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EDITORS:

Satyen K. Deb

Solar Energy Research Institute, Golden, Colorado, U.S.A.

Alex Zunger

Solar Energy Research Institute, Golden, Colorado, U.S.A.

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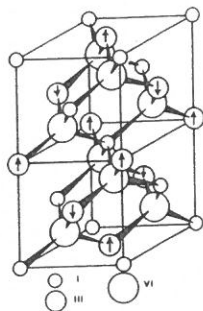
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PHASE STABILITY AND BAND STRUCTURE OF THE SEMIMAGNETIC
Cd_{1-x}Mn_xTe SEMICONDUCTOR ALLOY

Su-Huai Wei and Alex Zunger
Solar Energy Research Institute, Golden, Colorado 80401

ABSTRACT

Spin-polarized, self-consistent local spin density total energy and band structure calculations have been performed for Cd_{1-x}Mn_xTe alloy and its binary constituents in various phases. We discuss the phase stability and unusual electronic structure of this semimagnetic semiconductor.

INTRODUCTION

Manganese doped II-VI compounds have recently attracted considerable attention[1] as they exhibit the interesting combinations of magnetism and semiconductivity. Cd_{1-x}Mn_xTe is probably the most extensively studied member in this group. It crystallizes in a single-phase zincblende (ZB) structure up to a composition[2] of x=0.7. In this alloy the cadmium atoms, located on a face-centered cubic sublattice, are substituted by manganese atoms. We drew attention[3] to two interesting anomalies in Cd_{1-x}Mn_xTe. First, whereas most conventional octet isovalent semiconductor alloys retain in solution the underlying crystal structure of their end-point constituents, Cd_{1-x}Mn_xTe exhibit over a wide composition range the zincblende crystal structure of CdTe, rather than that of MnTe (the hexagonal NiAs-type structure)[2]. Second, whereas the band gap of conventional octet isovalent alloys is equal to or smaller than the concentration weighted average $\bar{E}(x) = (1-x)E_{AC} + xE_{BC}$ of the band gaps E_{AC} and E_{BC} of its end-point components, the band gap of Cd_{1-x}Mn_xTe (1.6-2.2 eV) is larger than both that of CdTe (1.6 eV at low temperature) or MnTe (1.3 eV). In this paper we explore the nature of these two anomalies, using a total energy and band structure approach. The self-consistent, first principle, spin-polarized, general potential linearized augmented plane wave (FLAPW) method[4] within the local spin density functional formalism[5] is used.

TOTAL ENERGIES AND STRUCTURAL STABILITY

We have modeled the ferromagnetic 50%-50% Cd_{1-x}Mn_xTe alloy by an ordered structure (space group D_{2d}^7) whose cation sublattice corresponds to the CuAu-I phase (space group D_{4h}^1). In addition to its cubic lattice constant a, the tetragonal structure has an internal structural degree of freedom $u = 1/4 + (R_{AC}^2 - R_{BC}^2)/\eta^2 a^2$ (with $\eta = c/a$) which measures the possible mismatch in the two bond lengths R_{AC} and R_{BC} in the unit cell.[3]

Table I compares the calculated equilibrium ground state properties with the experimental data.[6] The calculated results for the hypothetical MnTe in zincblende structure with ferromagnetic (F) and antiferromagnetic (AF) ordering and nonmagnetic CdTe are also listed in Table I.

A number of conclusions are apparent from these results: (i) the AF phase of cubic MnTe is stabler than the F phase by the spin-polarization-induced ferromagnetic-antiferromagnetic stabilization energy $\Delta E_{MnTe}^{F,AF} = -0.19$ eV/atom-pair. The two phases have similar bond lengths $-R(MnTe) = 2.70 \pm 0.02$ Å---very close to the value of 2.73 Å extrapolated from the experimental data for the "limiting phase".[6] (ii) We find that the

the chalcopyrite and cubic these atoms are distributed at room temperature the Mn shows otherwise, the Mn atoms will still be in the lattice of the cation sites, so ordered. To consider what the order at the chalcopyrite materials, or T_d) tend to indicate that Mn sites. Since no extra ordering lines is that the Mn occupy only the entering the other sublattice. For the sublattice would then be 2z temperature. The question of behaviour is involved here as can cation sites, the usual face a spin-glass results. However Mn atoms enter, say, the III and hence an antiferromagnetic the comments above. For the T_d would indicate a different ordering lines observed in the on along a preferred [111] axis alloys resulting in hexagonal the present cubic alloys could for the T_0 values observed. No been completed at present but 1.

