Potential Resolution to the “Doping Puzzle” in Iron Pyrite: 
Carrier Type Determination by Hall Effect and Thermopower

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Pyrite FeS₂ has outstanding potential as an earth-abundant, low-cost, non-toxic photovoltaic, but underperforms dramatically in solar cells. While the full reasons for this are not clear, one certain factor is the inability to understand and control doping in FeS₂. This is exemplified by the widely accepted but unexplained observation that unintentionally-doped FeS₂ single crystals are predominantly n-type, whereas thin films are p-type. Here we provide a potential resolution to this “doping puzzle”, arrived at via Hall effect, thermopower, and resistivity measurements on a large set of FeS₂ single crystals and films that span five orders of magnitude in mobility. The results reveal three main findings. First, in addition to crystals, the highest mobility thin films in this study are shown to be definitively n-type, from both Hall effect and thermopower. Second, as mobility decreases an apparent crossover to p-type occurs, first in thermopower, then in Hall measurements. This can be understood, however, in terms of the crossover from diffusive to hopping transport that is clearly reflected in resistivity. Third, universal behavior is found for both crystals and films, suggesting a common n-dopant, possibly sulfur vacancies. We thus argue that n-type doping is facile in FeS₂ films, that apparent p-type behavior in low mobility samples can be an artifact of hopping, and that the prevailing notion of predominantly p-type films must be revised. These conclusions have deep implications, both for interpretation of prior work on FeS₂ solar cells and for the design of future studies.

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I. Introduction

Pyrite structure FeS$_2$ has long been acknowledged as a semiconductor with significant potential as a photovoltaic (PV). A substantial effort to develop pyrite PV began in the mid 1980’s, stimulated by pyrite’s useful energy gap ($E_g \approx 0.95$ eV) and outstanding visible absorption coefficient ($\alpha > 10^5$ cm$^{-1}$ above 1.2-1.4 eV), which render a 100-nm-thick film capable of absorbing >90 % of the sun’s light.$^1$ Electron mobilities over 300 cm$^2$V$^{-1}$s$^{-1}$ and minority carrier diffusion lengths of 100-1000 nm were also demonstrated in pyrite crystals,$^1$ but the FeS$_2$ PV effort was nevertheless unsuccessful. Various forms of Schottky and photoelectrochemical solar cells were fabricated from both thin films and bulk crystals, and while the high internal quantum efficiencies and short circuit current densities were promising, open circuit voltages ($V_{oc}$) remained below 0.2 V, less than 20 % of $E_g$.$^1$ Power conversion efficiencies in FeS$_2$-based solar cells thus never exceeded 3 %,$^1$ an order of magnitude below the Shockley-Queisser limit. As other thin film PV materials such as CdTe and Cu(In,Ga)Se$_2$ began to show promise in the mid 1990’s,$^2$ interest in pyrite PV waned.

Recently, however, a second wave of interest in FeS$_2$ for PV applications has emerged.$^{3-23}$ This is in large part due to the identification of sulfides, particularly FeS$_2$, as near-ideal choices for large-scale deployment of solar cells from the perspectives of earth abundance, toxicity, and cost.$^3$ Sulfur is a waste product, while iron remains one of the cheaper metallic elements to recover from ore. A significant number of researchers are thus applying fresh approaches to the synthesis, characterization, and property measurement of FeS$_2$-based materials and devices.$^{3-23}$

A notable feature of this second wave of effort with FeS$_2$ is a focus on fundamental problems, as opposed to the device efforts that have proven unsuccessful.$^{1-13}$ Three main issues have emerged:
The origin of the low $V_{oc}$ in pyrite-based solar cells;\textsuperscript{1,11,14,17,18,20,24,25} questions regarding phase purity, defects, and stoichiometry;\textsuperscript{1,6-12,17,18,20,21,24,25} and the understanding and control of doping.\textsuperscript{1,6,7,9-12,17,18,20-22,25} While much remains to be done to address these complex (and often inter-related) issues, significant progress has recently been made, particularly with the first two. Careful studies of $n$-type pyrite single crystals have clearly elucidated surface electronic properties that differ significantly from the bulk, including conductive surface layers,\textsuperscript{20} a high density of surface acceptors,\textsuperscript{18} and even surface inversion.\textsuperscript{20} Such phenomena offer hypotheses for the low $V_{oc}$ in pyrite, which will no doubt be explored. Similar progress has been made with phase purity and stoichiometry. Despite suggestions that secondary phases such as pyrrhotite Fe$_{1-x}$S or marcasite FeS$_2$ could be deleterious and widespread,\textsuperscript{8} several studies have established phase-pure pyrite crystals,\textsuperscript{18,20,21} films,\textsuperscript{9,12,19,21} and nanostructures,\textsuperscript{11,15,17,22} also clarifying stability limits.\textsuperscript{21} In terms of stoichiometry, evidence for S vacancies ($V_S$) as the origin of $n$-type behavior in unintentionally-doped crystals is also accumulating.\textsuperscript{18,20}

