Coexistence of ferroelectricity and ferromagnetism in hex-GeS nanowires

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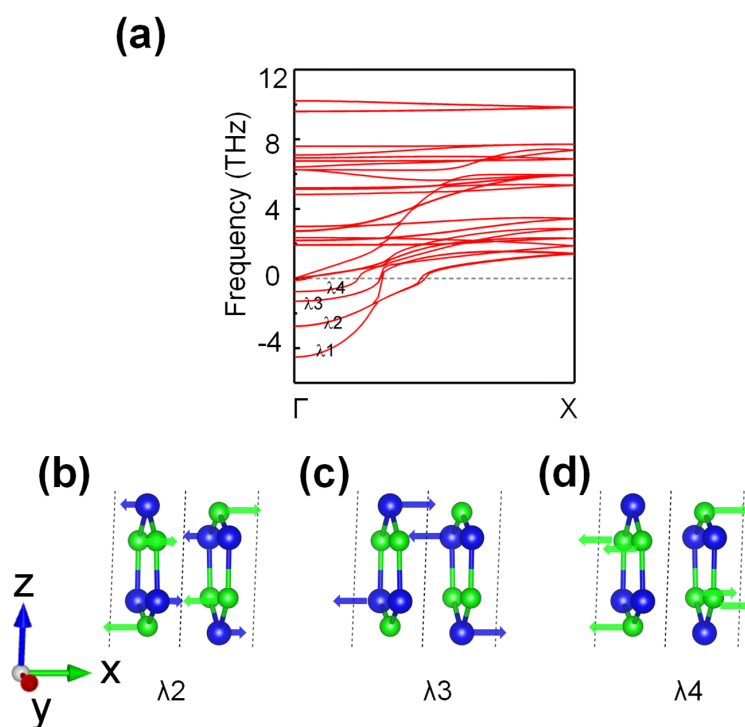
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FIG. S1: (a) Phonon dispersion of hex-GeS nanowires (b)-(d) imaginnary frequency model of hex-GeS nanowires. Blue atoms is Ge and green atoms is S.

The phonon dispersions indicate that hex-GeS and structures are dynamically unstable, where four optical modes have negative frequency (λ_1-λ_4) at Γ point. The structural with space inversion will be removed via λ_1-λ_4 soft optical modes, leading to the structural transition.

TABLE S1: Fitted parameters in Equation 1. The units are meV/(C/m)^2, meV/(C/m)^4, and meV/(C/m)^2.

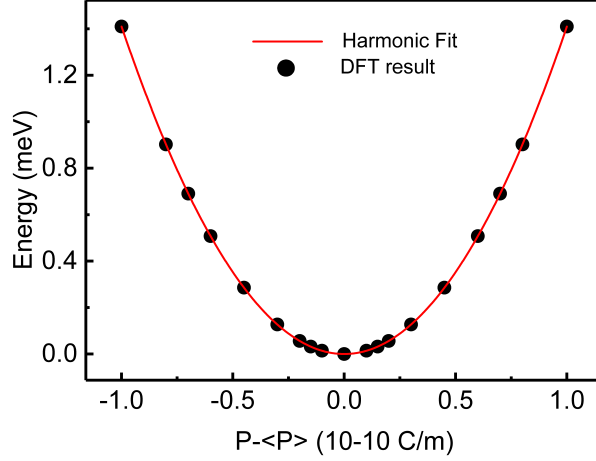|	A	B	C
hex-GeS	-216	25	1.41

FIG. S2: The dipole-dipole interaction of hex-GeS calculated by DFT. The red line is the harmonic approximation fit and black dots are DFT results

The value of Born effective charges (Z*) is 4.7e and the atomic distortion (τ) is $0.407\mathring{A}$ for FE hex-GeS nanowires. There are six GeS ion pairs in the unit cell. Thus, the polarization value by the expression, $P = 6*Z^**\tau$. which is 11.47 $e\mathring{A}$ for hex-GeS nanowires. The value is akin to the polarization value by Berry phase method: 12.2 eÅ.

