

Supporting Information

**The correlation of the liquidus curves and valence electron structures of ternary
lithium halide molten-salt electrolyte for liquid metal battery**

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Empirical electron theory of solids and molecules

EET, which is consisted by three basic hypotheses and a calculation method, is used for determining the valence electron structures of atom, and calculating the multiple physical properties based on the valence electron structural parameters.¹⁻³

Hypothesis 1

In solid and molecule, each atom is generally hybridized by two atomic states, which are so-called h and t respectively. For the two states, one of them is in the excited state or near to the ground state. The hybrid state is consisted by various electrons and single-bond radius $R(1)$, where the numbers of various electrons include the covalent electron number n_c , lattice electron number n_l , $3d$ magnetic electron m^{3d} , and dumb-pair electron n_{dp} .

Hypothesis 2

The hybrid states of atoms are discontinuous, which can be calculated by the weighted average of state proportions of h and t states with Eqs s1- s2:

$$C_t = 1 / (1 + K^2), C_h = 1 - C_t \quad \backslash * \text{MERGEFORMAT (s1)}$$

$$K = \frac{\tau' l' + m' + n'}{\tau l + m + n} \sqrt{\frac{l' + m' + n'}{l + m + n}} \frac{l \pm \sqrt{3m} \pm \sqrt{5n}}{l' + \sqrt{3m'} \pm \sqrt{5n'}} \backslash * \text{MERGEFORMAT}$$

(s2)

where C_h and C_t denote the state proportions of h and t state; the letters of (l, m, n) and (l', m', n') represent the numbers of valence electrons distributed on $s, p,$ and d orbits in the h and t states, respectively. The introduction of τ and τ' is to distinguish the lattice electron and

covalence electrons on s orbit in h and t states, and the electron is defined as the valence electron for the case of $\tau=1$ or $\tau'=1$, otherwise, it is the lattice electron for $\tau=0$ or $\tau'=0$.

When h -state electrons are all lattice electrons ($\tau=0$ or $\tau'=0$), the K formula is modified as Eq. s3:

$$K = \frac{l'+m'+n'}{l} \frac{l'+m'+n'}{\sqrt{l'+\sqrt{3m'} \pm \sqrt{5n'}}} \quad \backslash * \text{ MERGEFORMAT (s3)}$$

The hybrid states can be determined by the K formula as above, and various electrons and single-bond radius can be calculated by weighted average of state proportions of two states with Eqs s4-s7 :

$$n_{T\sigma} = n_{Th}C_{h\sigma} + n_{Tt}C_{t\sigma} = (l+m+n)C_{h\sigma} + (l'+m'+n')C_{t\sigma} \quad \backslash *$$

MERGEFORMAT (s4)

$$n_{l\sigma} = n_{lh}C_{h\sigma} + n_{lt}C_{t\sigma} = (l-\tau)C_{h\sigma} + (l'-\tau')C_{t\sigma} \quad \backslash * \text{ MERGEFORMAT}$$

(s5)

$$n_{c\sigma} = n_{ch}C_{h\sigma} + n_{ct}C_{t\sigma} = (\tau l + m + n)C_{h\sigma} + (\tau' l' + m' + n')C_{t\sigma} \quad \backslash *$$

MERGEFORMAT (s6)

$$R(1)_{\sigma} = R(1)_{h\sigma}C_{h\sigma} + R(1)_{t\sigma}C_{t\sigma} \quad \backslash * \text{ MERGEFORMAT (s7)}$$

where $C_{h\sigma}$ and $C_{t\sigma}$ represent the proportions of h and t states in the σ -th hybrid state, respectively. Therefore, all atomic hybrid states, which is called as hybrid table of element, are built according to the calculations of numbers of various electrons and single-bond radii.

The detail information is supplied in TableS1-S3.

