

9`YVWfcb]Wghfi Wfi fY`UbX`ghUV]`]micZ= J `gYa]Wt`bXi Wtcf`UbX`h\Y]f`U`cmg. `H\Y`fc`Y`cZ
a YhU`X`VUbXg

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5fhjWYg`mci `a UmVY`]bhYfYghYX`]b

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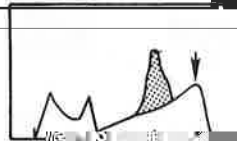


FIG. 1. Observed photoemission spectra (Refs. 1-3) of cation d states (shaded regions) in the II-VI compounds. The arrow at $E = 0$ points to the valence-band maximum.

It has been traditionally accepted in various theoretical approaches to II-VI semiconductors (e.g., tight binding, pseudopotentials) to neglect the effects of the cation d bands, hoping that in some sense they are "deep," "localized," and hence, unresponsive to many perturbations of

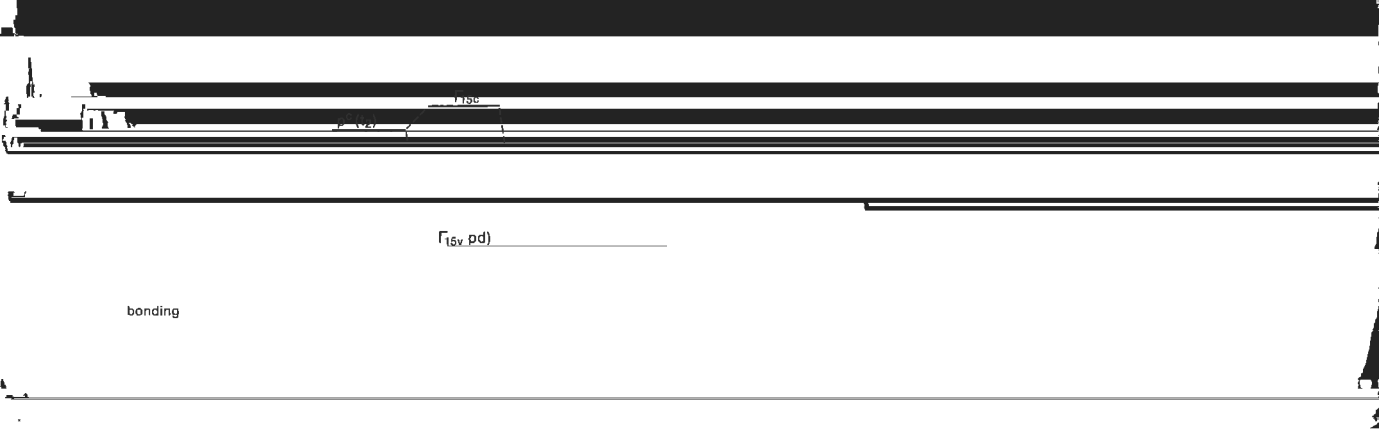
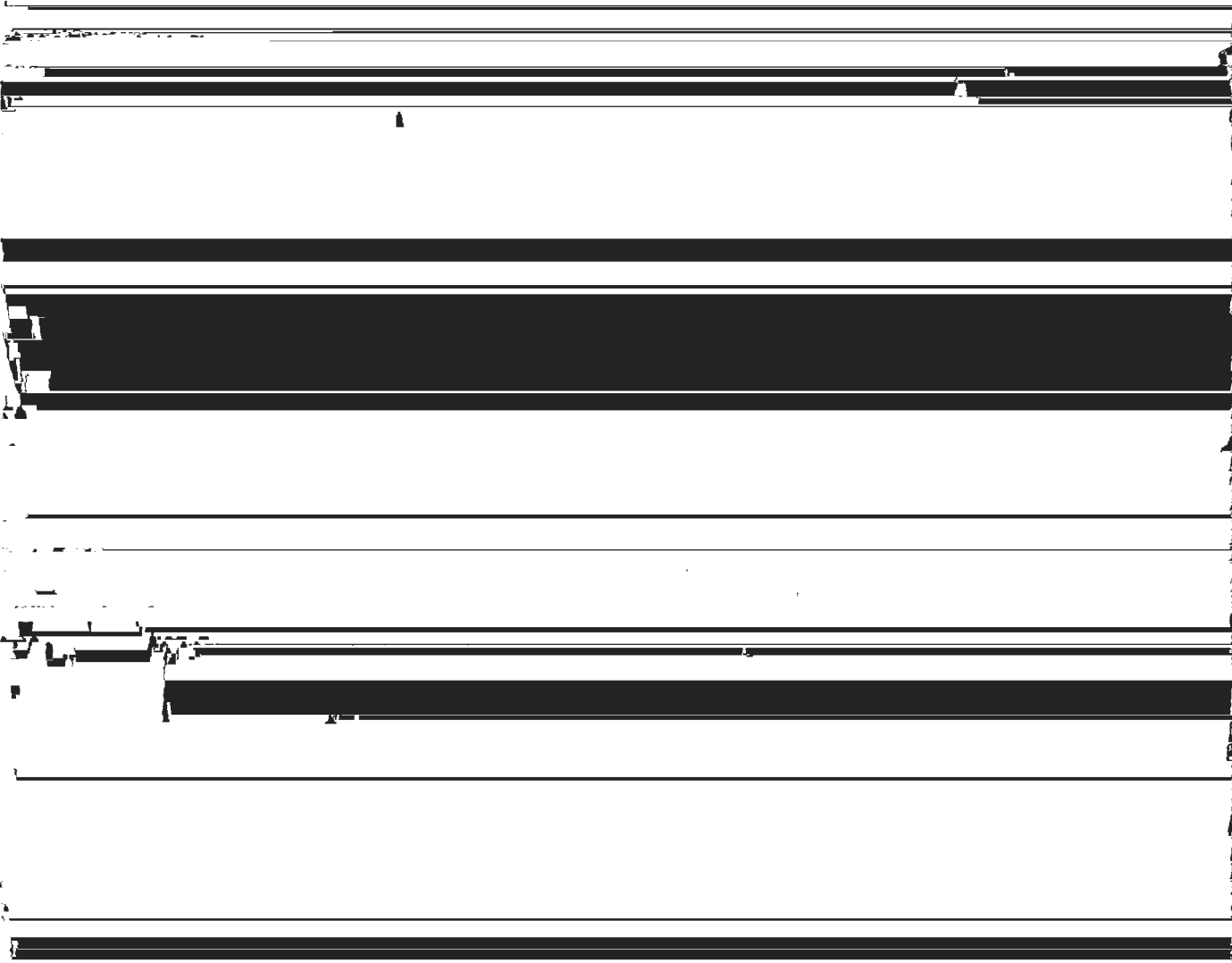