Progress with the third issue, however (\textit{i.e.}, control and understanding of doping in pyrite), has not been so forthcoming. We note first in this respect that recent high purity, unintentionally-doped pyrite single crystals have been shown to be unambiguously $n$-type,\textsuperscript{18,20} with $V_S$ as the suspected dopants,\textsuperscript{18,20} consistent with the large majority of the literature. Specifically, unintentionally-doped pyrite crystals are overwhelmingly found from Hall effect measurements to be $n$-type. This is illustrated in Figure 1(a), which plots the magnitude of the room temperature Hall coefficient, $R_H$, as a function of the carrier mobility, $\mu$, from literature reports on both pyrite films and bulk crystals.\textsuperscript{18,20,22,23,26-30} On this plot blue symbols are for electron-like (\textit{i.e.}, apparently $n$-type ($R_H < 0$)) behavior, whereas red symbols are used for hole-like (\textit{i.e.}, apparently $p$-type ($R_H > 0$)) behavior. For bulk crystals, which typically have relatively high $\mu$ and thus
populate the top right corner of Figure 1(a), \( n \)-type majority carriers prevail. The small number of counter-examples often occur in naturally-occurring crystals, where impurities are a concern, or in cases where the Hall effect disagrees with the other premier means to determine the sign of majority carriers, \( i.e., \) thermopower, as returned to below.\textsuperscript{26,29}

The complexity arises when considering unintentionally-doped \textit{thin films} of FeS\(_2\). The first point here is that the electronic quality of pyrite thin films, as judged from \( \mu \), is highly variable. Thin film mobilities up to 200-280 cm\(^2\)V\(^-1\)s\(^-1\) have been claimed \textit{via} spray pyrolysis\textsuperscript{27} and chemical vapor deposition,\textsuperscript{31} with an additional handful of other values in the 2 – 80 cm\(^2\)V\(^-1\)s\(^-1\) range.\textsuperscript{5,19,28,29,30} In the great majority of cases, however, pyrite films have \( \mu \) sufficiently low that they cannot be determined straightforwardly from Hall measurements.\textsuperscript{9,12,22,23,28,29,32,33} Some ubiquitous uncontrolled impurity, generating high doping and low \( \mu \) in pyrite films, is thus often hypothesized, although a high \( V_S \) density also seems plausible.\textsuperscript{7,22,32-34} This situation explains the modest number of thin film data points in Figure 1(a), exacerbated by the fact that raw data (\textit{i.e.,} Hall coefficient, voltage, or resistance) are often not reported. Notably, and in contrast to bulk crystals, what data are available suggest \textit{p}-type behavior in films. Specifically, as shown in Figure 1(a), while the Hall effect has been reported to indicate either \( n \)-\textsuperscript{29} or \textit{p}-type\textsuperscript{19,22,23,27,28,30} majority carriers in FeS\(_2\) films, \textit{p}-type behavior apparently dominates.