Hypothesis 3

The covalent bond length between atoms u and v is calculated according to the number of covalent electron pair n_α and single-bond radius, as below:

$$D_{uv}(n_\alpha) = R_u(1) + R_v(1) - \beta \log n_\alpha \quad (\alpha = A, B, C, \dots, N) \setminus *$$

MERGEFORMAT (s8)

where $R_u(1)$ and $R_v(1)$ denote the radii of single-bond for u and v atoms, respectively. n_α denotes the number of covalence electron pair on the α -th bond. The parameter β can reflect the overlap-ability of the electron clouds between the u and v atoms, the value of β is initially defended to be 0.6 for metals and alloys, and 0.71 for the other nonmetal compounds according to Pauling's theory. However, in EET, the value of β is modified according to the maximum of n_α ($\alpha=A, B, C, \dots, N$), as below:

$$\beta = \begin{cases} 0.60 & -0.30 \leq n_\alpha \leq 0.70 \\ 0.71 & -n_\alpha \leq 0.25 \text{ or } n_\alpha \geq 0.25 \\ 0.71 - 2.2\varepsilon & -n_\alpha = 0.25 + \varepsilon \text{ or } n_\alpha = 0.75 - \varepsilon \end{cases} \setminus *$$

MERGEFORMAT (s9)

Equivalent electron

For the transition metals in B group and AIII group metals (Ga, In, and Tl), their d orbits with long-Cross form can be extended along the long line and touch with their spherical s orbits, and cause part overlap of two orbitals, it is so-called hybridization of d and s orbits, which can supply a tunnel for transporting electrons from d into s orbit, and the d electron also has the possibility to enter the p orbit by the hybridization of s and p orbits formed by partly overlap of spindle p and spherical s orbits. Thus, these d electrons, which have entered

into the s or p orbit by d - s or s - p hybridizations, are equivalent to the s or p electrons distributed in atomic out-shell. Therefore, these d electrons are called as equivalent s or p electron. For Cu, Ag, and Au, the orientation of the electrons in p orbit is so chaotically distributed in the different cells of the lattice space, which causes that their average effect is equivalent to that of the s -electrons. However, the phase angle distribution of these equivalent electrons and their contribution to the binding energy still retain their original properties.

Bond Length Difference Method

BLD method is used to solve n equations as listed in Eq. s10 for determining the valence electron structures, which include the atomic hybrid states and the numbers of various electrons. ¹⁻

³ For the 1st bond:

$$D_{uv}(n_A) = R_u(1) + R_v(1) - \beta \lg n_A \quad \backslash * \text{MERGEFORMAT (s10)}$$

For the i^{th} bond:

$$D_{uv}(n_i) = R_{ui}(1) + R_{vi}(1) - \beta \lg n_i \quad \backslash * \text{MERGEFORMAT (s11)}$$

Then have:

$$\Delta D_i = \Delta R_i - \beta \lg \gamma_i \quad \backslash * \text{MERGEFORMAT (s12)}$$

where, $\Delta D_i = D_{uv}(n_A) - D_{uv}(n_i)$; $\Delta R_i = R_u(1) + R_v(1) - R_{ui}(1) - R_{vi}(1)$; $\gamma_i = n_A / n_i$;

$$\gamma_i = 10^{(\Delta R_i - \Delta D_i) / \beta} \quad (i = A, B, \dots, N) \quad \backslash * \text{MERGEFORMAT (s13)}$$

The total covalent electrons can be estimated by the sum of all covalent electrons for all atoms in formula unit.

$$n_c = \sum_i^n n_{ci} \quad \backslash * \text{MERGEFORMAT (s14)}$$

On the other hand, the covalent electrons are also the sum of covalent electrons in all equivalent bonds, as listed in Eq. s15.

$$n_c = \sum_{\alpha=A}^N n_\alpha I_\alpha = n_A \sum_{\alpha=A}^N \gamma_\alpha I_\alpha \quad \backslash* \text{MERGEFORMAT (s15)}$$

Then have:

$$n_A = \sum_i^n n_{ci} / \sum_{\alpha=A}^N \gamma_\alpha I_\alpha, \quad n_\alpha = \gamma_\alpha n_A \quad \backslash* \text{MERGEFORMAT (s16)}$$

The theoretical bond length $\overline{D}_{uv}(n_\alpha)$ is estimated by putting Eq. s16 into L.Pauling's equations as below:

$$\overline{D}_{uv}(n_\alpha) = R_u(1) + R_v(1) - \beta \lg n_\alpha \quad (\alpha = A, B, \dots, N) \backslash*$$

MERGEFORMAT (s17)

The hybrid state with various electronic numbers can be determined by a criterion of $\Delta D \leq 0.05 \text{ \AA}$ under the first order approximation. In this case, the valence electron structures of each atom in a structural formula are determined, which can supply the various electron numbers for building the models of multiple physical properties such as melting point, cohesive energy, and magnetic moments *etc* for calculating the multiple physical properties.

