# Supplementary Information

## Toward Two-Dimensional Ionic Crystals with Intrinsic Ferromagnetism


Li-Rong Cheng, Zheng-Zhe Lin*

*School of Physics and Optoelectronic Engineering, Xidian University, Xi'an 710071, China*

* Corresponding Author. E-mail address: zzlin@xidian.edu.cn


### 1. Total energy of EuS lattice

EuS bulk is an ionic lattice of NaCl type. The energy of one primitive cell reads $E=-\frac{\alpha q^2}{4\pi\varepsilon_0 r}+\frac{mB}{r^n}$, where $\alpha$ = 1.748 is the Madelung constant and $m$ = 6 is the number of nearest $S^{2-}$ for one $Eu^{2+}$. We perform DFT calculations with different Eu-S bond length $r = a/\sqrt{2}$ ($a$ is the lattice constant) while keeping the lattice type. The repulsion energy $\frac{mB}{r^n}$ is then obtained by subtracting the Madelung energy $-\frac{\alpha q^2}{4\pi\varepsilon_0 r}$ from the total energy $E$. The values of $B$ = 904.9 (for $r$ in units of Å) and $n$ = 6.36 is gotten by data fitting. The data are listed below.

**Table S1. Energy of EuS bulk under different Eu-S bond lengths.**

| lattice constant $a$ (Å) | Eu-S bond length $r$(Å) | $-\frac{\alpha q^2}{4\pi\varepsilon_0 r}$ (eV) | $\frac{mB}{r^n}$ (eV) | $E=-\frac{\alpha q^2}{4\pi\varepsilon_0 r}+\frac{mB}{r^n}$ (eV) | DFT energy (eV) |
|---|---|---|---|---|---|
| 3.732 | 2.639 | -38.153 | 11.343 | -26.810 | -26.984 |
| 3.939 | 2.785 | -36.145 | 8.042 | -28.103 | -28.040 |
| 4.146 | 2.932 | -34.338 | 5.804 | -28.534 | -28.441 |
| 4.354 | 3.078 | -32.702 | 4.255 | -28.447 | -28.405 |
| 4.561 | 3.225 | -31.216 | 3.165 | -28.050 | -28.087 |

## 2. Energy bands of EuS bulk

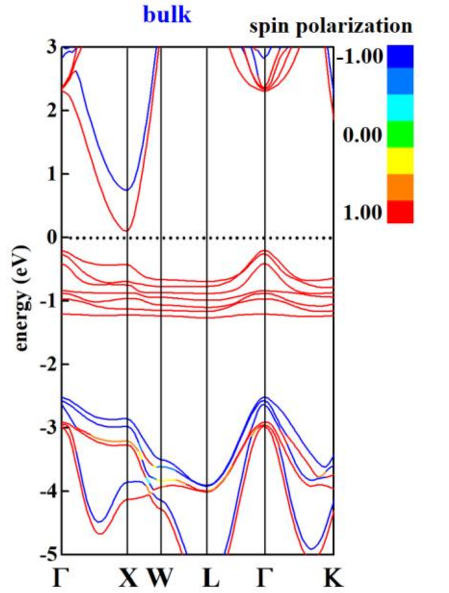


**Fig. S1 The energy bands of EuS bulk with SOC.** The bands are plotted at the level of HSE06.

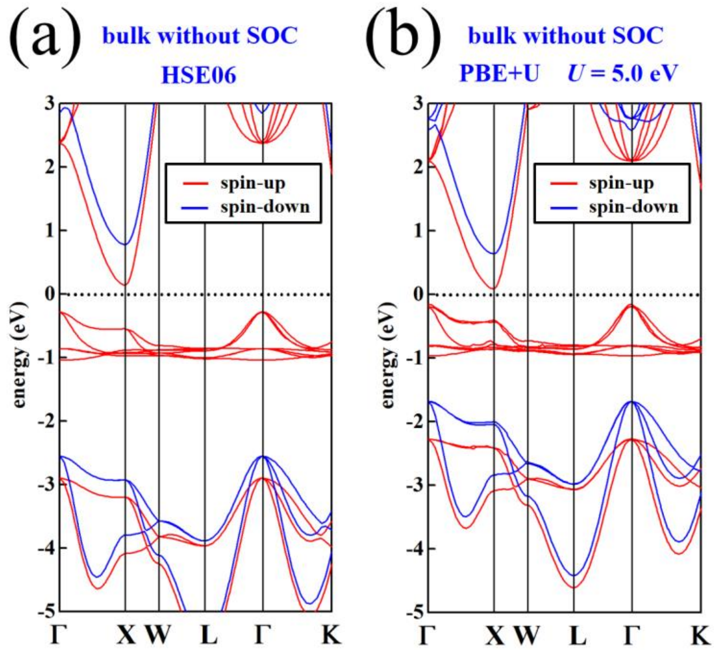


**Fig. S2 The energy bands of EuS bulk without SOC. (a)** The bands at the level of HSE06. **(b)** The bands at the level of PBE+U with $U$ = 5.0 eV.