Similar conclusions can be reached from thermopower or Seebeck coefficient (\( S \)) measurements, often employed when the Hall effect is difficult to measure due to low \( \mu \).\textsuperscript{29} As shown in Figure 1(b), such measurements confirm \( n \)-type behavior (\textit{i.e.,} \( S < 0 \), blue points) in bulk single crystals,\textsuperscript{26} but appear to support \textit{p}-type conduction (\textit{i.e.,} \( S > 0 \), red points) in films.\textsuperscript{28,29} The number of data points in Figure 1(b) is not impressive, however, due to the large fraction of
cases in the pyrite film literature where “qualitative thermopower” or “hot point probe” measurements are performed. In those measurements, only the sign of $S$ is recorded, and thus no data points can be plotted in Figure 1(b). As shown in Table I these “qualitative thermopower” or “hot point probe” measurements (where a carrier type from thermopower is listed but with no value for $S$) are in almost universal support of $p$-type conduction in low mobility FeS$_2$ thin films. On aggregate, the observations summarized in Figure 1 and Table I have led to the now widely accepted notion that unintentionally-doped bulk single crystals of pyrite are $n$-type, whereas unintentionally-doped thin films are $p$-type. While some ubiquitous unintentionally-introduced thin film defect or impurity is often cited, the fundamental explanation remains unknown. It is additionally worthwhile to highlight that there are a number of cases, specifically in low $\mu$ samples, where $R_H$ and $S$ disagree on the sign of the majority carriers, as shown in Figure 1(b) and Table I (highlighted in orange), another unresolved issue in pyrite.

Herein we provide a potential resolution to the “doping puzzle” in pyrite FeS$_2$, i.e., the apparent inversion in sign of the majority carriers from single crystals to films. We do this by comparing 300 K measurements of $R_H$ and $S$ on a large set (~100 samples) of unintentionally-doped pyrite single crystals and polycrystalline films, spanning five orders-of-magnitude in apparent $\mu$. Consistent with prior work, the single crystals are found to be unambiguously $n$-type, from both $R_H$ and $S$. In stark contrast to the prevailing view, however, the highest mobility thin films in this study are also shown to be unambiguously $n$-type, confirmed by $R_H$ and $S$. As the $\mu$ of the thin films decreases an apparent transition from electron-like to hole-like majority carriers takes place, first in $S$ and then in $R_H$. While this could be naively interpreted in terms of an $n \rightarrow p$ crossover, we find that the crossover points in $R_H$ and $S$ are well correlated with a crossover from
diffusive to hopping transport. This crossover, which is known to be capable of inverting the sign of $R_H$ and $S$ in disordered semiconductors, is tracked in detail via temperature-dependent resistivity measurements. We thus conclude that apparent $p$-type behavior in low mobility FeS$_2$ thin films, whether indicated by $R_H$ or $S$, can easily be an artifact of hopping. We contend that such films are actually $n$-type, much like higher $\mu$ films, challenging the belief that pyrite thin films are predominantly $p$-type and providing a potential resolution to the pyrite “doping puzzle”.

II. Experimental Details

II.A Materials synthesis and characterization. Pyrite FeS$_2$ thin films were synthesized by ex situ sulfidation of Fe, as described in greater detail in prior work.$^{16,21}$ Briefly, Fe thin films (33 nm thick) were first deposited on chemically-cleaned substrates by either high vacuum DC magnetron sputtering or ultra-high vacuum electron-beam evaporation. Sputtering was done at $\sim$1 Å/s from targets of nominal purity 99.9 or 99.99 %, in 2.3 mTorr of Ar, in a system with a base pressure in the $10^{-8}$ Torr range. The deposition temperatures were either ambient or 300 °C. Electron beam evaporation was done at 0.5 Å/s from source material of nominal purity 99.99 %, at ambient substrate temperature, in a system with a base pressure in the $10^{-10}$ Torr range. A wide variety of substrates were explored, including Al$_2$O$_3$(0001), soda lime glass, pyrex glass, crystalline quartz (SiO$_2$), fused quartz (SiO$_2$), Si(001)/a-Si-N, and MgF$_2$(001). As described earlier,$^{16,21}$ sulfidation was achieved in sealed and evacuated ($1\times10^{-6}$ Torr) quartz tubes containing 1 mg of 99.999 % pure S, at temperatures of 200 to 600 °C. The majority of the films were sulfidized at 600 °C; some were annealed at temperatures $<400$ °C.

Pyrite FeS$_2$ single crystals were grown via the chemical vapor transport (CVT) method, as also described earlier.$^{21}$ This employed a sealed and evacuated ($1\times10^{-6}$ Torr) quartz vessel in a two-
zone tube furnace, loaded with 2.2 g of FeS$_2$ powder (99.9 %), 100 mg of FeBr$_2$ (99.999 %) transport agent, and 580 mg of S powder (99.999 %). After an initial 3 day period with an inverted temperature gradient to “clean” the growth zone, hot and cold zone temperatures were set to 670 and 590 °C, respectively, for around 20 days. This resulted in crystals up to 360 mg, with approximately 5 mm (111) facets.