Calculation model of Physical Properties

Calculation model of cohesive energy

The physical model of cohesive energy is built based on the parameters of valence electron structures, which consists of the bonding energy, electric potential, magnetic potential, and condensing energy, as below:⁴⁻⁶

$$E_c = \sum_{\alpha} \frac{b_{\alpha} I_{\alpha} n_{\alpha}}{D_{\alpha}} f_{\alpha} + \frac{b_1 \sum n_1}{D} f' + \sum_i b_i a m_i^{3d} - \sum_i b_i C_i W_i \backslash*$$

MERGEFORMAT (s18)

In the first term of Eq s18, the parameter b represents the shielding ability of the electrons to atomic nucleon, b_{α} is the geometrical mean of b for bonding atoms u and v . \overline{D}_{α} is the calculated bond length for the α th bond, f_{α} is bonding factor, which denotes the bonding ability between the two atoms. The parameter b_{α} and f_{α} can be obtained by Eqs s19-s20.

$$b_{\alpha} = \sqrt{b_u b_v}, b = 313.95 / (n - 0.36\delta) \text{ (kJ} \cdot \text{Å/mol)} \backslash *$$

MERGEFORMAT (s19)

$$f_{\alpha} = 0.5 * (f_u + f_v), f = \sqrt{n_s / n_T} + \sqrt{3n_p / n_T} + g * \sqrt{5n_d / n_T} \backslash *$$

MERGEFORMAT (s20)

where $n=1, 2, 3, 4, 5, 6, 7$ or 13 , $\delta=2, 1, 0$; n_T is the total number of covalence electrons and lattice electrons, n_s and n_p, n_d are the numbers of covalence electrons in $s, p,$ and d orbitals, respectively; g is defined as $1, 1.35,$ and 1.7 for elements in the 4th, 5th, and 6th periods, respectively.

For the second term, b_1 represents the weighted geometrical mean of b for u and v atoms as given in Eq s21.

$$b_1 = \sqrt[x+y]{b_A^x b_B^y} \quad \backslash * \text{ MERGEFORMAT (s21)}$$

where x and y are the number of A and B atoms in a formula. \bar{D} is averaged bond length by weight of bond numbers.

$$\bar{D} = \sum I_{\alpha} \bar{D}_{\alpha} / \sum I_{\alpha} \quad \backslash * \text{ MERGEFORMAT (s22)}$$

f' represents itinerant ability of the lattice electron in lattice space.

$$f' = \sqrt{2n_1 / n_T} \quad \backslash * \text{ MERGEFORMAT (s23)}$$

For the third term, m_i^{3d} represent $3d$ magnetic electrons of the i -th atom. The parameter of a is relative to the equivalent molecular field, it is defined as 0.1542 for $3d$ transition metals Fe, Co and Ni.

For the final term, the parameter $C=0.907P$ and the value of P is 6 for elements in VB, 5 for elements in VIIB, 4 for elements in VIIIB, 3 for Fe, 2 for Co, 1 for Ni, and 0 for elements in IB and IIB, respectively. The parameter W can be obtained by Eq s24.

$$W = (n_{dp} + m^{3d}) / Z \quad \backslash * \text{ MERGEFORMAT (s24)}$$

where n_{dp} and Z are the numbers of dumb-pair electron and all electrons distributed in the most out -shell of atom.

Calculation model of melting points

The model of melting point is built on an assumption of the strongest bond broken by heat vibration energy at the critical temperature (melting point). As long as the vibrating energy of thermal phonon is just equal to the bonding energy of the strongest bond, the strongest bond is broken by the vibration of the thermal phonon, the other bonds are also simultaneously broken, which lead to the collapse of the structural skeleton, and induce a phase transition from solid to liquid state. The solid state structure is melting. ^{5,6}

The bond energy of the strongest bond can be estimated by Eq. s25.

$$U_B = b \frac{n_A}{D_A} f + b_1 \frac{n_1}{I^\sigma D} f' - \frac{\sum b_i C_i W_i}{I^\sigma} \quad \text{* MERGEFORMAT (s25)}$$