FIG. 3. Schematic plot of pp and pd coupling in zinc-blende semiconductor: (a) pp coupling only and (b) inclusion of pp and pd coupling



(iv) Whereas classical point-ion crystal-field models³³ predict for T_d symmetry that the e level is below the t_2 level,

formalism itself is not free of error; for example, we find $\epsilon_{\text{calc}} = 49$ and the numerical integrals involved in obtaining

TABLE II. Comparison of calculated ground-state properties of II-VI compounds (lattice parameter a , cohesive energy E_c and bulk modulus B) using the

FIG. 5. Wave-function amplitude for d band states in HgTe: (a) Γ_{15d} and (b) Γ_{12d} . Note the bonding buildup of charge along the bond in (a) and the nonbonding character in (b). **HgTe**

orbitals are effectively removed from the basis set. This was done by setting the LAPW energy parameters³⁶ $E_{l=2}^{\text{Cd}}$ and $E_{l=2}^{\text{Hg}}$ for the d -wave basis functions inside the Cd and Hg

To directly isolate the effect of p - d repulsion

ture calculations for CdTe and HgTe where the cation d

If p - d mixing is allowed, the spin-orbit splitting can be described³⁹ as a linear combination of the splittings for pure p and pure d orbitals Δ_p and Δ_d , weighed by the fraction Q_d

of Δ_0 for HgTe is complicated by the inverted band structure of this compound [see Fig. 2(c), showing Γ_{1c} below Γ_{15v}]. Unfortunately, only *indirect* measurements⁶¹⁻⁶⁸ have been