Films and crystals were characterized structurally and chemically via wide-angle X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), depth-profiled Auger electron spectroscopy (AES), superconducting quantum interference device (SQUID) magnetometry, and optical absorption spectroscopy. XRD on crystals was performed on a Bruker-AXS D5005 system (powdered crystals) and a Panalytical X-Pert Pro high resolution diffractometer (bulk crystals), using Cu K$_\alpha$ radiation. Films were measured using Bruker-AXS PLATFORM and Bruker D8 Discover systems using area detectors, again with Cu K$_\alpha$. Raman spectroscopy employed a WiTec alpha300R confocal microscope equipped with a UHTS 300 spectrometer and a DV401 CCD detector, SEM and EDS a JEOL field-emission microscope (operated at 15 kV) with a Thermo-Noran Vantage X-ray detector, and AES a Physical Electronics Model 545 with a differentially-pumped Ar sputter source. SQUID magnetometry was done at 200 K in a Quantum Design MPMS XL7, and optical absorption was done in a Cary 5000UV-Vis-NIR spectrophotometer in dual beam mode. As discussed in more detail below (Section III), a summary of characterization results on films and crystals is provided in Supplemental Material (Figures S1, S2).

II.B Electronic and thermal transport measurements. Temperature-dependent resistivity measurements were made in a Janis cryostat and/or a Quantum Design PPMS, between 2 and
300 K. Indium contacts were employed in a van der Pauw configuration, using both AC (13.7 Hz) and DC excitation depending on the absolute resistance. Extensive checks of contact resistance, current-voltage curves, and AC resistance-current curves were made to ensure Ohmic response and the absence of self-heating. Hall effect measurements were made at 300 K, in applied magnetic fields to ± 90 kOe, using phase-sensitive AC excitation and optimized temperature stability of ± 10 mK. Seebeck coefficient (thermopower) measurements were performed in a vacuum of 10 mTorr in a home-built system at 315 K. FeS₂ samples with coplanar 4-mm-gap electrodes were placed across two thermally isolated Cu blocks, also separated by 4 mm. The temperature of each block was controlled independently (to ± 50 mK) with a dual-channel temperature controller, using thermocouples anchored on each block. As different block temperatures were regulated, the induced thermoelectric voltage was measured via Cu leads attached to the blocks. The Seebeck coefficient was then obtained from the slope of thermoelectric voltage vs. temperature gradient curves, which extended to 16 K temperature differences. As discussed in more detail below (Section III.A), different substrates were employed (see Supplemental Material Figure S3⁴⁰) to rule out substrate effects as the origin of Seebeck coefficient sign inversion. Any contribution to $S$ from the contacts and leads was also investigated, by measuring the thermopower of the electrode metal deposited on a substrate with no pyrite film. The observed $S$ was $n$-type and on the order of 0.1-1 $\mu$V/K, in contrast to the over 10 times higher $n$- or $p$-type $S$ of the polycrystalline FeS₂ films.

III. Results and Analysis

Extensive structural and chemical characterization of our unintentionally-doped pyrite bulk single crystals and polycrystalline thin films has been provided in prior publications.¹⁶,²¹ In Supplemental Material Figures S1 and S2⁴⁰ we provide a brief summary of these characterization
results. In Figure S1, for single crystals, optical imaging, XRD, Raman spectroscopy, and EDS data are shown, confirming the single crystal, single phase, stoichiometric nature of the samples. In Figure S2, for polycrystalline thin films, XRD, Raman spectroscopy, EDS, depth-profiled AES, SQUID magnetometry, optical absorption, and SEM data are shown. These data confirm single-phase, close to stoichiometric, large grain polycrystalline films with the expected optical absorption properties.