$$E = \sum_i \frac{A}{2}(P_i)^2 + \frac{B}{2}(P_i)^4 + \frac{C}{2}\sum_{i,j}(P_i - P_j)^2 \tag{1}$$
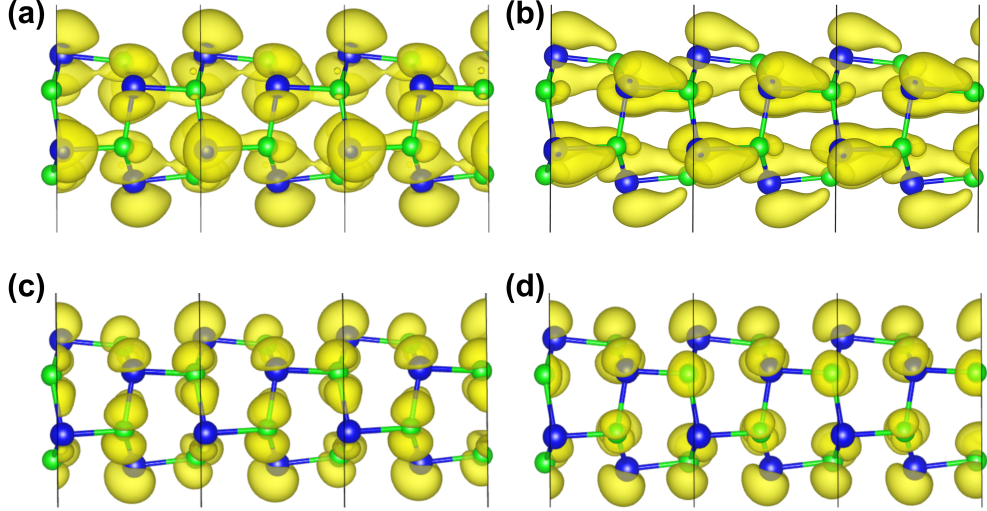
FIG. S3: (a)-(d) The electron density distributions of states ACD. (a) shows bonding nature in state A; (b),(c),(d) show antibonding nature in state B, C, D

In order to understanding the underlying mechanism of the different trends under strain, we make the charge density distributions and analyse their bonding nature. The energy level shifts of the bonding and antibonding states exhibit opposite trends under external strain. According to the Heitler-London model, the energies of the bonding and antibonding states are given as:

$$E_{\text{bonding}} = 2E_0 + \frac{e^2}{R} + \frac{K + H}{1 + S^2} \qquad (2)$$

$$E_{\text{antibonding}} = 2E_0 + \frac{e^2}{R} + \frac{K - H}{1 - S^2}, \qquad (3)$$

where E_0 is the energy of an isolated atom, K includes the classical Coulomb energy of the electron-electron and electron-ion interactions, and S is the overlap integral of the orbitals between different atomic sites, which is usually much smaller than 1 and thus S^2 can be neglected in most cases. Therefore, the exchange integral term H plays a dominant role in determining the different energy variation behaviors with strain in the bonding and antibonding situations. The exchange H is written as

$$H = \iint \psi_a^*(r_1)\psi_b^*(r_2)(\frac{1}{r_{12}} - \frac{1}{r_{2a}} - \frac{1}{r_{1b}})$$
$$\times \psi_b(r_1)\psi_a(r_2)\,dr_1 dr_2, \qquad (4)$$

Generally, for non-localized s and p orbitals, the contribution of the electron-ion interactions is dominant over that of the electron-electron interactions. Thus, as the atomic distance increases (corresponding to tensile strain), the energy contribution from the electron-ion interactions increases more rapidly compared to the reduction of the electron-electron contributions, which results in an increased value of H. Then, an increase in H will lead to an increase in bonding energy $E_{bonding}$ and a decrease in antibonding energy $E_{antibonding}$, according to eqn (2) and (3).