The vibrating energy of thermal phonon with n mol is $1.5nRT$. At the melting point (T_m), the vibrating energy just equals to the energy of the strongest bond, *i.e.*, $1.5nRT_m = U_B$. Therefore, the melting point can be calculated as follows:

$$T_m = (b \frac{n_A}{D_A} f + b_1 \frac{n_1}{I^\sigma D} f' - \frac{\sum b_i C_i W_i}{I^\sigma}) / 1.5nR \quad \text{* MERGEFORMAT}$$

(s26)

Table S1 The calculated and experimental bond lengths of selected compositions on the liquidus line at 641K

compositions	Bonds	I_α	n_α	$D_{uv}(n\alpha)/\text{\AA}$	$\bar{D}_{uv}(n\alpha)/\text{\AA}$	$\Delta D(\text{\AA})$
A1	Li1-Cl	12	0.1383	2.5646	2.5690	-0.0044
	Li1-Li1	12	0.0100	3.6287	3.6331	-0.0044
	Cl-Cl	12	0.0019	3.6287	3.6331	-0.0044
	Li2-Br	12	0.1047	2.7406	2.7450	-0.0044
	Li2-Li2	12	0.0054	3.8177	3.8221	-0.0044
	Br-Br	12	0.0019	3.8177	3.8221	-0.0044
	Li3-I	12	0.1459	2.9956	3.0000	-0.0044
	Li3-Li3	12	0.0014	4.2382	4.2426	-0.0044
	I-I	12	0.0048	4.2382	4.2426	-0.0044
A2	Li1-Cl	12	0.1374	2.5667	2.5690	-0.0023
	Li1-Li1	12	0.0099	3.6308	3.6331	-0.0023
	Cl-Cl	12	0.0019	3.6308	3.6331	-0.0023
	Li2-Br	12	0.1039	2.7427	2.7450	-0.0023
	Li2-Li2	12	0.0054	3.8197	3.8220	-0.0023
	Br-Br	12	0.0019	3.8197	3.8220	-0.0023
	Li3-I	12	0.1449	2.9977	3.0000	-0.0023
	Li3-Li3	12	0.0014	4.2403	4.2426	-0.0023
	I-I	12	0.0048	4.2403	4.2426	-0.0023
A3	Li1-Cl	12	0.1364	2.5689	2.5690	-0.0001
	Li1-Li1	12	0.0099	3.6330	3.6331	-0.0001
	Cl-Cl	12	0.0019	3.6330	3.6331	-0.0001
	Li2-Br	12	0.1032	2.7449	2.7450	-0.0001
	Li2-Li2	12	0.0054	3.8219	3.8220	-0.0001
	Br-Br	12	0.0018	3.8219	3.8220	-0.0001
	Li3-I	12	0.1439	2.9999	3.0000	-0.0001
	Li3-Li3	12	0.0014	4.2425	4.2426	-0.0001
	I-I	12	0.0048	4.2425	4.2426	-0.0001

Table S1.Continued

compositions	Bonds	I_α	n_α	$D_{uv}(n\alpha)/\text{\AA}$	$\bar{D}_{uv}(n\alpha)/\text{\AA}$	$\Delta D(\text{\AA})$
A4	Li1-Cl	12	0.1355	2.5710	2.5690	0.0020
	Li1-Li1	12	0.0099	3.6351	3.6331	0.0020
	Cl-Cl	12	0.0019	3.6351	3.6331	0.0020
	Li2-Br	12	0.1025	2.7470	2.7450	0.0020
	Li2-Li2	12	0.0053	3.8240	3.8220	0.0020
	Br-Br	12	0.0019	3.8240	3.8220	0.0020
	Li3-I	12	0.1429	3.0020	3.0000	0.0020
	Li3-Li3	12	0.0014	4.2446	4.2426	0.0020
A5	I-I	12	0.0047	4.2446	4.2426	0.0020
	Li1-Cl	12	0.1346	2.5730	2.5690	0.0040
	Li1-Li1	12	0.0097	3.6371	3.6331	0.0040
	Cl-Cl	12	0.0019	3.6371	3.6331	0.0040
	Li2-Br	12	0.1018	2.7490	2.7450	0.0040
	Li2-Li2	12	0.0053	3.8260	3.8220	0.0040
	Br-Br	12	0.0018	3.8260	3.8220	0.0040
	Li3-I	12	0.1419	3.0040	3.0000	0.0040
	Li3-Li3	12	0.0014	4.2466	4.2426	0.0040
I-I	12	0.0047	4.2466	4.2426	0.0040	