TABLE IV. Calculated spin-orbit splittings at Γ (denoted Δ_0) and L (denoted Δ_1)

where α and β are the geometrical coefficient depends on the charge distribution of the state. In CuCl, having a very strong p - d mixing, Δ_0 is *negative*.³⁵

We have calculated the spin-orbit splitting Δ_0 at Γ_{15v} and Δ_1 at L_{3v} directly from the band structure through a second variation procedure.^{39(b)} The results [Δ_0 (band calculation) and Δ_1 (band calculation)] are given in Table IV. In addition, we have calculated Δ_0 and Δ_1 from Eq. (4). We find that if we consider Δ_p as the SO splitting of the Γ_{15v} states with no pd hybridization and Δ_d as the SO splitting of the

uncertainties exist. First, in calculating Δ_0 from the band structure we assumed that the $j = l + 1/2$ and $j = l - 1/2$ radial orbitals can be averaged.³⁹ This approximation could introduce an error of ≤ 0.2 eV for the Hg $6p_{1/2}$ state, hence the spin-orbit splitting of the Hg $6p$ level is underestimated by this amount. Since the Γ_{15v} valence-band maximum of HgTe includes but 6% Hg $6p$ character, the value of Δ_0 is underestimated by ≤ 0.02 eV. This correction can be added to our directly calculated value of Table IV. The second potential source of error in the theory may arise from the fact that the calculated d band energies (Table III) are less bound than photoemission studies indicate (Table I); hence,

noted Δ_1), in eV. Q_d denotes the fraction of d character in the respective wave functions. Δ (band calc.) is the value obtained from direct band-structure results, using the approach of Ref. 39. Δ [Eq. (5)] corresponds to the simple approximation of Eq. (5) where the SO splitting is expressed as a combination of the p -orbital contributions Δ_p and the d -orbital contributions Δ_d . Here Δ is obtained from band calculations at Γ where $\alpha = 1$

in contrast with the currently accepted experimental results

8(a)] and *depleted* from the Cd-Te bond [negative dashed areas in Fig. 8(b)]. However, the "overloading" of the Hg

The difference between our predictions of E_g (7) and the

Table 1 (1) and (2) of CdTe, HgTe, and Hg_{1-x}Cd_xTe

currently accepted experimental values showing $\Delta_0(\text{CdTe}) < \Delta_0(\text{HgTe})$ has an important implication: cur-

is but an artifact of the omission of the contributions of the cation *d* bands to the charge densities, as evidenced by Figs.

TABLE V. Calculated and observed valence-band offsets (in eV) for II-VI semiconductor pairs. The right-hand compound in each pair has the higher VBM. Comparison is given with the tight-binding (TB) and Tersoff's results.

	CdTe/ZnTe	CdTe/HgTe	ZnTe/HgTe	MnTe/CdTe
ΔE_{VBM} (with d) ^a	0.13 + 0.02	0.37 + 0.03	0.26 + 0.04	0.25 + 0.10 ^b
Expt.	0.10 + 0.06 ^c	0.35 + 0.06 ^d 0.36 + 0.05 ^e	0.25 + 0.05 ^e	< 0.1 ^e
ΔE_{VBM} (TB, no d) ^f	-0.07	0.00	0.07	0.04

^a Present study; spin-orbit splitting effects are included; see Ref. 70.

^b Averaged over spin-up and spin-down states.

^c Reference 73.

^d Reference 72.

^e Reference 74.