Further, we find that the state A shows bonding nature and antibonding nature for state B-D under uniaxial strain by the checking the electronic charge distributions of states A-D in figS3.
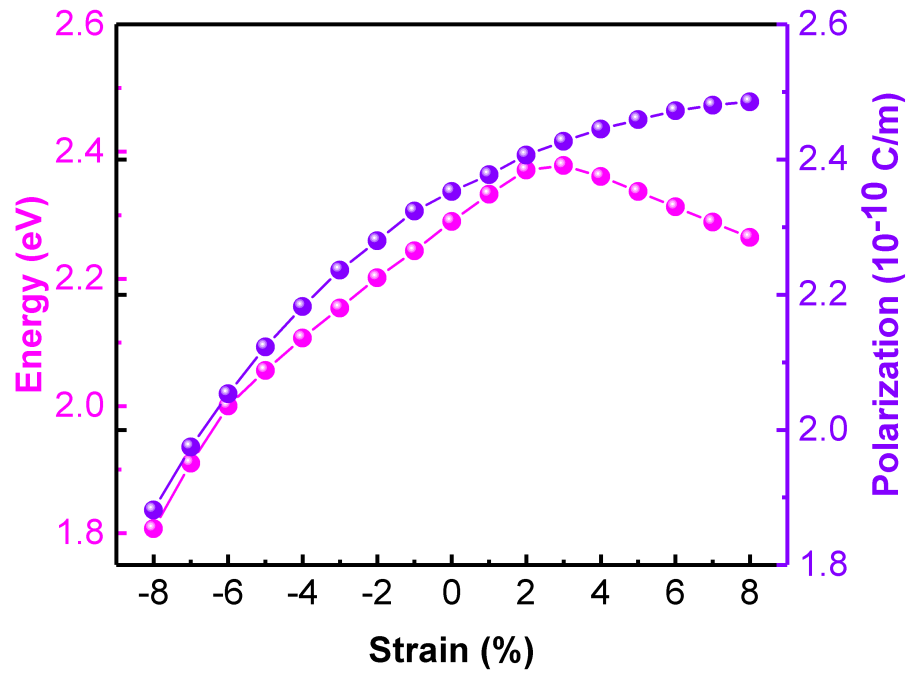
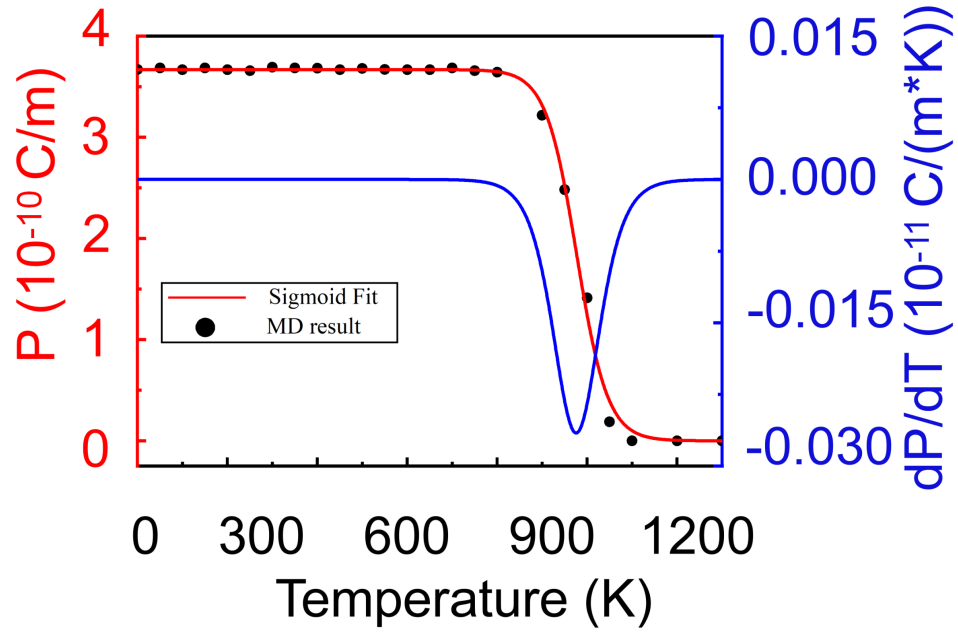FIG. S4: Alteration of band gaps and polarization with regard to strain.

