

Unveiling the Room-Temperature Magnetoelectricity of Troilite FeS

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We report on a first-principles study of the troilite phase of iron sulfide (FeS). We show that even if, a few decades ago, this material was thought to be ferroelectric, the structural transition from the high $P6_3/mmc$ to the low $P\bar{6}2c$ symmetry phase does not involve polar instabilities, though the space inversion center symmetry is broken. Our calculations and symmetry analysis nevertheless reveal that FeS is magnetoelectric at room temperature with a response larger than the prototypical room-temperature magnetoelectric crystal Cr_2O_3 . We also show that the spin channel decomposition of the polarization exhibits nonzero values in the opposite direction in FeS, which is actually a general hint of the presence of a magnetoelectric monopole in diagonal magnetoelectrics.

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The troilite phase of FeS was first depicted by an Italian Jesuit, Domenico Troili, during his analysis of a meteorite which fell down in Italy in 1766 [1]. This particular phase among iron sulfide minerals is indeed commonly found in meteorites originating from the Moon [2] or Mars [3] and it is also naturally found in Earth's crust [4], though most of them have a meteoritic origin. Understanding the crystal properties of FeS is thus of high importance for planetary and geophysical studies such as planetary evolution [5]. Numerous research investigations have focused on FeS in order to understand its complex temperature and pressure phase diagram [6–9]. At high temperature, FeS is metallic and crystallizes in the high symmetry hexagonal $P6_3/mmc$ (No. 194) space group, the so-called NiAs-type structure. Below $T_N \sim 588$ K, FeS undergoes an antiferromagnetic (AFM) phase transition with spins perpendicular to the hexagonal axis (the c axis), and around $T_s \sim 445$ K a spin-flip transition occurs where the spins align toward the c axis [10]. A structural phase transition arises at $T_\alpha = 415$ K, modifying the crystal structure from the $P6_3/mmc$ space group to the so-called troilite structure with the space group $P\bar{6}2c$ [11,12]. Interestingly, this structural phase change is accompanied by the opening of an electronic band gap so that FeS also experiences a metal-insulator transition at T_α .

Previous studies debated without a clear conclusion whether the troilite phase of FeS is ferroelectric or not [11–17]. This argument was questioned because of the loss of the space inversion center symmetry during the troilite phase transition (the $P\bar{6}2c$ space group is noncentrosymmetric) and also because electrical studies measured a ferroelectric polarization in this crystal [15,18], though no full evidence of ferroelectricity has been established [11,13–17]. In addition, a very recent study also observed a possible onset of a superconducting phase in troilite FeS from a meteoritic sample at a temperature as high as 117 K [19]. FeS has, then, unique multifunctional properties of tremendous potential for technological applications, with

the possibility of obtaining samples with relatively cheap techniques directly from Earth's crust and meteorites.

In this Letter, we cast light on the structural and magnetoelectric properties of troilite FeS through first-principles studies. The analysis of the phonon band structure of the high symmetry phase allows us to prove that FeS is not ferroelectric but nevertheless is piezoelectric and magnetoelectric. We show that the structural transition is driven by a zone boundary instability that couples to a zone center mode, which breaks the space inversion symmetry, but without inducing an overall polarization. While ferroelectricity is not induced, we prove that the crystallographic and AFM symmetries allow for magnetoelectricity. Our analysis of the magnetoelectric properties shows that the amplitude of the response is about 2 times larger than Cr_2O_3 , where the spin-up and -down channels can be seen as electrically polarized in opposite directions and thus at the source of magnetoelectric monopoles [20].