III.A Room temperature Hall effect and thermopower measurements. We first focus on 300 K $R_H$ and $S$ measurements performed on bulk single crystals and thin films with a wide range of $\mu$. To this end, Figure 2(a,b) plots $R_H$ and $S$ as a function of the apparent Hall mobility, $\mu_H$, following identical conventions to Figure 1, i.e., blue points for electron-like signs, red points for hole-like signs, and solid triangles and open diamonds for films and crystals, respectively. We explicitly refer to $\mu_H$ as an apparent mobility because, as we shall see, some of these $\mu_H$ values are sufficiently low that diffusive transport cannot be assumed, and naïve interpretation of $R_H$ is thus hazardous; this will form a key point of our work. The first points to note about Figure 2 are the wide range of $\mu_H$ probed (five orders of magnitude) and the substantial reduction in scatter compared to Figure 1. Crystals and films appear to exhibit universal behavior, in fact. Considering first the single crystals, the results are simple, and as expected. These crystals have relatively high $\mu_H$ (40-250 cm$^2$V$^{-1}$s$^{-1}$) with clearly electron-like $R_H$ and $S$. Representative raw data to support this are provided in Figure 3(a,b), where the Hall resistivity ($\rho_{xy}$) is plotted vs. applied magnetic field ($H$) (yielding $R_H = d\rho_{xy}/d\mu_0H$), and the negative thermovoltage (-$\Delta V$) is plotted vs. temperature difference ($\Delta T$) (yielding $S = -\Delta V/\Delta T$). (-$\Delta V$ is plotted to facilitate comparison between Hall and thermopower data). For the representative crystal shown, the slope
of both curves is large and negative, indicating $n$-type majority carriers. The Hall response is also linear at all $H$ probed, with no evidence of a second carrier type.

The results for polycrystalline thin films are more interesting. As shown in Figure 2, the films studied in this work span a range in $\mu_H$ from almost 10 cm$^2$V$^{-1}$s$^{-1}$ down to $\sim$10$^{-3}$ cm$^2$V$^{-1}$s$^{-1}$. There are two important points to emphasize about this. First, while $R_H$ and $S$ are relatively straightforward to measure in high $\mu_H$ samples, this is not so at the low $\mu_H$ end of this range. In this regime care must be taken to accurately determine very low $R_H$, including AC detection, a wide $H$ range (-90 to + 90 kOe in this case), high $T$ stability ($\pm$ 10 mK at 300 K in this case), and minimization of noise, drift, and contact resistance. Interpretation of low $R_H$ is also challenging, as diffusive transport can no longer be assumed. For thermopower measurements, contributions from the leads, and from substrate effects, must be considered as $S$ decreases, as discussed above (Section II.B) and in Supplemental Material Figure S3. Interpretation of low $S$ values is also challenging, again due to the possibility of non-diffusive transport. Second, it must be emphasized that complete control over the $\mu_H$ of polycrystalline thin films by tuning ex situ sulfidation was not achieved in this work. The wide range in $\mu_H$ in Figure 2 was rather obtained by synthesizing a large quantity of polycrystalline films, which had variable carrier density, and thus $\mu_H$. As detailed above (Section II.A), the films shown in Figure 2 were in fact synthesized on seven different substrates, using two Fe deposition methods, and variable sulfidation temperatures. While control over carrier density was not obtained, as shown in Supplemental Material Figure S4 these films nevertheless exhibit a consistent $\mu_H$-carrier density relation, $\mu_H$ scaling as $n^{-1}$, where $n$ is the Hall electron density.
The films exhibit clear and systematic trends in Figure 2, evidencing three distinct regimes. In Regime I, at $\mu_H > 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, we find, in stark contrast to claims of predominantly $p$-type conduction in pyrite films, *clear electron-like behavior in both $R_H$ (Figure 2(a)) and $S$ (Figure 2(b)).* Raw data to support this are provided in Figure 3(a,b), where Hall and Seebeck data on a representative film with $\mu_H = 2.2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ are shown. While $R_H$ and $S$ are smaller than in single crystals, both $R_H$ and $S$ agree on $n$-type transport in these higher $\mu_H$ films. $\rho_{xy}$ is again linear in $H$. In terms of the *origin* of this behavior, note that higher mobility ($\geq 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) $n$-type films were obtained on a variety of substrates (Si/Si-N, MgF$_2$, soda lime glass, quartz, and Al$_2$O$_3$), meaning that interdiffusion of some donor impurity is an unlikely explanation. Moreover, as shown in Supplemental Material Figure S5, while Co, Ni, and Cu impurities were detected in these films by Secondary Ion Mass Spectrometry (SIMS), many films have $n$ up to 100 times the concentrations of these elements, implicating an intrinsic rather than extrinsic defect as the dominant $n$-dopant. As in single crystals, $V_S$ appears a likely culprit. Regardless of the precise origin, however, what is most important is that the higher $\mu_H$ films in this study are definitively $n$-type, in contrast to the prevailing notion.

