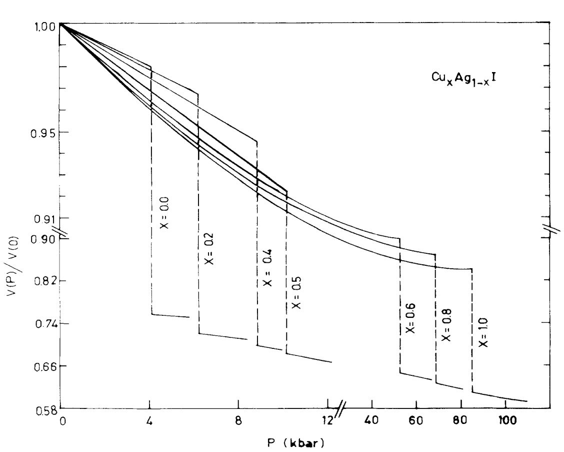

FIG. 3. The variation of $V(P)/V(0)$ with pressure (P in kbar) for $Cu_xAg_{1-x}I$ mixed crystals.

It is also clear from Fig. 2 that the P_t values up to $x \leq 0.5$ are closer to that of AgI. This feature reflects that there might be a ploytype structure of $Cu_xAg_{1-x}I$ mixed crystals up to these concentrations and it is in keeping with the remark of Livescu and Brafman.[1]

The volume collapses $\Delta V(P_t)/V(0)$ obtained from Fig. 3 and reported in Table III show that our values are in closer agreement with their measured data available only for the host and dopant crystals. These values for their mixed crystals ($Cu_xAg_{1-x}I$) are of only academic interest, at present, but they lie within the Phillips criteria[12] (i.e., 19±2 %) laid down for the covalent to ionic transitions. It is also seen from Table III that the values of the relative volumes $V(P_t)/V(0)$ are in reasonably good agreement with their experimental data[5] available only for AgI. Their values for the rest of the crystals under consideration will be deferred until the report of their measured data values.

Finally, it may be concluded that $Cu_xAg_{1-x}I$ mixed crystals (with $x \leq 0.5$) transform from ZB to RS phase at pressures up to 11.00 kbar, which is lower than that of the crystals with $x > 0.5$. This might be so mainly because at $x > 0.5$, the ZB phase of CuI seems to be more stable. At $x \leq 0.5$, the TBP model has predicted the presence of a polytypic structure of $Cu_xAg_{1-x}I$. The present TBP model has thus been found to explain the phase-transition properties of mixed $Cu_xAg_{1-x}I$ crystals with success as it has done in the cases of pure crystals.[11,16,17]

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