Table S2. The calculated and experimental bond lengths of selected compositions on the liquidus curve at 723K

compositions	bonds	I_α	n_α	$D_{uv}(n_\alpha)/\text{\AA}$	$\bar{D}_{uv}(n_\alpha)/\text{\AA}$	$\Delta D(\text{\AA})$
B1	Li-X	12	0.1309	2.7885	2.7543	0.0341
	Li-Li	12	0.0038	3.9263	3.8922	0.0341
	X-X	12	0.0028	3.9263	3.8922	0.0341
B2	Li-X	12	0.1308	2.7790	2.7464	0.0325
	Li-Li	12	0.0040	3.9109	3.8783	0.0325
	X-X	12	0.0027	3.9109	3.8783	0.0325
B3	Li-X	12	0.1306	2.7709	2.7399	0.0310
	Li-Li	12	0.0041	3.8969	3.8659	0.0310
	X-X	12	0.0027	3.8969	3.8659	0.0310
B4	Li-X	12	0.1305	2.7646	2.7349	0.0296
	Li-Li	12	0.0043	3.8852	3.8556	0.0296
	X-X	12	0.0027	3.8852	3.8556	0.0296
B5	Li-X	12	0.1303	2.7602	2.7320	0.0281
	Li-Li	12	0.0044	3.8756	3.8474	0.0281
	X-X	12	0.0027	3.8756	3.8474	0.0281
B6	Li-X	12	0.1302	2.7601	2.7335	0.0266
	Li-Li	12	0.0045	3.8712	3.8446	0.0266
	X-X	12	0.0027	3.8712	3.8446	0.0266
B7	Li-X	12	0.1302	2.7636	2.7373	0.0263
	Li-Li	12	0.0045	3.8737	3.8474	0.0263
	X-X	12	0.0027	3.8737	3.8474	0.0263
B8	Li-X	12	0.1302	2.7670	2.7409	0.0261
	Li-Li	12	0.0044	3.8766	3.8504	0.0261
	X-X	12	0.0028	3.8766	3.8504	0.0261
B9	Li-X	12	0.1303	2.7747	2.7487	0.0260
	Li-Li	12	0.0043	3.8848	3.8587	0.0260
	X-X	12	0.0029	3.8848	3.8587	0.0260
B10	Li-X	12	0.1304	2.7884	2.7621	0.0262
	Li-Li	12	0.0041	3.9007	3.8744	0.0262
	X-X	12	0.0030	3.9007	3.8744	0.0262

Table S2.Continued

compositions	bonds	I_α	n_α	$D_{uv}(n_\alpha)/\text{\AA}$	$\bar{D}_{uv}(n_\alpha)/\text{\AA}$	$\Delta D(\text{\AA})$
	Li-X	12	0.1306	2.8114	2.7840	0.0274
B11	Li-Li	12	0.0037	3.9297	3.9023	0.0274
	X-X	12	0.0032	3.9297	3.9023	0.0274
	Li-X	12	0.1308	2.8460	2.8157	0.0302
B12	Li-Li	12	0.0032	3.9763	3.9460	0.0302
	X-X	12	0.0034	3.9763	3.9460	0.0302

Table S3. The calculated and experimental bond lengths of selected compositions on the liquidus curve at 773K