At lower $\mu_H$ Regime II is entered ($10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1} < \mu_H < 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), where $R_H$ decreases and maintains an electron-like sign, but both positive and negative signs of $S$ occur (Figure 2(b)), in an apparently chaotic fashion. This is illustrated in Figure 3(c,d) using two representative films, with $\mu_H$ of 0.10 and 0.13 cm$^2$V$^{-1}$s$^{-1}$. Despite their nearly identical $\mu_H$, the former exhibits electron-like $R_H$ and $S$, while the latter shows electron-like $R_H$ and hole-like $S$. As already noted, opposing signs of $R_H$ and $S$ have been sporadically observed before in FeS$_2$, one proposed explanation relying on two-band transport. Below, we will provide an alternative explanation, acknowledging the significance of low $\mu$. As $\mu_H$ decreases further, a final regime of behavior is
found in Figure 2, Regime III, where $\mu_H < 10^{-2}$ cm$^2$V$^{-1}$s$^{-1}$. Here, $R_H$ also inverts sign, both $R_H$ and $S$ suggesting hole-like behavior. This is further illustrated in Figure 3(e,f) where raw $R_H$ and $S$ data are shown for a representative film with a low $\mu_H$ of $10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$. Again, $\rho_{xy}$ is linear in $H$.

It should be emphasized that the basic structural and chemical characterization data on these films reveal no significant differences over the entire span of $\mu_H$ in Figure 2 (see Supplemental Material Figure S6$^{40}$).

**III.B Temperature-dependent electronic transport measurements.** As already noted, a critical issue for the interpretation of Figure 2 is the low $R_H$, $S$, and $\mu_H$ found in the lower left region. While $R_H$ and $S$ in higher $\mu_H$ samples, in which transport is clearly diffusive, are simple to interpret, this is not so at low $\mu_H$ where diffusive band transport can no longer be assumed. In particular, the crossover from diffusive to hopping transport that would be expected in any material as $\mu$ decreases (typically below $\sim 1$ cm$^2$V$^{-1}$s$^{-1}$, notably close to the Regime I / II boundary) is known to suppress $R_H$ and can even invert its sign. Similar complications arise for the interpretation of $S$. It is thus essential to consider Figure 2 alongside data that elucidate the transport mechanism, making temperature-dependent resistivity ($\rho$) measurements indispensable.

Figure 4 shows such data, plotting in the top panels (a-c) $\rho$ (log scale) vs. $T$ for representative samples in each of the regimes shown in Figure 2. This includes a bulk crystal and a high $\mu_H$ (2.2 cm$^2$V$^{-1}$s$^{-1}$) film in Regime I (Figure 4(a)), three intermediate $\mu_H$ (0.03 – 0.13 cm$^2$V$^{-1}$s$^{-1}$) films in Regime II (Figure 4(b)), and a low $\mu_H$ ($10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$) film in Regime III (Figure 4(c)). Additional insight is provided in Figure 3(d-f) which shows the same data on Zabrodskii plots.$^{42}$ These are plots of $\ln W$ vs. $\ln T$, where $W$, the reduced activation energy, is defined as $W = -\frac{d\ln \rho}{d\ln T}$. This linearizes the $\rho = \rho_0\exp(T_0/T)^m$ form typically expected at low $T$ in
semiconductors, where $\rho_0$ is the $T \to \infty$ limit of $\rho$, $T_0$ is a characteristic temperature, and $m$ reveals the conduction mechanism. Briefly, $m = 1$ indicates activated, diffusive transport,\textsuperscript{43} while $m = \frac{1}{2}$ and $\frac{1}{4}$ indicate Efros-Shklovskii\textsuperscript{44} and 3D Mott variable-range hopping (VRH),\textsuperscript{45} respectively. VRH is common in doped semiconductors, Mott VRH applying when the density-of-states (DOS) around the Fermi energy ($E_F$) is approximately constant, Efros-Shklovskii VRH when electron-electron interactions induce a soft-gap in the DOS around $E_F$.\textsuperscript{44,45}