^f Reference 75 and Eq. (8).

cannot be neglected. If these orbitals are *below* the anion p states (e.g., Cu-3d, Zn-3d, Al-3d, Ga-3d, In-5s, Hg-5s) four common-anion semiconductors CdTe/HgTe,

$$\Delta E^{(n)}(V) = E [A_n B_{4-n} C_4; V] - (n/4)E [AC] - [(4-n)/4]E [BC]. \quad (11)$$

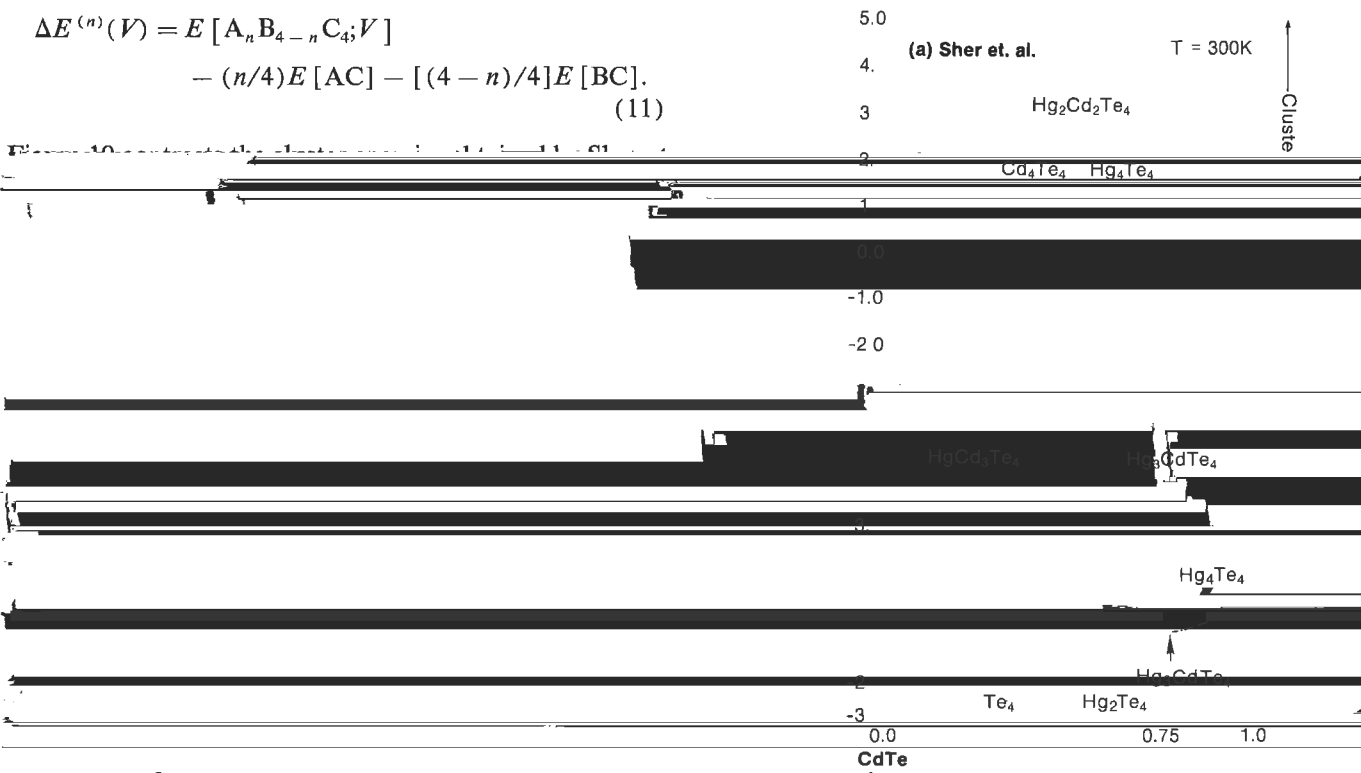


FIG. 11. Calculated excess cluster probabilities [Eq. (10)] for CdTe-HgTe alloys. The results of Sher *et al.* (Ref. 49) are shown in (a), whereas (b) gives the present first-principles results.

