Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Correlation between the Electronic Structure, Topologic Structure and Dynamic Properties of Liquid Ce

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1. Methods

Radial distribution function. The normalized total radial distribution function (TRDF) and partial radial distribution functions (PRDFs) are defined as:

$$g(r) = \frac{V}{N^2}\left\langle \sum_{i}^{N} \frac{h_{ij}}{4\pi r^2 \Delta r} \right\rangle \quad (1)$$

$$g_i(r) = \frac{V}{N^2}\left\langle \sum_{i=1}^{N_i} \frac{h_{ij}}{4\pi r^2 \Delta r} \right\rangle \quad (2)$$

Where V is the volume of the simulation supercell; N is the total number of atoms in the supercell; N_i is the number of the atoms of i species; h_{ij} is the number of atoms of j species which locate in the spherical shell with radius from r to $r+\Delta r$ around an atom of i species. $g(r)$ is the normalized total radial distribution function; $g_i(r)$ is the partial radial distribution function of i specie atoms.

Chemical order parameter. Chemical short range order (CSRO) is described in terms of the micro-chemical inhomogeneity (MCI) parameter ξ which can be used to reflect the CSRO's quantitatively of a binary system as well as for a general multi-component system. The MCI parameter of the component i, ξ_i and the MCI parameter of the system ξ, are defined respectively as

follows:

$$\xi_i = CN_{ii} - \frac{1}{N-1}\sum_{j\neq i}^{N} CN_{ji} \tag{3}$$

$$\xi = \sum_i c_i \cdot \xi_i \tag{4}$$

Where CN_{ji} is the number of atoms of j species around an atom of i species, and c_i is the concentration of i species. For a system with a positive MCI parameters ξ, it has a tendency to undergo segregation or phase separation at those compositions, since atoms prefer to have atoms of similar species as their neighbors. In a system with negative MCI parameters ξ, there is a preference for each atom to have distinct atoms as neighbors.

Diffusion coefficient. The diffusion coefficient is defined as:

$$D_j = \frac{\left\langle \sum_{i=1}^{N_j} \left[r_i(t) - r_i(0) \right]^2 \right\rangle}{6N_j t} \tag{5}$$

Where N_j is the number of the j-th kind of Ce atoms, $r_i(0)$ and $r_i(t)$ are the position of *i-th* atom at the start and end of the interval t. Since different kinds of Ce are interchangeable during the structure evolution, it is challenging to calculate the diffusion coefficient for each kind of Ce. In our calculation, a Ce atom is considered as a larger-magnetic-moment one if its average magnetic moment is larger than $0.6\,\mu_B$ in 2 ps, otherwise it is considered as a smaller-magnetic-moment Ce atom.

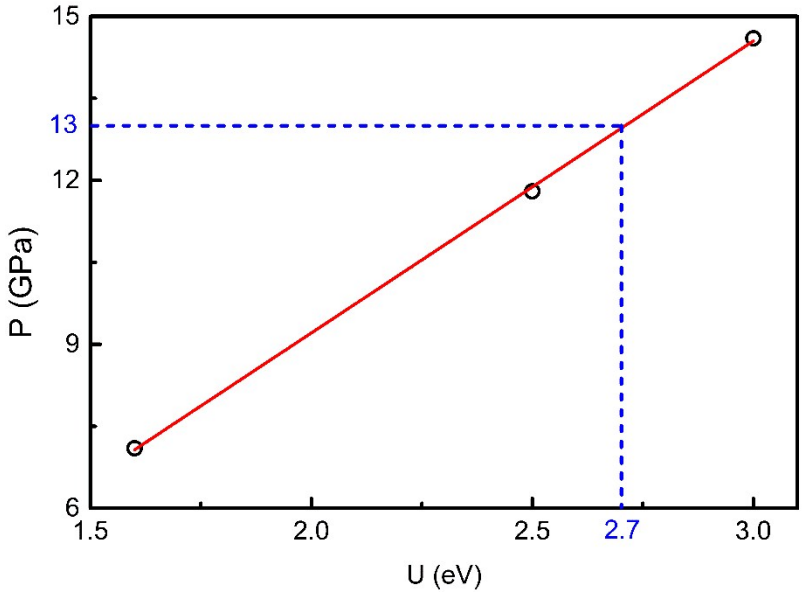

Figure S1 | The external pressure changes with U at fixed volume. Here, we calculate the pressure with different U at fixed volume which 14% larger than the HDL phase at 13 GPa and 1550 K. The U=2.7 eV are derived by liner interpolation method as illustrated in figure S1.