With a mobility of 141 cm$^2$V$^{-1}$s$^{-1}$, conduction in the single crystal shown in Figure 4(a,d) would certainly be expected to be diffusive. This is complicated, however, by the anomalous $T$ dependence in Figure 4(a) (note the inflection around 90 K, also evident in Figure 4(d)), which occurs due to the surface conduction documented by Limpinsel et al.\textsuperscript{20} In essence the insulating FeS$_2$ interior “freezes out” around this $T$, the more conductive surface shunting the current at low $T$. We have made a thorough investigation of this, the results of which will appear elsewhere.\textsuperscript{46}

Moving on to the relatively high $\mu_H$ film in Figure 4(a,d), $\rho$ can be seen to be weakly $T$-dependent. Considering Figure 4(d), a straight line with negative slope (the black dashed line indicates $m = \frac{1}{2}$) is observed at low $T$ (below $\sim$30 K), indicating Efros-Shklovskii VRH. At higher $T$, however, $\ln W$ becomes negative, and increases with $T$. This indicates conduction close to the insulator-metal transition,\textsuperscript{42} certainly not in the hopping regime at 300 K, where the data in Figure 2 were obtained. Both the crystals and films in Regime I are thus clearly in the diffusive transport regime, confirming that $R_H$ and $S$ can be simply interpreted in terms of $n$-type conduction.

Skipping to Regime III, as illustrated in Figure 4(c,f), the situation is different. In this very low apparent $\mu_H$ regime, Figure 4(f) shows adherence to the Efros-Shklovskii form over the entire
range (more than an order of magnitude in $T$ and four orders in $\rho$), indicating that such films are deep in the VRH regime even at 300 K. Regime III in Figure 2, where both $R_H$ and $S$ have hole-like signs, must thus be interpreted with this in mind, as returned to below. The situation at intermediate $\mu_H$, in Regime II, represents a crossover between Regimes I and III. In this region a spectrum of behaviors is found, evolving non-monotonically with $\mu_H$. Three films are thus shown in Figure 4(b,e), representing three distinct behaviors. The behavior of the film with $\mu_H = 0.13$ cm$^2$V$^{-1}$s$^{-1}$ is similar to that seen in Regime III. Efros-Shklovskii VRH is evidenced over the entire $T$ range, indicating that this film is in the hopping regime at 300 K. Vitally, this film (see Figure 3(c,d)) is one in which $R_H$ remains electron-like, while $S$ inverts. On the other hand, the film with $\mu_H = 0.10$ cm$^2$V$^{-1}$s$^{-1}$ has behavior similar to Regime I; Efros-Shklovskii VRH occurs at low $T$, but gives way to diffusive transport by 300 K. In this case (see Figure 3(c,d)), both $R_H$ and $S$ remain electron-like. A final example is provided by the 0.03 cm$^2$V$^{-1}$s$^{-1}$ film in Figure 4(b,e), which, despite the slightly lower $\mu_H$, exhibits simple activation at low $T$ ($i.e., m = 1$) and is clearly not in the Efros-Shklovskii regime at 300 K. This sample also exhibits electron-like $R_H$.

The apparently complicated behavior in Regime II is thus quite straightforward. While some sample-to-sample variation occurs, films exhibiting diffusive transport at 300 K based on $\rho(T)$ invariably display electron-like $R_H$ and $S$. When hopping is active at 300 K, however, a sign reversal occurs, first in $S$. As $\mu_H$ decreases further, into Regime III, both $R_H$ and $S$ invert, generating the behavior shown in Figures 3(e,f) and 4(c,f). This correlation is reinforced for a large number of films in Supplemental Material Figure S7. The occurrence of hopping conduction is thus essential to understand the signs of $R_H$ and $S$, a factor not taken into account in prior explanations based on two-band conduction.
IV. Discussion

We now provide a consistent interpretation of Figures 2-4. Beginning with Regime I, specifically with single crystals, the fact that $\mu_H >> 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, that the Hall effect is linear, and that $\rho(T)$ provides no evidence of hopping at 300 K, clearly indicate that $R_H$ and $S$ can be simply interpreted. We thus apply $R_H = -1/ne$ (where $e$ is the magnitude of the electronic charge (a positive number)), based on diffusive transport with a dominant majority carrier type. Correspondingly, we interpret $S$ via the usual non-degenerate semiconductor approach, $S = -\frac{(k_B/e)[(E_C - E_F)/k_BT + a_c]}{(k_B/e)}$, where $k_B$ is Boltzmann’s constant, $E_C$ is the conduction band onset energy, and $a_c$ is a small constant. Both $R_H$ and $S$ are thus negative, reflecting electrons as majority carriers. This is as expected based on prior work, the $n$-type doping likely being due to $V_S$; future work to definitively establish this would clearly be worthwhile.