compositions	bonds	I_α	n_α	$D_{uv}(n_\alpha)/\text{\AA}$	$\bar{D}_{uv}(n_\alpha)/\text{\AA}$	$\Delta D(\text{\AA})$
C1	Li-X	12	0.1300	2.7234	2.6945	0.0288
	Li-Li	12	0.0051	3.8363	3.8074	0.0288
	X-X	12	0.0024	3.8363	3.8074	0.0288
C2	Li-X	12	0.1298	2.7135	2.6863	0.0272
	Li-Li	12	0.0053	3.8194	3.7922	0.0272
	X-X	12	0.0023	3.8194	3.7922	0.0272
C3	Li-X	12	0.1295	2.7041	2.6786	0.0254
	Li-Li	12	0.0056	3.8027	3.7772	0.0254
	X-X	12	0.0023	3.8027	3.7772	0.0254
C4	Li-X	12	0.1294	2.7004	2.6758	0.0245
	Li-Li	12	0.0058	3.7956	3.7711	0.0245
	X-X	12	0.0023	3.7956	3.7711	0.0245
C5	Li-X	12	0.1292	2.6960	2.6725	0.0234
	Li-Li	12	0.0060	3.7868	3.7633	0.0234
	X-X	12	0.0023	3.7868	3.7633	0.0234
C6	Li-X	12	0.1291	2.6942	2.6714	0.0227
	Li-Li	12	0.0060	3.7818	3.7591	0.0227
	X-X	12	0.0023	3.7818	3.7591	0.0227
C7	Li-X	12	0.1290	2.6945	2.6728	0.0217
	Li-Li	12	0.0061	3.7791	3.7573	0.0217
	X-X	12	0.0023	3.7791	3.7573	0.0217
C8	Li-X	12	0.1290	2.6960	2.6747	0.0212
	Li-Li	12	0.0061	3.7790	3.7577	0.0212
	X-X	12	0.0024	3.7790	3.7577	0.0212
C9	Li-X	12	0.1290	2.6993	2.6786	0.0206
	Li-Li	12	0.0061	3.7809	3.7602	0.0206
	X-X	12	0.0024	3.7809	3.7602	0.0206
C10	Li-X	12	0.1290	2.7053	2.6851	0.0201
	Li-Li	12	0.0060	3.7862	3.7660	0.0201
	X-X	12	0.0025	3.7862	3.7660	0.0201

Table S3.Continued

compositions	bonds	I_α	n_α	$D_{uv}(n_\alpha)/\text{\AA}$	$\bar{D}_{uv}(n_\alpha)/\text{\AA}$	$\Delta D(\text{\AA})$
C11	Li-X	12	0.1292	2.7142	2.6943	0.0199
	Li-Li	12	0.0058	3.7959	3.7759	0.0199
	X-X	12	0.0025	3.7959	3.7759	0.0199
C12	Li-X	12	0.1294	2.7323	2.7123	0.0200
	Li-Li	12	0.0054	3.8171	3.7970	0.0200
	X-X	12	0.0027	3.8171	3.7970	0.0200
C13	Li-X	12	0.1296	2.7457	2.7253	0.0204
	Li-Li	12	0.0051	3.8331	3.8127	0.0204
	X-X	12	0.0028	3.8331	3.8127	0.0204
C14	Li-X	12	0.1298	2.7667	2.7456	0.0211
	Li-Li	12	0.0047	3.8597	3.8386	0.0211
	X-X	12	0.0029	3.8597	3.8386	0.0211
C15	Li-X	12	0.1302	2.7974	2.7743	0.0230
	Li-Li	12	0.0041	3.8999	3.8769	0.0230
	X-X	12	0.0031	3.8999	3.8769	0.0230

Table S4. The calculated and experimental bond lengths of selected compositions on the liquidus curve at 823K

composition	bonds	I_α	n_A	$D_{uv}(n_\alpha)/\text{Å}$	$\bar{D}_{uv}(n_\alpha)/\text{Å}$	$\Delta D(\text{Å})$
1	Li-X	12	0.1288	2.6629	2.6375	0.0254
	Li-Li	12	0.0066	3.7542	3.7287	0.0254
	X-X	12	0.0021	3.7542	3.7287	0.0254
2	Li-X	12	0.1286	2.6570	2.6325	0.0244
	Li-Li	12	0.0069	3.7435	3.7190	0.0244
	X-X	12	0.0020	3.7435	3.7190	0.0244
3	Li-X	12	0.1283	2.6517	2.6283	0.0233
	Li-Li	12	0.0071	3.7334	3.7100	0.0233
	X-X	12	0.0020	3.7334	3.7100	0.0233
4	Li-X	12	0.1281	2.6462	3.6999	0.0219
	Li-Li	12	0.0074	3.7219	3.6999	0.0219
	X-X	12	0.0020	3.7219	2.6243	0.0219
5	Li-X	12	0.1280	2.6445	2.6232	0.0212
	Li-Li	12	0.0075	3.7172	3.6959	0.0212
	X-X	12	0.0020	3.7172	3.6959	0.0212
6	Li-X	12	0.1279	2.6451	2.6248	0.0202
	Li-Li	12	0.0075	3.7143	3.6941	0.0202
	X-X	12	0.0020	3.7143	3.6941	0.0202