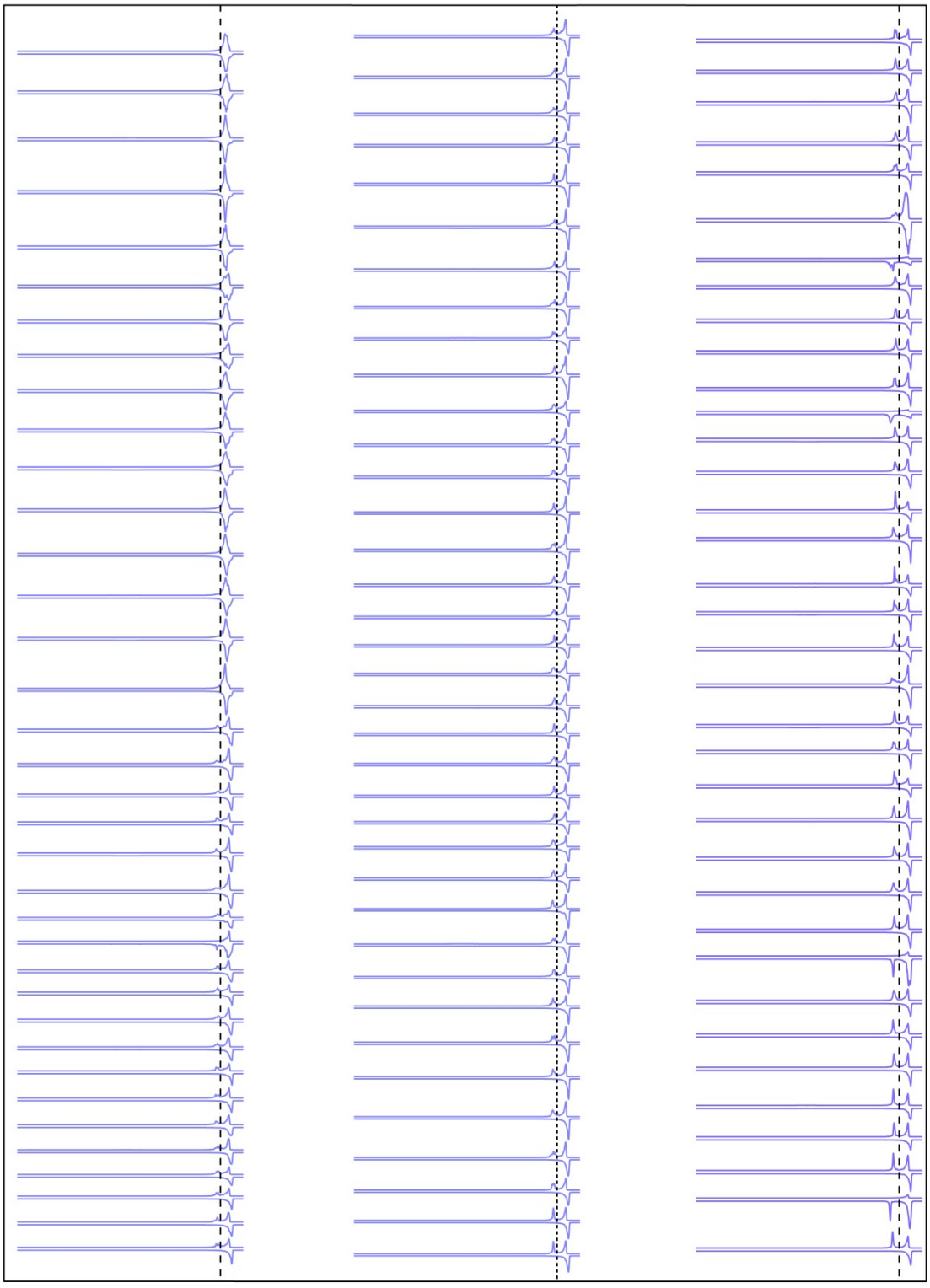

Figure S2 | Each atomic f-PDOS of the given structure for LDL Ce.