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Table I. Calculated ground state properties of F-MnTe, F-CdMnTe₂, CdTe and AF-MnTe compared with the experimental data. The calculated cohesive energy for AF-MnTe in the NiAs structure at a=4.143 Å, c=6.705 Å is 7.77 eV.

Property	F-MnTe		F-CdMnTe ₂ (D _{2d} ⁵)		CdTe (ZB)		AF-MnTe (ZB)	
	Calc.	Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.	Exptl.
a _{eq} (Å)	6.26	6.33 ^a	6.37	6.39 ^b	6.46	6.48 ^c	6.23	6.33 ^a
u _{eq}	-	-	0.243	0.242 ^b	-	-	-	-
E _c (eV)/cell	7.37	-	12.03	-	4.61	4.12 ^d	7.56	-
R(Mn-Te)(Å)	2.71	2.73 ^a	2.73	2.75 ^b	-	-	2.70	2.73 ^a
R(Cd-Te)(Å)	-	-	2.79	2.80 ^b	2.80	2.80 ^c	-	-

(a) Extrapolated from the alloy data to x=1, see Ref. 6. T=300K.

(b) Alloy data at x=1/2, see Ref. 6. T=300 K; (c) Ref. 12; (d) Ref. 13.

observed NiAs structure of MnTe is stabler by the hexagonal-cubic stabilization energy $\Delta E_{\text{MnTe}}^{\text{ZB}} = -0.40 \pm 0.1$ and -0.21 ± 0.1 eV/atom-pair relative to the zincblende F and AF forms, respectively. Hence, we will not expect to find the isolated ZB phase under conditions where equilibration to the NiAs form is not hindered by kinetic activation barriers. (iii) Fitting the total energy $E[\text{CdMnTe}_2, a, u, \eta=1]$ as a quadratic function of u and a , we find at equilibrium $a_{\text{eq}} = 6.370$ Å and $u_{\text{eq}} = 0.242$. These values correspond to $R(\text{Mn-Te}) = 2.73$ Å and $R(\text{Cd-Te}) = 2.79$ Å, which are within 1% of the values observed for the 50%-50% alloy in extended x-ray absorption fine structure (EXAFS) measurements.[6] The non-ideal anion displacement ($u \neq 1/4$) in the F-CdMnTe₂ structure (i.e., the Te anion moves away from the center of its tetrahedron toward the pair of Mn atoms and away from the pair of Cd atoms) leads to the formation of Mn-Te and Cd-Te bond lengths similar to those found in the respective binary systems [$R^\circ(\text{Mn-Te}) = 2.71$ Å and $R^\circ(\text{Cd-Te}) = 2.80$ Å, calculated for pure F-MnTe and CdTe, respectively (Table I)], but are considerably different from what a virtual crystal approximation (VCA) would have predicted, [i.e., $u=1/4$ and $R(\text{VCA})(\text{Mn-Te}) = R(\text{VCA})(\text{Cd-Te}) = 2.758$ Å]. The fact that our calculated equilibrium bond lengths are close to those of the pure end-point compounds indicates that the system has used its internal degree of freedom u to achieve nearly ideal tetrahedral bond lengths (at the expense of somewhat distorting the bond angles), thereby lowering its strain energy. (iv) We evaluate the enthalpy of formation (per four atoms) $\Delta H^{\text{(F)}}$ for the ferromagnetic phases relative to the equilibrium ZB forms of CdTe and F-MnTe as

$$\Delta H^{\text{(F)}} = E[\text{F-CdMnTe}_2] - E[\text{CdTe}] - E[\text{F-MnTe}]. \quad (1)$$

For the AF phase we have the formation enthalpy

$$\Delta H^{\text{(AF)}} = E[\text{AF-CdMnTe}_2] - E[\text{CdTe}] - E[\text{AF-MnTe}]. \quad (2)$$