FeS is not ferroelectric or multiferroic.—In this first section we propose elucidating the ferroelectric character of the room-temperature phase of FeS. The troilite phase of FeS is found experimentally to crystallize in the hexagonal $P\bar{6}2c$ space group with 12 Fe and 12 S atoms in the unit cell [see Figs. 1(a) and 1(b)] and it is a semiconductor with a small band gap of about 0.04 eV at room temperature. We emphasize that this gap value was measured on Fe-deficient samples, namely, $\text{Fe}_{0.996}\text{S}$, since Fe-chalcogenides often show Fe vacancies [21,22]. For these reasons, it is difficult to make a quantitative comparison between the calculated and experimental values. The Fe atoms order antiferromagnetically with spins collinearly aligned along the c axis, where the magnetic structure can be seen as alternating planes of spin-up and spin-down along the c direction [see Fig. 1(c)]. Performing a full-cell relaxation from first-principles calculations without any Hubbard U correction on the Fe- d orbitals [23], we recover the insulating state with the generalized gradient approximation (GGA)

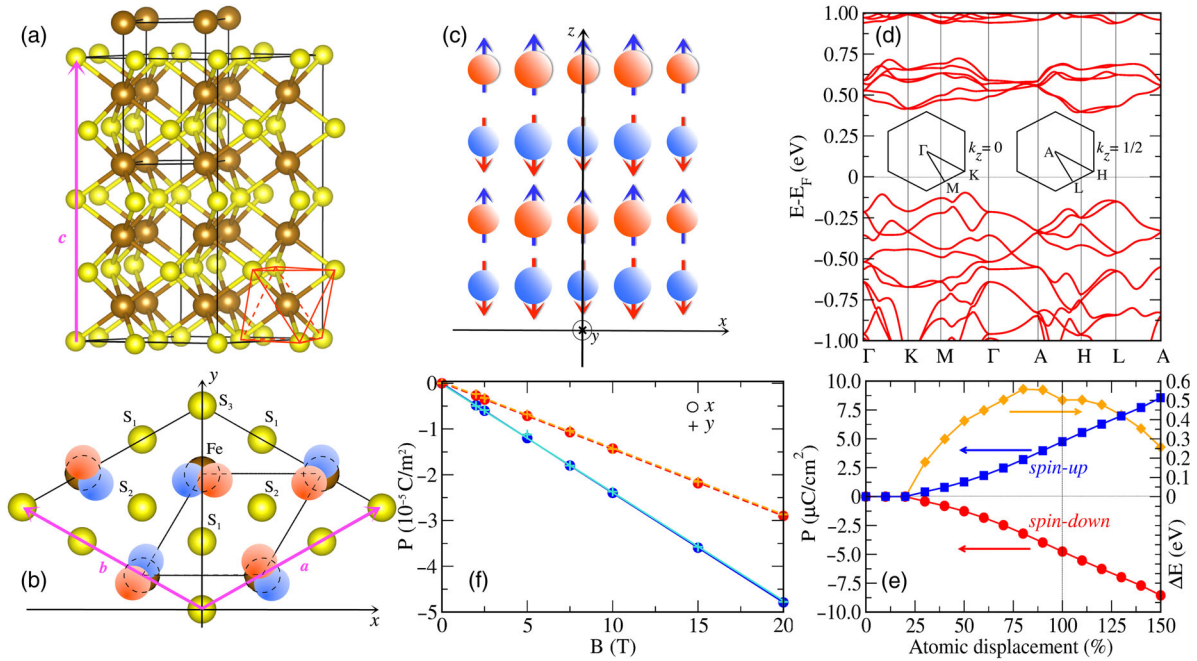


FIG. 1. (a) Schematic view of the troilite cell (Fe, brown spheres, S, yellow spheres). The smaller cell defined by black lines is relative to the high symmetry $P6_3/mmc$ phase. The red lines highlight the octahedral coordination of one Fe. (b) Top view of the troilite cell where the Fe and the S are in the high symmetry positions. The blue and red circles (distinguishing two different Fe planes along the c axis) represent the displacement of the Fe atoms away from their initial positions (the dashed circles). (c) Fe AFM arrangement. Red and blue highlight different Fe spin planes (the S atoms are not shown). (d) Electronic band structure for the $P6_2c$ phase, with a top view of the $k_z = 0$ and $k_z = 1/2$ Brillouin zone planes. (e) Spin-up (blue squares) and spin-down (red circles) contributions to the electric polarization and energy gap (the orange diamonds) as a function of the fraction of the atomic distortions between the ground state $P6_2c$ (100%, dashed line) and $P6_3/mmc$ (0%) phases. (f) Electric polarization as a function of an applied magnetic field along the x (circles) and y (plus signs) directions. Solid lines represent the total contribution and a dashed line the electronic one.