## 3. Quantum Monte Carlo simulations

The magnetic moment $M$ is simulated via Quantum Monte Carlo simulations. The thermal average value of $M$ in the canonical ensemble reads

$$M = \mu_B \frac{Tr\hat{S}_z e^{-\hat{H}/kT}}{Tre^{-\hat{H}/kT}} = \mu_B \frac{\sum_i < i|\hat{S}_z e^{-\hat{H}/kT}|i>}{\sum_i < i|e^{-\hat{H}/kT}|i>} = \mu_B \frac{\sum_{i,j} < i|\hat{S}_z|j>< j|e^{-\hat{H}/kT}|i>}{\sum_i < i|e^{-\hat{H}/kT}|i>}.$$

Taking the basis states $|\, i >$ as the eigenstates of spin $S_z$, we have

$$M = \mu_B \frac{\sum_i < i|\hat{S}_z|i>< i|e^{-\hat{H}/kT}|i>}{\sum_i < i|e^{-\hat{H}/kT}|i>}.$$

At a given temperature $T$, the term $< i|e^{-\hat{H}/kT}|i>$ is calculated by stochastic series expansion [S1, S2]. The sampling in the spin eigenstates $|\, i >$ is performed using the Metropolis Monte Carlo method with relative probability $< i|e^{-\hat{H}/kT}|i>$. We take 20 $\times$ 20 EuS supercells. The results are shown in **Fig. S3**.

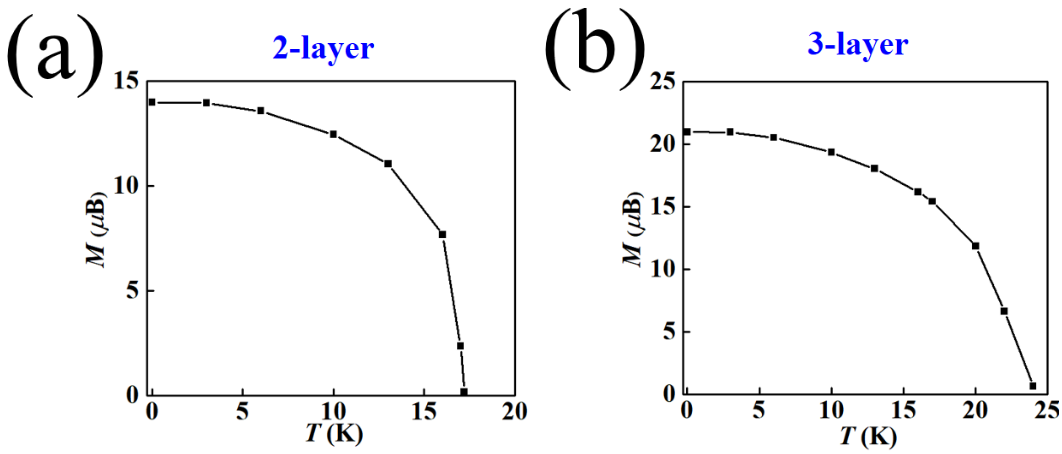


**Fig. S3** Quantum Monte Carlo simulations of the magnetic moment of 2-layer **(a)** and 3-layer **(b)** EuS varying with temperature $T$.

**4. Magnon-phonon interaction and the self-energy**

To understand how the phonons influence the magnon spectrum, we import a Hamiltonian to describe the spin-phonon interactions. The longitudinal acoustic (LA) phonons lead to the stretching of lattice, and give rise to the change of Heisenberg coupling $J$. For LA phonons near the Γ point, the migration $\vec{u}$ of Eu atoms locating at position $\vec{r}$ can be describe by long-wave approximation as

$$\vec{u}(\vec{r}) = \sum_{\vec{q}} \frac{\vec{q}}{q} \sqrt{\frac{\hbar}{2\sigma A \omega(\vec{q})}} (a_{\vec{q}} e^{i\vec{q}\bullet\vec{r}} + a_{\vec{q}}^{+} e^{-i\vec{q}\bullet\vec{r}}) .$$