FIG. S5: The polarization variation along with temperature obtained from AIMD for oct-GeS nanowires
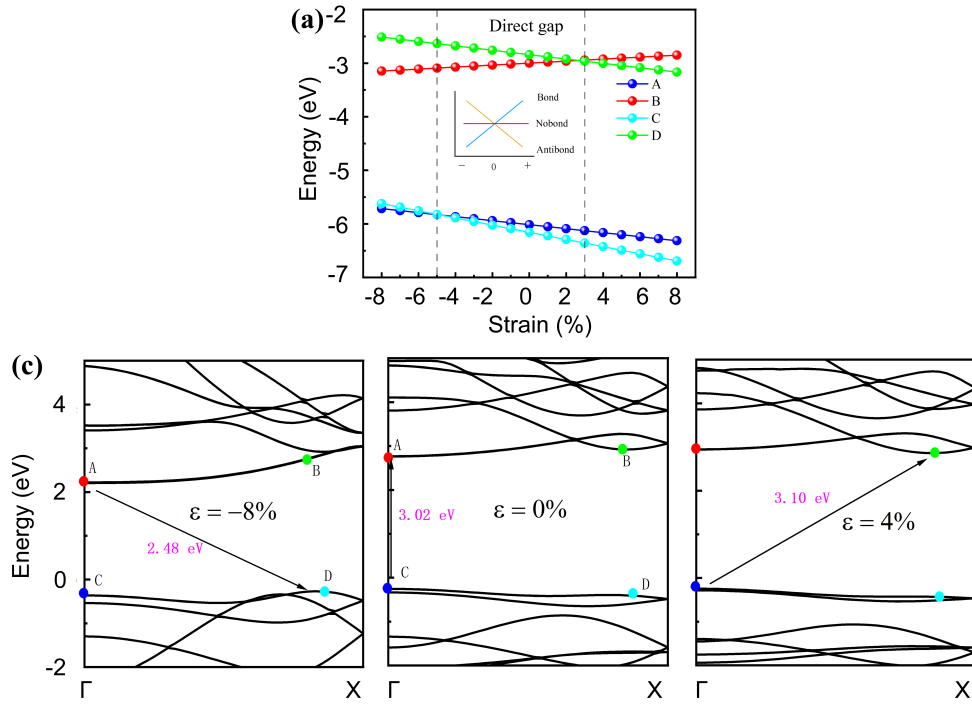
FIG. S6: (a) the band edge is regulated by the strain for A-D state at HSE06 level . (b) The band structure variations at = -8 %, 0%, +4% at HSE06 level.

hex-GeS

1.00000000000000

15.0000000000000000 0.0000000000000000 0.0000000000000000

0.0000000000000000 5.7245002174000010 0.0000000000000000

0.0000000000000000 0.0000000000000000 15.0000000000000000

Ge S

6 6

Direct

0.4655554479441186 0.9647113717854465 0.6641519962144710

0.3406567977788008 0.4647070740184296 0.5522911114077927

0.5343952338254910 0.4647073511485849 0.3358388500091215

0.3750820695819530 0.9647056484558661 0.3880921552968111

0.6249626775404609 0.4647035008923832 0.6118654324971167

0.6593673650159185 0.9647007509490771 0.4477709154048671

0.3573509455377735 0.0353006153850198 0.5467522199631233

0.5308328507617518 0.0352903923769054 0.3530560002226403

0.6426272216963627 0.5352953057133490 0.4531858981670946

0.4692098516873899 0.5352938845651651 0.6469524007005166

0.6118207602905026 0.0352908351337713 0.6001827424571832

0.3881388083394791 0.5352932405759959 0.3998602486592701

Regular octagon-GeS

1.00000000000000

15.0000000000000000 0.0000000000000000 0.0000000000000000

0.0000000000000000 5.8450000760000034 0.0000000000000000

0.0000000000000000 0.0000000000000000 15.0000000000000000

Ge S

8 8

Direct

0.5505727436363375 0.4562106069907294 0.2910702136085880

0.6983487721084717 0.9545601284221207 0.3708514669963741

0.7481644981883696 0.4545775733328477 0.5314957710599632

0.6715027809800622 0.9562812460199375 0.6808855306845158

0.5114358961347417 0.4562372508337063 0.7304958626441933

0.3636854698605935 0.9545328499649516 0.6506969791821466

0.3138339275422687 0.4545658182771803 0.4900642365833372

0.3905102669377697 0.9562479545118964 0.3406834961537059

0.5477545605105766 0.0474130810136761 0.3214497992777380

0.6721051406264884 0.5490009024553537 0.3925438659313603

0.7143007240986059 0.0490114999234813 0.5284344552265016

0.6520955202992905 0.5473146347662960 0.6575638892095762

0.5142634579360917 0.0473649777799231 0.7001988437999291

0.3899943972841778 0.5490614751126227 0.6289209771780047

0.3477318683561125 0.0490155592753201 0.4931028070899915

0.4099699775000729 0.5473444413199560 0.3640518053740557

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