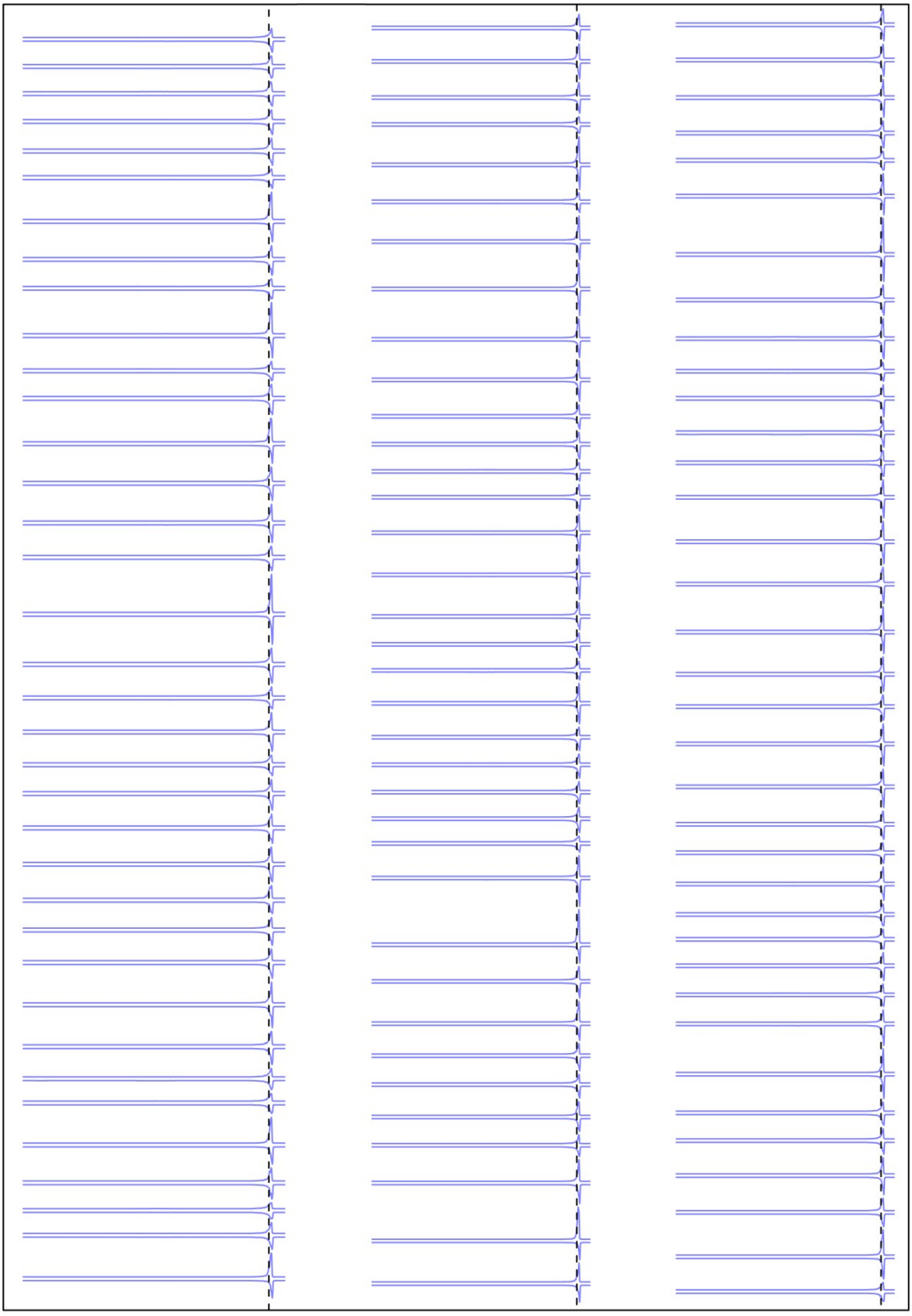

Figure S3 | Each atomic f-PDOS of the given structure for HDL Ce.

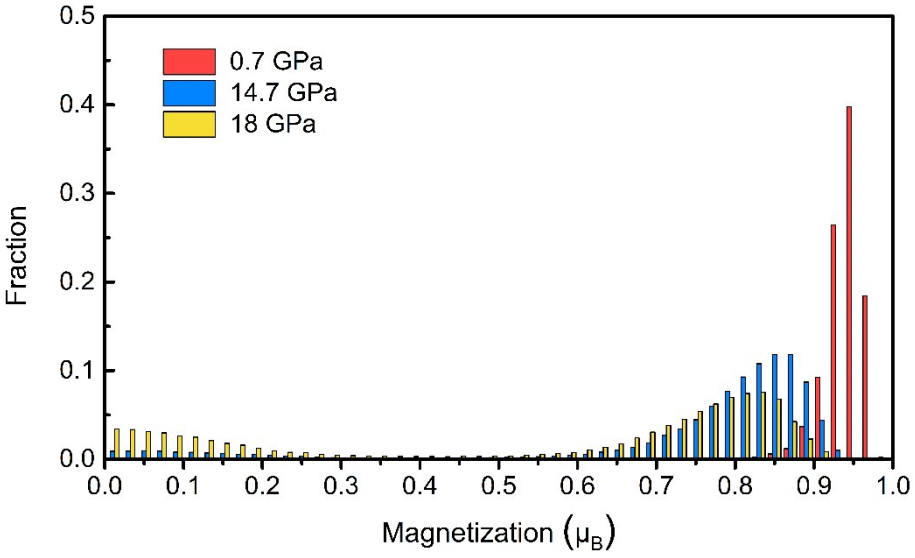

Figure S4 | Atomic magnetic moment changes with pressure in LDL phase at 1900 K.

Supplemental video

For clarity, yellow represents the smallest 15 local magnetic moments of Ce atoms, whereas the other atoms represent the larger-magnetic-moment ones. From the video, we see it visually that Ce atoms with similar degree of 4f-electron-locality tend to gather together.