Here, $\vec{q}$ is the phonon wave vector, $a_{\vec{q}}$ ($a_{\vec{q}}^{+}$) is the phonon annihilation (creation) operator, $\sigma$ is mass areal density and $A$ is the area. The LA phonon frequency $\omega(\vec{q}) = cq$ ($c$ is the longitudinal wave velocity in EuS). Based on the Heisenberg Hamiltonian $H = -J \sum_{ij\in \mathrm{NN}} \vec{S}_i \bullet \vec{S}_j$, the magnon-phonon interaction Hamiltonian reads

$$\begin{aligned} H_{m-p} &= -|\nabla J| \sum_{ij\in \mathrm{NN}} |\vec{u}_j - \vec{u}_i| \vec{S}_i \bullet \vec{S}_j \\ &= -|\nabla J| \sum_{ij\in \mathrm{NN}} |\vec{u}_j - \vec{u}_i| [(S_i^{+} S_j^{-} + S_i^{-} S_j^{+})/2 + S_{iz} S_{jz}] \\ &\approx -S|\nabla J| \sum_{ij\in \mathrm{NN}} |\vec{u}_j - \vec{u}_i| (b_i^{+} b_j + b_i b_j^{+} - b_i^{+} b_i - b_j^{+} b_j) . \end{aligned}$$

The last step employs the Holstein–Primakoff representation. The atomic migration can be approximately written as

$$\vec{u}_j - \vec{u}_i \approx \frac{\partial \vec{u}(\vec{r})}{\partial \vec{r}} \bullet (\vec{R}_j - \vec{R}_i) = \sum_{\vec{q}} \frac{\vec{q}}{q} \sqrt{\frac{\hbar}{2\sigma A \omega(\vec{q})}} i\vec{q} \bullet (\vec{R}_j - \vec{R}_i)(a_{\vec{q}} e^{i\vec{q}\bullet\vec{r}} - a_{\vec{q}}^{+} e^{-i\vec{q}\bullet\vec{r}}) .$$

Then, with the Fourier transform $b_i = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{i\vec{k}\bullet\vec{R}_i} b_{\vec{k}}$ to the magnons, for long-wave phonon $\vec{q}$ (i.e. $e^{i\vec{q}\bullet(\vec{R}_j - \vec{R}_i)} \approx 1$) we have

$$H_{m-p} \approx S|\nabla J| \sum_{NN,\vec{q},\vec{k}} \sqrt{\frac{\hbar}{2\sigma A \omega(\vec{q})}} 2i |\vec{q} \bullet \vec{R}_{NN}| (1 - \cos \vec{k} \bullet \vec{R}_{NN})(a_{\vec{q}} b_{\vec{k}+\vec{q}}^{+} b_{\vec{k}} - a_{\vec{q}}^{+} b_{\vec{k}-\vec{q}}^{+} b_{\vec{k}}) .$$

This Hamiltonian $H_{m\text{-}p}$ represents that a magnon of momentum $\vec{k}$ can adsorb (release) a phonon of momentum $\vec{q}$, and then becomes a magnon of momentum

$\vec{k}+\vec{q}$ ($\vec{k}-\vec{q}$). At low temperature, the environment is close to phonon vacuum, and the term $a_{\vec{q}}^{+}b_{\vec{k}-\vec{q}}^{+}b_{\vec{k}}$ is the main process. In the process of transmission, a $\vec{k}$-magnon may release a $\vec{q}$-phonon and then adsorb it soon (i.e. $|\vec{k},0\vec{q}> \to |\vec{k}-\vec{q},1\vec{q}> \to |\vec{k},0\vec{q}>$, see **Fig. S4(a)**), which leads to a self-energy correction of magnons. At the level of second-order perturbation, the energy correction of $\vec{k}$-magnon reads

$$E_{m-p}^{(2)}(\vec{k}) = -\sum_{\vec{q}} \frac{|<\vec{k},0\vec{q}\,|H_{m-p}|\,\vec{k},0\vec{q}>|^2}{\hbar\omega(\vec{q})+E(\vec{k}-\vec{q})-E(\vec{k})}$$

$$= -S^2|\nabla J|^2 \sum_{NN,\vec{q}} \frac{2\hbar}{\sigma A\omega(\vec{q})} \frac{|\vec{q}\bullet\vec{R}_{NN}|^2 (1-\cos\vec{k}\bullet\vec{R}_{NN})^2}{\hbar\omega(\vec{q})+E(\vec{k}-\vec{q})-E(\vec{k})}$$

$$> -S^2|\nabla J|^2 \sum_{\vec{q}} \frac{2\hbar}{\sigma A\omega(\vec{q})} \frac{nq^2a^2}{\hbar\omega(\vec{q})+E(\vec{k}-\vec{q})-E(\vec{k})}.$$