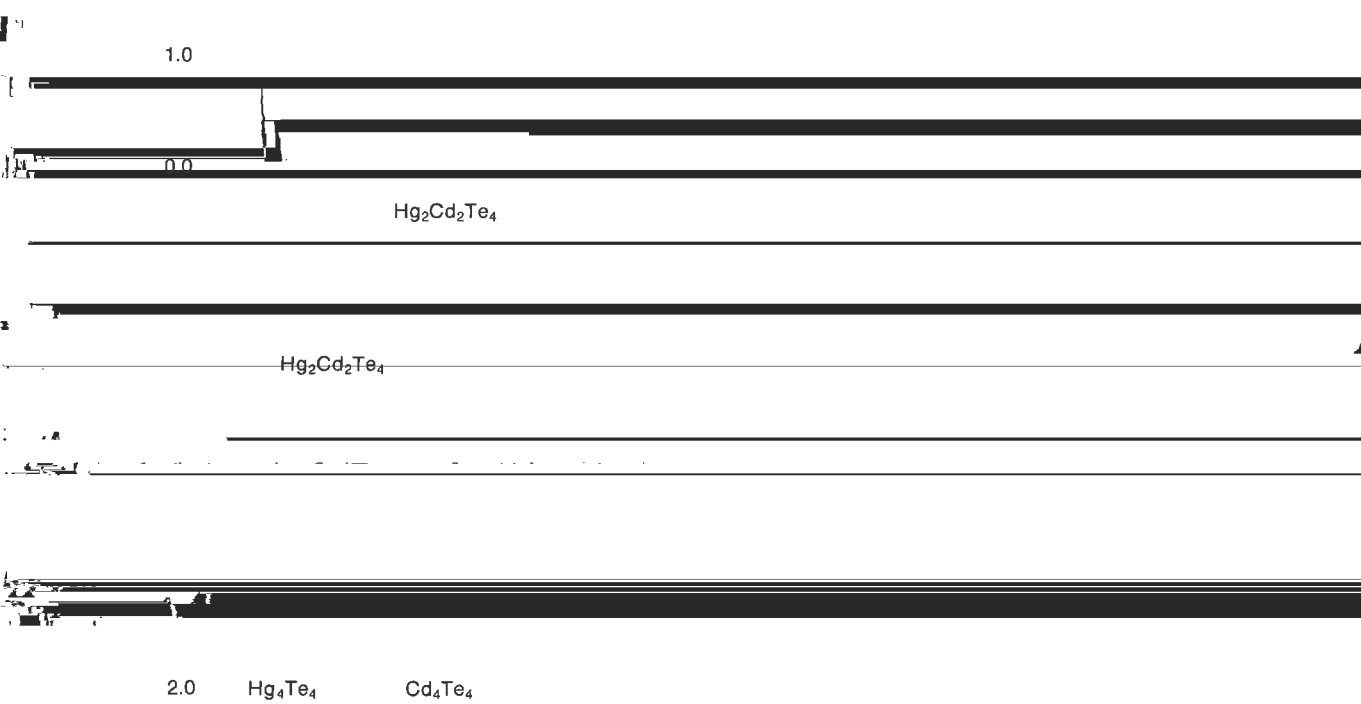


FIG. 10. Calculated excess cluster probabilities [Eq. (10)] for CdTe-HgTe alloys. Results of Sher *et al.* (Ref. 49) are shown in (a), whereas (b) shows the present first-principles results.

TABLE VI. Comparison between theory and experiment in the predicted trends in clustering [Eq. (10)]

Hg-rich $Hg_{1-x}Zn_xTe$		Hg-poor $Hg_{1-x}Zn_xTe$	
Cluster type		Sher <i>et al.</i> ^a	
Hg_4	Deficiency (-)		
Hg_3Zn	Excess (+)		
$HgZn_3$	Deficiency (-)	Excess (+)	
Zn_4		Deficiency (-)	
Cd-rich $Cd_{1-x}Zn_xTe$		Cd-poor $Cd_{1-x}Zn_xTe$	
	Exptl. ($x < 0.12$)	Sher <i>et al.</i> ^a	Exptl. ($x = 0.9$)
Cd	Deficiency (-)		
Cd_3Zn	Excess (+)		
$CdZn_3$	Deficiency (-)	Excess (+)	Deficiency (-)
Zn_4		Deficiency (-)	Excess (+)
Hg-rich $Hg_{1-x}Cd_xTe$		Hg-poor $Hg_{1-x}Cd_xTe$	
Cluster type	Sher <i>et al.</i> ^d Wei and Zunger	Wei and Zunger	Exptl. ^d ($x = 0.75$)