exchange-correlation functionals, but not with the local density approximation. Over the different approximations, we found that the GGA Perdew-Burke-Ernzerhof (PBE) functional with $U = 1$ eV gives the best agreement with the experimental results [23] for the structural parameters. In the following, we will present results within this approximation, unless otherwise stated. We found that the ferromagnetic (FM) order is 10 meV higher in energy than the AFM one and that our noncollinear calculations stabilize the out-of-plane alignment of the spins with no canting, which is in agreement with experimental observations [40]. In Fig. 1(d), we report the electronic band structure of the relaxed $P6_2c$ phase around the last occupied bands. We found an indirect band gap of 0.49 eV, which is one order of magnitude larger than the experimental gap but in agreement with previous calculations [41]. We note that the overestimation of the band gap can originate from the exchange-correlation approximation used in our density functional theory (DFT) simulations, but also from experimental band gap underestimation due to the presence of defects or off stoichiometry, as discussed above [15,22]. Regarding the character of the bands in Fig. 1(c), we remark that close to the band gap the bands are mostly of Fe- d character, with

low weight S- p bands [23]. This orbital character of the band structure, also found in the metallic FeS high symmetry phase (see below), is typical of iron-based superconductors [42], and it might be the source of the recent observation of a possible superconducting transition in troilite FeS [19]. Nevertheless, while we do not observe metallicity in the troilite FeS ground state, we argue that the source of a superconducting phase might come from vacancies and polarons, as observed, for example, in WO_3 [43].

To understand whether this alloy has a ferroelectric polarization in its ground state, we performed Berry phase calculations to compute the polarization in the $P6_2c$ phase, and we found that the total polarization is zero. However, when decomposing the spin channel contributions to the polarization, we found an absolute value of about $5 \mu\text{C}/\text{cm}^2$ for each spin direction with opposite sign; therefore, the total polarization is zero. To exemplify this effect, we computed (within the collinear magnetic scheme) the spin-up and -down electric polarizations at different amplitudes of the pattern of displacements that drives FeS from the $P6_3/mmc$ phase to the $P6_2c$ phase; we show the results in Fig. 1(e). Interestingly, from 0% to 25% of distortion, no electric polarization develops in the two spin

channels. The system is still metallic in this range of distortions [see Fig. 1(e) for the gap versus the amplitude of the distortion], forbidding any polarization onset. Beyond 25% of distortion, the band gap opens and an electric polarization develops in each spin channel, but with opposite directions.

Using a classical picture, the polarization corresponds to the integration of the charge times the position operator \mathbf{r} . Within the DFT scheme, it can be expressed through the density times the position operator: $\rho(\mathbf{r}) \cdot \mathbf{r}$, where $\rho(\mathbf{r}) = \rho^\uparrow(\mathbf{r}) + \rho^\downarrow(\mathbf{r})$, in terms of spin-up $\rho^\uparrow(\mathbf{r})$ and spin-down $\rho^\downarrow(\mathbf{r})$ contributions. On the other hand, replacing the charge density $\rho(\mathbf{r})$ by the magnetization density $m(\mathbf{r}) = [\rho^\uparrow(\mathbf{r}) - \rho^\downarrow(\mathbf{r})]$, we obtain the definition of the magnetoelectric monopole, A , which is given by the space integration of $m(\mathbf{r}) \cdot \mathbf{r}$, similarly to the electric polarization [20]. Interestingly, we see that in FeS the electric polarization is zero, but it has a nonzero magnetoelectric monopolarization $A = 5.9 \times 10^{-3} \mu_B/\text{\AA}^2$, which means that it is not ferroelectric but is nevertheless magnetoelectric.