We find a negative value of $\Delta H^{\text{(F)}} = -0.05 \pm 0.01$ eV. Hence, the ordered CuAu-I phase of F-CdMnTe₂ is predicted to be stable against disproportionation into its ZB constituents. (v) In contrast, we find that because of the large AF stabilization of MnTe relative to the F phase ($\Delta E_{\text{MnTe}}^{\text{F,AF}} = -0.19$ eV/pair), $\Delta H^{\text{(AF)}}$ is positive (at least +0.04 eV/pair). This is so because the AF stabilization of the mixed CdMnTe₂ compound ($\Delta E_{\text{CdMnTe}_2}^{\text{F,AF}}$) is smaller than the AF stabilization in pure MnTe due to the

F-MnTe, F-CdMnTe₂, CdTe and calculated cohesive energy = 6.705 eV is 7.77 eV.

CdTe		AF-MnTe	
(ZB)		(ZB)	
Calc.	Exptl.	Calc.	Exptl.
6.46	6.48 ^c	6.23	6.33 ^a
-	-	-	-
4.61	4.12 ^d	7.56	-
-	-	2.70	2.73 ^a
2.80	2.80 ^c	-	-

Ref. 6. T=300K.
) Ref. 12; (d) Ref. 13.

by the hexagonal-cubic d -0.21 ± 0.1 eV/atom-pair tively. Hence, we will not ions where equilibration to on barriers. (iii) Fitting tic function of u and a, we 2. These values correspond hich are within 1% of the nded x-ray absorption fine -ideal anion displacement Te anion moves away from the atoms and away from the Cd-Te bond lengths similar ms [R^o(Mn-Te) = 2.71 Å and e and CdTe, respectively m what a virtual crystal , u=1/4 and R(VCA)(Mn-Te) = calculated equilibrium bond at compounds indicates that m u to achieve nearly ideal somewhat distorting the bond v) We evaluate the enthalpy magnetic phases relative to

$$E[\text{F-MnTe}] . \quad (1)$$

$$E[\text{AF-MnTe}] . \quad (2)$$

0.1 eV. Hence, the ordered be stable against dispro- In contrast, we find that Te relative to the F phase at least +0.04 eV/ pair). the mixed CdMnTe₂ compound on in pure MnTe due to the

more dilute magnetic interactions (i.e., fewer nearest neighbor Mn atoms and a larger Mn-Mn interatomic distance).

Figure 1 summarizes our calculated total energy differences (solid horizontal lines) relative to the pair [F-ZB-MnTe + CdTe] used as a reference energy. These calculated total energies suggest a number of observations on the relative stabilities of the various species. First, if complete thermodynamic equilibrium can exist in the alloy between all of its constituents, the system at T = 0 K will separate into hexagonal MnTe plus CdTe, which are the lowest energy species. Second, in actuality one might expect strong elastic activation barriers[7] (depicted schematically in Fig. 1 by the dotted lines) against disproportionation of an alloy with a lattice constant a(Cd_{1-x}Mn_xTe) to its constituents having radically different lattice constants (Table I). If one then considers such a "constrained equilibrium", then the only ordered phase possible at x=1/2 is F-CdMnTe₂, (since ΔH^F < 0, which makes its disproportionation into F-ZB-MnTe + CdTe unfavorable). This phase could spontaneously (activationlessly) become antiferromagnetic (since AF-CdMnTe₂ has a lower energy than F-CdMnTe₂); however, once formed, AF-CdMnTe₂ might disproportionate into its stabler constituents AF-MnTe + CdTe (since ΔH^{AF} > 0). This suggests that such Mn-rich alloys might in fact show clustering of AF-MnTe domains with strongly coupled Mn atoms. These have indeed reported[8]. Third, at finite temperatures the disordered alloy gains stability on account of its negative entropy term -TΔS; hence, above some critical temperature T_c it will be the stablest species. It is likely that conventional growth temperatures exceed T_c; hence, only a disordered, quenched-in phase is formed. At low temperatures and slow growth rates, the x=1/2 alloy might produce a crystallographically ordered CdMnTe₂ stable compound. Experiments in this direction are called for.