Table S5 Hybridization Table of H, Li with A type

h	\oplus	○○○	l, m, n, τ	1	0	0	0
t	●	●○○	l', m', n', τ'	0.94879	0.05121	0	0
				$k = \frac{1}{a^2 \pm \sqrt{1-a^2}}$			
		a^2	$1-a^2$				
σ			1	2	3	4	
$C_{h\sigma}$			1	0.7469	0.3489	0	
$C_{t\sigma}$			0	0.2531	0.6511	1	
$n_{T\sigma}$			1	1	1	1	
$n_{l\sigma}$			1	0.7469	0.3489	0	
$n_{e\sigma}$			0	0.2531	0.6511	1	
R_{σ} (1	H			0.3708	0.3479	0.3110	0.2800
)	Li			1.3260	1.2400	1.1046	0.9860

Table S6 Hybridization Table of IA group with B type

h	\oplus	o o o	l, m, n, τ	1	0	0	0
t	•	• o o	l', m', n', τ'	0.9982	0.0018	0	0
		a^2	$1-a^2$	$k = \frac{1}{a^2 \pm \sqrt{1-a^2}}$			
σ		1	2	3	4		
C_{hσ}		1	0.5384	0.4650	0		
C_{tσ}		0	0.4616	0.5350	1		
n_{Tσ}		1	1	1	1		
n_{lσ}		1	0.5384	0.4650	0		
n_{cσ}		0	0.4616	0.5350	1		
R_{σ} (1)	H	0.3708	0.3289	0.3222	0.2800		
	Li	1.3260	1.2089	1.1440	0.9860		
	Na	1.5133	1.4551	1.4308	1.3070		
	K	1.9628	1.8794	1.8601	1.7820		
	Rb	2.0870	2.0270	2.0175	1.9570		
	Cs	2.2140	2.2260	2.2279	2.2400		

Table S7 Hybridization Table of halide group with B type

h	● ● ● ● l, m, n, τ	0.26751	0.73758	0	0
t	○ ● ● ● l', m', n', τ'	0	1	0	0

$$k = \frac{a \pm \sqrt{3(1-a^2)}}{\sqrt{3}}$$

σ	a^2	$1-a^2$		
σ	1	2	3	4
$C_{h\sigma}$	1	0.5713	0.2372	0
$C_{t\sigma}$	0	0.4287	0.7628	1
$n_{T\sigma}$	1	1	1	1
$n_{l\sigma}$	0	0	0	0
$n_{c\sigma}$	7	7	7	7
R_{σ} (1 F)	0.4500	0.5649	0.6544	0.7180
Cl	0.8500	0.9117	0.9598	0.9940
Br	0.9400	1.0266	1.0941	1.1420
I	1.270	1.2974	1.3188	1.3340

- 1 X. P. Guo, Y. Q. Guo and L. H. Yin, Valence Electron Structures and Mechanical and Thermal Properties of Single-Phase Refractory High-Entropy Alloys, *J. Phys. Chem. C*, 2021, **125**, 20503–20511.
- 2 Y. Guo, T. Su, J. Zhang, X. Wang, Y. Chen and X. Zhao, Correlation of Valence Electron Structures and Thermal and Electric Properties in Li||Sb-Based Liquid Metal Batteries, *ACS Appl. Energy Mater.*, 2020, **3**, 5361–5374.
- 3 Y. Guo, R. Yü, R. Zhang, X. Zhang and K. Tao, Calculation of Magnetic Properties and Analysis of Valence Electronic Structures of $LaT_{13-x}Al_x$ (T = Fe, Co) Compounds, *J. Phys. Chem. B*, 1998, **102**, 9–16.
- 4 Z.-Q. Xue and Y.-Q. Guo, Correlation between valence electronic structure and magnetic properties in RCo_5 (R = rare earth) intermetallic compound, *Chin. Phys. B*, 2016, **25**, 063101.
- 5 T. Wang, Y.-Q. Guo and S. Li, Correlation between electronic structure and energy band in Eu-doped $CuInTe_2$ semiconductor compound with chalcopyrite structure, *Chin. Phys. B*, 2017, **26**, 103101.
- 6 L. Yin, Y. Guo and X. Guo, Strong Dependence of Thermal and Magnetic Properties on Valence Electron Structures in R_2Co_{17} (R = Rare Earth) Intermetallics, *Inorg. Chem.*, 2022, **61**, 2402–2408.