Magnetoelectricity is a spin-orbit driven crystal response (when disregarding exchange-striction effects) and it is observed either by a magnetic field induced electric polarization or by an electric field induced magnetization [44]. In order to estimate the amplitude of the magnetoelectric response, we made noncollinear calculations with the spin-orbit interaction and performed a full relaxation under a finite magnetic field and computed the induced polarization [23]. We present these results in Fig. 1(f), where we show the total induced polarization and its electronic contribution versus the amplitude of the magnetic field. The electronic contribution is obtained by applying the field without letting the atoms relax. In this way, only the electrons respond to the field (clamped ions or high frequency response [45]). From Fig. 1(f), we see that applied magnetic fields along the x and y directions induce an electric polarization in the same direction, while we do not see any induced polarization when the field is applied in the z direction (not shown). This behavior can be understood from simple arguments: the application of a Zeeman magnetic field parallel to the magnetic moments at 0 K will not induce any response besides a phase transition from AFM to FM order at large field amplitudes since the system is collinear with spins along the z direction. In addition, the induced responses along the x and y directions are identical [we show the response with a field along the x direction only on Fig. 1(f) for clarity] and linear. The magnetoelectric coefficients are thus simply given by the slope of these curves, and we found that $\alpha_{xx}^{\text{tot}} \approx \alpha_{yy}^{\text{tot}} = -3.00$ ps/m. We checked the U and J parameter dependence of α_{xx} and α_{yy} and we observed values going from -3 to -6 ps/m [23]. The magnetoelectric response of FeS is thus about 2 times larger than the one reported for Cr_2O_3 [45–47]. The electronic contribution to the response gives

$\alpha_{xx}^{\text{el}} \approx \alpha_{yy}^{\text{el}} = -1.83$ ps/m, which represents 61% of the total response. The electronic magnetoelectric response is thus large in FeS and it is more important than the one reported in Cr_2O_3 , where the electronic contribution represents about 25% of the total response [45]. This effect can be caused by the vicinity of a metallic phase, which will drive higher high frequency responses of the electrons [23].

Other related quantities to magnetoelectric crystals are the magnetic effective charges, which represent the change of magnetization against atomic displacement [46,48]. We calculated these magnetic effective charges in FeS and found that the largest components are $Z_{xx}^M = Z_{xz}^M = -Z_{yx}^M = 0.1 \mu_B/\text{\AA}$. Interestingly, these values are 2 times larger than those reported in Cr_2O_3 [48] and are thus in agreement with the amplitude of the magnetoelectric response.

We note that a previous study by Li and Franzen [17] proposed attributing the ferroelectric phase of FeS to being a polar subgroup of the $P\bar{6}2_c$ phase (the $P31c$ space group) in which a polar mode would induce a ferroelectric phase transition in the troilite phase. We explored the possibility of a $P31c$ polar phase by performing two tests: (i) condensing the polar mode in the $P\bar{6}2_c$ and relaxing the structure to see whether a lower energy polar phase can be reached and (ii) performing phonon calculations in the $P\bar{6}2_c$ phase to see if a polar unstable mode is present. We find that both tests contraindicate the existence of a $P31c$ polar phase. In (i) the full relaxation drives the system back to the $P\bar{6}2_c$ phase without any remaining polarization or gain of energy. In (ii) we do not find any unstable or soft mode in the $P\bar{6}2_c$ phase. These tests show that the troilite phase is at least locally stable against atomic and strain distortions.

From our DFT calculations, we are thus able to conclude that the troilite phase of FeS is not ferroelectric but is a new room-temperature magnetoelectric candidate, a sought after property of the last decade [44].