Our total energy calculation thus points to the existence of an alloy-stabilized ZB phase of MnTe, hitherto unknown to exist in its own phase diagram, with a bond length which is in excellent agreement with that inferred for the "limiting phase" from the data on Cd_{1-x}Mn_xTe. We now proceed to investigate the electronic structure of the Cd_{1-x}Mn_xTe system.

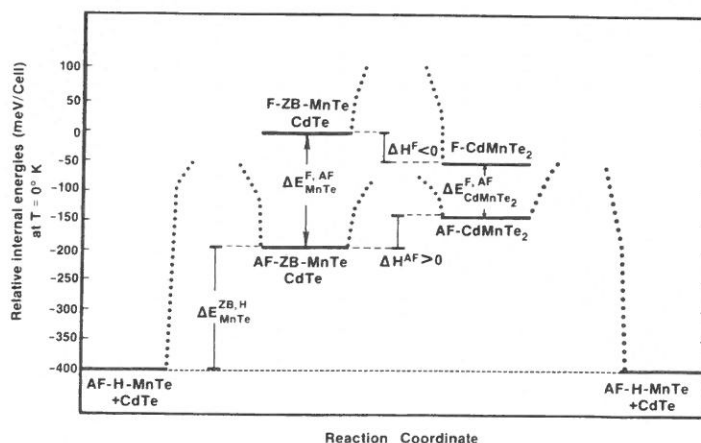


Fig. 1: Relative total energies (thick horizontal lines) of some possible structural and magnetic phases of the MnTe + CdTe system. Dotted lines indicate schematically possible activation barriers.

BAND STRUCTURE

The spin-polarized band structure of F-CdMnTe₂ at the lattice constant $a=6.255 \text{ \AA}$, and $u_{\text{eq}}=0.242$ is depicted in Fig. 2a, and b for spins up and down, respectively.

The lowest valence band in this system is constituted primarily from Te s orbitals, with a minor Cd d character. The next higher band is the Cd d band which peaks at $E_V^{\uparrow} - 9.2 \text{ eV}$ and $E_V^{\downarrow} - 7.5 \text{ eV}$ [where E_V^{\uparrow} and E_V^{\downarrow} denote the valence band maxima (VBM) for spin up and spin down, respectively]. We see that the upper valence band complex has a Mn d and Te p characteristic; those differs widely for spin up and spin down. Regarding its d components, we find that the spin-up Mn d band is occupied (Fig. 2a) and centered at $E_V^{\uparrow} - 3.7 \text{ eV}$, whereas the spin down d band is empty (Fig. 2b) and centered at $E_V^{\downarrow} + 2.9 \text{ eV}$. The $+4.9 \text{ eV}$ separation between them constitutes the effective d band exchange (x) splitting $\Delta_x(d)$. We find, however, that another important exchange splitting exists in the problem--the p-d exchange splitting $\Delta_x(pd) = E_V^{\downarrow} - E_V^{\uparrow}$ of the top of the valence bands for spin up (Fig. 2a) and spin down (Fig. 2b)--and that it is negative: the top of the valence band for spin-up (E_V^{\uparrow}) is 1.7 eV above the top of the valence band for spin down (E_V^{\downarrow}). This is at first surprising, given that we find the effective potential for the majority spin to be more attractive than that for the minority spin, as is usually the case in spin polarized systems. Figure 3 explains this phenomenon in terms of a simple p-d repulsion model. What is special about Mn and Te atoms is that the calculated atomic p⁺ and p⁻ orbital energies of the anion are bracketed by the atomic d⁺ and d⁻ levels of the cation. Indeed the atomic exchange splitting of Mn 3d is far larger (4.25 eV) than that of Te valence p orbitals (1.14 eV). We depict this situation in parts a and b of Fig. 3.