^a Results for clustering in $Hg_{1-x}Zn_xTe$ were presented by Sher *et al.* in Ref. 49, Fig. 5. Note that the labels for Hg_4 and Zn_4 were interchanged erroneously in this figure. The same error occurred in Fig. 5 of Sher *et al.* (Ref. 76).
^b Results for clustering in $Cd_{1-x}Zn_xTe$ were presented by Sher *et al.*, Ref. 76, Fig. 4. Note that the labels for Cd_4 and Zn_4 were erroneously interchanged in this figure.
^c Beshah *et al.*, Ref. 77.
^d Results for clustering in $Hg_{1-x}Cd_xTe$ were presented by Sher *et al.*, Ref. 49, Fig. 6. Note that the labels Hg_4 and Cd_4 were erroneously interchanged in that figure.
^e Zax *et al.*, Ref. 78.

Ordered compound	$a_{\text{eq}}^{(n)}$ (Å)	$R(\text{Zd-Te})$ (Å)	$R(\text{Cd-Te})$ (Å)	$R(\text{Hg-Te})$ (Å)	μ	$B^{(n)}$ (GPa)	$\Delta H^{(n)}$ (kcal/4-atom mole)
ZnTe	6.052				0.25		0
CdTe	6.470		2.802		0.25		0
HgTe	6.492				0.25		0
Cd ₃ ZnTe ₄	6.368	2.643	2.797		0.2397	47.3	0.76
CdZnTe ₂	6.263	2.638	2.790		0.2290	44.0	1.25
CdZn ₃ Te ₄	6.158	2.650	2.785		0.2609	50.2	1.08
Hg ₃ ZnTe ₄	6.383	2.645		2.806	0.2393	48.6	0.62
HgZnTe ₂	6.269	2.637		2.797	0.2279	45.2	0.98
HgZn ₃ Te ₄	6.163	2.632		2.787	0.2611	49.4	0.84
Cd ₃ HgTe ₄	6.476		2.802	2.810		44.8	0.24
CdHgTe ₂	6.481		2.801	2.812		44.2	0.28
CdHg ₃ Te ₄	6.485		2.804	2.810		46.2	0.17
		2.621				52.1	
						44.0	
			2.811			46.1	
						0.2485	
						0.2496	

Our results for HgCdTe₂ disagree with the results of Sher *et al.*⁴⁹ and Hass and Vanderbilt²⁰ who found that if the (destabilizing) *d* band is ignored, $\Delta H[\text{CdHgTe}_2] < 0$.

mismatch $R_{\text{BC}}[A\text{C:B}] - R_{\text{AC}}[B\text{C:A}]$ in the dilute alloy (or impurity) limit with respect to the size mismatch in the pure compounds, R_{BC}^0 and R_{AC}^0 :

TABLE VIII. Band gaps of binary and ternary II-VI compounds.

	E_g (LDA) (eV)	E_g (exptl.) 0 K (eV)	error (eV)	LDA corrected (eV)	b (exptl. at $x = 0.5$)	
ZnTe	1.02	2.39 ^a	1.37	2.39
CdTe	0.47	1.61 ^a	1.14	1.61
HgTe	-0.99	-0.30 ^a	0.69	-0.30
CdHgTe ₂	-0.27	0.60 ^b	(0.91)	0.64	0.23 ^b , 0 ^a	0.05
HgZnTe ₂	-0.09	1.01 ^c	(1.03)	0.94	0.14 ^c	0.41
CdZnTe	0.64	1.94 ^d	(1.35)	1.90	0.26 ^d	0.44

^a Reference 35.

^b Alloy data at $x = 0.5$, recommended $T = 0$ K values by Brice, from data compiled in Ref. 86.

^c Alloy data at $x = 0.5$, Ref. 87.

^d Reference 88.

LDA

b_{ord}
(calc. at
 $x = 0.5$)

0 K), and applying to our calculated LDA gaps of ABC₂ the

We further predict that $p-d$ repulsion will lead to a near

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