Microscopic origin and symmetry analysis.—To understand the phase transitions that occur in FeS and the microscopic origin of its magnetoelectric phase, we analyzed the electronic and vibrational properties of the high temperature $P6_3/mmc$ phase. As for the low symmetry phase, the GGA PBE approximation with $U = 1$ eV gives the best agreement on the relaxed structure against the experimental values [23].

In Fig. 2(a), we report on the electronic band structure of the $P6_3/mmc$ phase, where we recover the aforementioned property of the mostly Fe- d character of the bands around the Fermi level, with the interesting difference that the system is metallic, as observed experimentally at high temperature in this phase. In Fig. 2(b), we present the phonon dispersion curves of the $P6_3/mmc$ phase. These dispersions show the presence of several unstable phonon branches [imaginary frequencies plotted as negative values on Fig. 2(b)] at the zone boundary K , M , H , and L points.

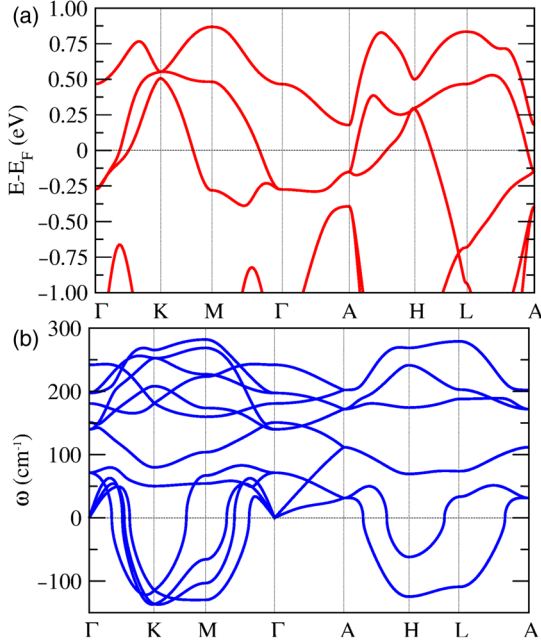


FIG. 2. (a) Electronic band structure and (b) phonon dispersion curves including the total and atom-projected density of states of the high symmetry $P6_3/mmc$ FeS phase. The special k points in the hexagonal Brillouin zone are (in reduced coordinates) $\Gamma(0, 0, 0)$, $K(\frac{1}{3}, \frac{1}{3}, 0)$, $M(\frac{1}{2}, 0, 0)$, $A(0, 0, \frac{1}{2})$, $H(\frac{1}{3}, \frac{1}{3}, \frac{1}{2})$, $L(\frac{1}{2}, 0, \frac{1}{2})$.

This means that the $P6_3/mmc$ phase is unstable over several types of atomic patterns of distortions. The strongest instabilities are observed at the K point with an irreducible representation (irrep.) K_5 ($138i \text{ cm}^{-1}$), at the M point with an M_2^- irrep. ($131i \text{ cm}^{-1}$), at the H point with an H_2 irrep. ($126i \text{ cm}^{-1}$), and at the L point with an L_1 irrep. ($111i \text{ cm}^{-1}$). We remark that the H_2 irrep. alone gives the subgroup $P\bar{6}2_c$ (see Table I), which is the ground state space group of the magnetoelectric troilite phase. This suggests that the condensation of the H_2 unstable mode in the $P6_3/mmc$ phase would directly drive the system to its ground state. We thus condensed the H_2 mode in the $P6_3/mmc$ phase, performed a full relaxation of the cell, and, indeed, obtained the $P\bar{6}2_c$ ground state phase with the same energy as the one we discussed in the previous section (confirming that the two phases are identical). We would thus conclude *a priori* that the H_2 mode alone is at the origin of the troilite phase. To check this hypothesis, we