In the tetrahedral crystalline environment, the anion p states transform as the $t_2(\Gamma_{15})$ representation, whereas the cation d states are split into a doublet $e(\Gamma_{12})$ representation and a triplet $t_2(\Gamma_{15})$ representation. In substitutional T_d symmetry, the e states are lower in energy than the t_2 states.[9] This is depicted in part c of Fig. 3. Since the Mn 3d e states transform differently from the Te 5p states, there is no p-d hybridization in this (Γ_{12}) channel, and hence the e_+ and e_- states are essentially unperturbed in the solid (Fig. 3d). On the other hand, the interaction between the anion and cation spin-up states of the same t_2 symmetry produces a lower bonding (B_+) and a higher anti-bonding (AB_+) band. Similarly, the coupling

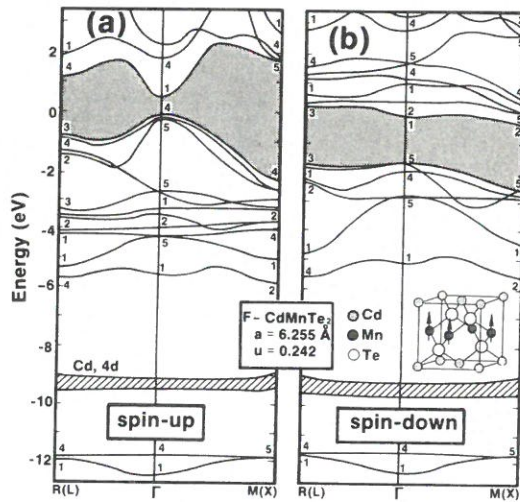


Fig. 2: Electronic band structure of F-CdMnTe₂ (a and b). The zero of the energy is at E_V^{\uparrow} . Symbols in parentheses are the points of fcc BZ. The band-gap regions are shaded.

Te_2 at the lattice constant a , and b for spins up and

constituted primarily from the next higher band is the $E_v^\uparrow - E_v^\downarrow = 7.5$ eV [where E_v^\uparrow and E_v^\downarrow are spin up and spin down, and the band complex has a Mn d and Te p spin up and spin down. The spin-up Mn d band is occupied and the spin-down d band is empty. The +4.9 eV separation between the e_+ and e_- states (splitting $\Delta_x(d)$). We find that the splitting exists in the $E_v^\uparrow - E_v^\downarrow$ of the top of the valence band (Fig. 2b)--and that it is $E_v^\uparrow - E_v^\downarrow = 1.7$ eV above the top of the valence band. This is at first surprising, since the majority spin to be more occupied is usually the case in spin splitting. The reason for this phenomenon in terms of a simple model involving Mn and Te atoms is that the Mn d and Te p orbitals on the anion are bracketed by the Mn d orbitals on the cation. Indeed the atomic exchange splitting is larger than that of Te valence p orbitals. This is shown in parts a and b of Fig. 3.

In the tetrahedral crystalline environment, the anion p states transform as the $t_2(\Gamma_{15})$ representation, whereas the cation d states are split into a doublet $e(\Gamma_{12})$ representation and a triplet $t_2(\Gamma_{15})$ representation. In substitutional T_d symmetry, the e states are lower in energy than the t_2 states.[9] This is depicted in part c of Fig. 3. Since the Mn 3d e states transform differently from the Te 5p states, there is no p-d hybridization in this (Γ_{12}) channel, and hence the e_+ and e_- states are essentially unperturbed in the solid (Fig. 3d). On the other hand, the interaction between the anion and cation spin-up states of the same t_2 symmetry produces a lower bonding (B_-) and a higher antibonding (AB_+) band. Similarly, the coupling

between the anion and cation spin-down states with the same t_2 symmetry produces a lower bonding (B_-) and a higher antibonding (AB_-) pair of bands (Fig. 3d). The order of these levels can be gathered from the atomic energy levels discussed above: since the unperturbed atomic d^+ is lower in energy than p^+ , but d^+ is above p^+ (Fig. 3c), simple perturbation theory leads to a situation in which B_- is below AB_+ ; hence, we have an effective negative p-d exchange splitting. This p-d coupling also suggests here a smaller spin-up band gap (calculated: 0.63 eV) than the spin-down band gap (1.64 eV), since AB_+ is repelled upward relative to B_- . Similar negative p-d exchange splitting is also observed in F-MnTe. We therefore predict that a spin-polarized photoemission experiment will show the emission of majority spin states (AB_+) at lower binding energies than that of the minority spin (B_-). Such experimental studies are called for.