In the last estimation formula, $a$ is the lattice constant and $n$ is the nearest neighbor number. Such estimation provides a lower bound of magnon self-energy. If the denominator can be near zero, i.e. $E(\vec{k})=E(\vec{k}-\vec{q})+\hbar\omega(\vec{q})$ (**Fig. S4(b)**), the self-energy correction would be large. Fortunately, the LA phonons in layered EuS are very "hard" (**Fig. S4(c)** and **(d)**) and the case of $E(\vec{k})=E(\vec{k}-\vec{q})+\hbar\omega(\vec{q})$ cannot appear. So the self-energy correction would be small.

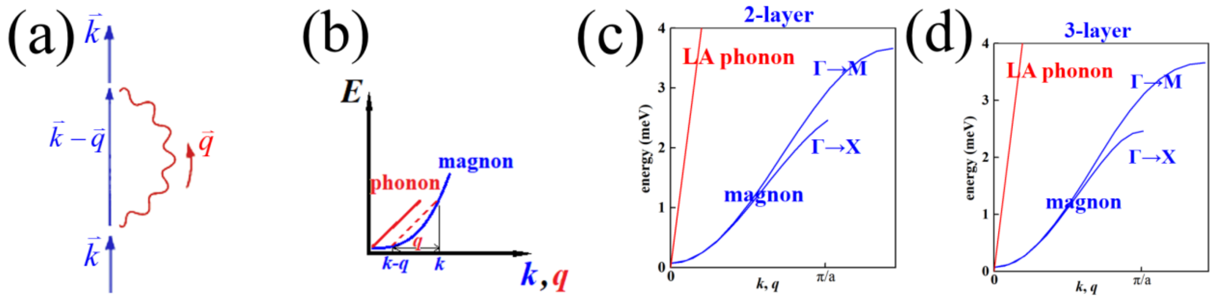


**Fig. S4 (a)** The Feynman diagram of magnon self-energy. **(b)** The magnon and LA phonon spectrum for when $E(\vec{k})=E(\vec{k}-\vec{q})+\hbar\omega(\vec{q})$ can be satisfied. **(c)** The magnon and LA phonon spectrum 2-layer EuS. **(d)** The magnon and LA phonon spectrum 3-layer EuS.

For the magnons near the $\Gamma$ point, the spectrum is close to $E(\vec{k})\approx\rho k^2$ and the denominator

$$\hbar\omega(\vec{q}) + E(\vec{k}-\vec{q}) - E(\vec{k}) \approx \hbar\omega(\vec{q}) + \rho(q^2 - 2\vec{k}\bullet\vec{q})$$

$$\geq \hbar\omega(\vec{q}) - 2\rho\vec{k}\bullet\vec{q}$$

$$\geq (\hbar c - 2\rho k)q\,.$$

So we can estimate that

$$E^{(2)}_{m-p}(\vec{k}) > -S^2|\nabla J|^2 \sum_{\vec{q}} \frac{2\hbar}{\sigma A c}\frac{na^2}{(\hbar c - 2\rho k)} = -\frac{2n\hbar S^2|\nabla J|^2}{\sigma c(\hbar c - 2\rho k)}\,.$$

By DFT calculations, we obtain $|\nabla J| = 0.12$ (0.14) meV/Å for 2-layer (3-layer) EuS.

By the calculations of Young's modulus, we obtain $c$ = $4.01\times10^3$ ($4.18\times10^3$) m/s for 2-layer (3-layer) EuS. We mainly care about the magnons near the Γ point whose self-energy correction may influence the low-energy gap. For $k \approx 0$, $E^{(2)}_{m-p} > -\frac{2nS^2|\nabla J|^2}{\sigma c^2}$. For 2- and 3-layer EuS, we finally obtain a rough estimation of $E^{(2)}_{m-p} >$ $-8\times10^{-4}$ meV. Such small value ensures that the low-energy gap of magnon is protected from the thermal disturbance of phonons.

**References**


[S1] A.W. Sandvik and J. Kurkijärvi, **Quantum Monte Carlo simulation method for spin systems**. *Phys. Rev. B* **43**, 5950 (1991).

[S2] O.F. Syljuasen and A.W. Sandvik, **Quantum Monte Carlo with directed loops**. *Phys. Rev. E* **66**, 046701 (2002).