performed a symmetry adapted mode decomposition of the $P\bar{6}2_c$ phase against the $P6_3/mmc$ phase using AMPLIMODES software [49]; we present the results in Table I. Interestingly, we observe that the H_2 mode is certainly contributing the most to the distortions (1.46 \AA), but we also observe the unstable K_5 mode and the stable Γ_4^- mode—contributing 0.53 and 0.18 \AA , respectively. This indicates that the $P\bar{6}2_c$ is driven by the H_2 unstable mode, but its condensation allows the development of the additional K_5 and Γ_4^- modes. These mode combinations can be explained by symmetry analysis: if one expands the energy with respect to the H_2 , K_5 , and Γ_4^- mode distortions, it must respect the invariance of the energy with respect to the symmetries of the $P6_3/mmc$ phase. If we consider the H_2 domain reported in Table I, we find the terms $a \times b^2$ and $c \times b^2$ at the third order, with a and c being the amplitudes of the Γ_4^- and K_5 modes, respectively (see Table I). The H_2 mode drives the Γ_4^- and K_5 modes through an improper coupling in a similar way to the trimerization observed in YMnO_3 [50,51] and in MoS_2 [52]. We note that Γ_4^- is a mode that breaks the space inversion symmetry, but it is not infrared active and is thus nonpolar, confirming that the $P\bar{6}2_c$ phase is not ferroelectric. Regarding the magnetic space group, we obtain the $P\bar{6}'2c'$ magnetic point group when the spins lie along the c direction, which allows for a diagonal magnetoelectric tensor $\alpha_{xx} = \alpha_{yy} \neq \alpha_{zz}$. The symmetry analysis confirms that the troilite phase is magnetoelectric, as obtained from our DFT calculations.

Discussion.—In spite of the last decade of effort in search of the magnetoelectric materials influenced by the exciting possibilities brought on by spintronic applications, we are still facing a scarcity of room-temperature crystal candidates [53]. While most studies in the field of magnetoelectrics have focused on oxide materials, here we showed that the common iron sulphide troilite mineral found on Earth, the Moon, and Mars and in meteors is magnetoelectric up to $\sim 415 \text{ K}$. Our DFT calculations demonstrate that the amplitude of the magnetoelectric response of FeS is of the same order as Cr_2O_3 . We also showed that the room-temperature phase comes from a displacive phase transition in which a zone boundary soft mode condenses in the high temperature metallic phase, driving the opening of the band gap. Additionally, our electronic structure analysis pointed toward a similar electronic structure character of FeS as the one observed in the Fe-based superconductors, which

TABLE I. Symmetry adapted mode decomposition of the relaxed $P\bar{6}2_c$ phase with respect to the $P6_3/mmc$ phase, as obtained from the AMPLIMODES software [49]. From the left to right columns, we show the k -vector coordinates, the irreducible representation of the symmetry adapted mode, the direction of the mode condensation, the corresponding subgroup, and the amplitude of the distortion.

k vector	Irreducible representation	Direction	Subgroup	Amplitude (\AA)
(0,0,0)	Γ_4^-	(a)	$P\bar{6}m2$ (187)	0.18
$(\frac{1}{3}, \frac{1}{3}, \frac{1}{2})$	H_2	$(-\sqrt{2}/2b, -1/2b, 0, 0)$	$P\bar{6}2_c$ (190)	1.46
$(\frac{1}{3}, \frac{1}{3}, 0)$	K_5	$(0, 0, -1/2c, -\sqrt{2}/2c)$	$P\bar{6}2_m$ (189)	0.53

might explain the recent observation of a possible superconducting phase at 117 K. We also highlighted that a diagonal magnetoelectric can be identified at the collinear level through a spin channel decomposition of the polarization where opposite values sum up in the calculation of the magnetoelectric monopolarization. These results are thus of primary importance in a widespread field of research, going from Earth and planetary studies to multifunctional applications, and further theoretical and experimental studies of FeS are highly appealing.

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