Comparing the band eigenvalues of CdTe, F-MnTe, and F-CdMnTe₂, we find that introducing Mn into CdTe has little effect on states that are localized on the Te and Cd atoms (e.g., Te 5s, Cd 4d states). Furthermore, the energy levels of CdMnTe₂ can be predicted within a few tenths of an eV by averaging the corresponding energy levels of the end-point compounds CdTe and F-MnTe, implying a small optical bowing in CdMnTe₂. For instance, we find the calculated interband p-s transition [$(\Gamma_{4v}, \Gamma_{5v}) + \Gamma_{1c}$] to be at 1.43 eV[10]; this value is close to the average (1.48 eV) of our calculated p-s ($\Gamma_{15v} - \Gamma_{1c}$) transition energies of the end-point compounds; i.e., $E_{p-s}(\text{CdTe}) = 0.44$ eV and $E_{p-s}(\text{F-MnTe}) = 2.53$ eV[10], indicating a small optical bowing for Cd_{1-x}Mn_xTe if the correct MnTe phase is used (i.e., ZB, not NiAs).

Our calculation indicates that AF-ZB-MnTe is a semiconductor rather than a metal, because the intra-atomic exchange splitting for the Mn ion is large enough to keep the unoccupied spin states above the top of the Te p bands. The AF ordering increases the band gap. In contrast with the ferromagnetic

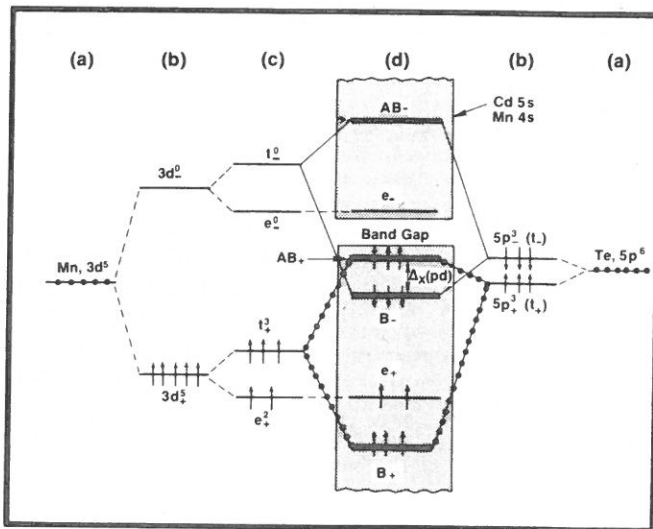


Fig. 3: A schematic diagram of the p-d repulsion effects for a ferromagnetic system with anion p states bracketed by the cation d states. (a) shows the atomic unpolarized levels, (b) shows the exchange-split atomic levels, (c) shows the crystal field split levels, and (d) shows the final interacting states. Shaded areas denote the host crystal bands.

case, there is no p-d exchange splitting in the AF spin arrangement. This is so because in the AF phase there is an equal number of Mn atoms with 3d levels below and above the Te p levels (compare, however, the ferromagnetic case in Fig. 3). Furthermore, since, in the AF ordering, states at the valence band edge are more bonded, the difference in spin symmetry between the F and AF phases also indicates the enhanced stability of the AF structure: the p-d repulsion in the F phase reduces the cohesion of the p bands.

We find the calculated localized Mn 3d⁺ states to be at about $E_V - 2.5$ eV for AF-MnTe. Taking into account the relaxation effects for localized states, we estimate that in the photoemission experiment the occupied Mn 3d⁺ states for $Cd_{1-x}Mn_xTe$ should have a binding energy of about $E_V^+ - 3.5$ eV. This value is in good agreement with recent data by Taniguchi et al.[11]

CONCLUSION

We have performed total energy and band structure calculations for the prototypical semimagnetic semiconductor $Cd_{1-x}Mn_xTe$. We find that the alloy environment stabilized a hitherto unknown ZB phase of MnTe and that the electronic structure of $Cd_{1-x}Mn_xTe$ is related to this ZB phase of MnTe, but not to the hexagonal phase. We find that the ZB phase of MnTe is metastable compared with its NiAs phase and predict that the ordered $CdMnTe_2$ can exist only in the ferromagnetic form. We find that in this ferromagnetic form the system has a negative p-d exchange splitting. The occupied Mn 3d states are predicted to be partially localized, located at $E_V - 2.5$ eV, and strongly hybridized with Te 5p states.

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