Moving on to the films in Regime I, we find $\mu_H \approx 1-10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, with $n \sim 10^{19} \text{ cm}^{-3}$ (Supplemental Material Figure S4). These electron densities are 2-3 orders-of-magnitude higher than in crystals, $\mu_H$ being 1-2 orders of magnitude lower. Even in Regime I our films thus have substantially heavier doping and higher disorder than single crystals. $S$ is also reduced, from the 100-200 $\mu\text{VK}^{-1}$ typical of crystals (Table I, Figures 1 and 2) to $\sim 20 \mu\text{VK}^{-1}$. The latter is in the range typically seen in pyrite films (10-80 $\mu\text{VK}^{-1}$, Table I, Figure 1). Critically, however, $\rho(T)$ again provides no evidence of hopping at 300 K, indicating that $R_H$ and $S$ can be interpreted much as for single crystals. Based on Figure 4(a), degenerate semiconductor transport is a possibility, however, meaning that $S = -\frac{\pi^2}{3}(k_B^2T/e)(dlnD(E)/dE)_{EF}$ may be more appropriate, where $D(E)$ is the available DOS. In any event, negative $R_H$ and $S$ indicates electrons as majority carriers, the major issue being the origin of this $n$-doping. Given that numerous films in this study have $n$ greatly in excess of the concentration of metal impurities (Supplemental
Material Figure S5\textsuperscript{40}, and that Figure 2 suggests universal behavior (\textit{i.e.}, a single $R_{H-n}$ or $\mu_{H} - n$ relationship) for both films and crystals, $V_S$ is again a strong possibility. The $V_S$ density may be difficult to control in FeS$_2$ films, certainly when synthesized by the methods employed here.

In Regime II, $\mu_{H} < 1 \text{ cm}^{2}\text{V}^{-1}\text{s}^{-1}$ is encountered for the first time, hopping transport becoming a possibility. Although not widely discussed in the pyrite literature, the influence of hopping on $R_H$ and $S$ has a long history. Consider first the Hall effect in hopping transport, which was studied in the context of amorphous (a) Si and Ge in the 1970’s. A first surprise was provided by Friedman\textsuperscript{47} in 1971 who showed that even when conduction proceeds by extended states, when these are near the mobility edge, $E_{\mu}$, $R_H$ can be suppressed by an order of magnitude and, most significantly, $R_H$ is always electron-like, even in $p$-type materials. Experiments by Le Comber \textit{et al}.\textsuperscript{48} further revealed a \textit{double} sign reversal, where a-Si films in the hopping regime doped $n$-type (with P) had $R_H > 0$, while films doped $p$-type (with B) had $R_H < 0$. Numerous theoretical works have been devoted to this topic, but it is fraught with complications. The three-site “triads” of Gal’perin \textit{et al}.\textsuperscript{49} are understood to be the elementary sources of the hopping Hall voltage,\textsuperscript{49} but both the magnitude and sign of $R_H$ are difficult to calculate, although the double sign reversal can be qualitatively reproduced.\textsuperscript{49,50} The relevance to low $\mu_{H}$ pyrite films was pointed out in our earlier work,\textsuperscript{16} where an apparent sign reversal in $R_H$ on entry into a regime of a specific type of intergranular hopping, due to nanoscale unreacted Fe clusters, was discovered. In the current work this is seen to be more generally important.

Thermopower in the hopping regime is similarly rich. An important fact, which has again not been widely discussed in the pyrite literature, is that hopping impacts both the magnitude and sign of $S$. In VRH this is because carriers with both positive and negative energies with respect to
$E_F$ contribute to thermopower.$^{51-53}$ $S$ thus vanishes for a DOS symmetric around $E_F$, DOS asymmetry being the essential factor, making sign reversal easily possible. This was handled by Zvyagin and Overhof in the 70’s by writing:$^{51,52}$

$$S = -\frac{k_B}{e} \int_{-W}^{W} \frac{E}{k_BT} N(E) dE / \int_{-W}^{W} N(E) dE$$

(1)

where $E$ is the energy with respect to $E_F$, and $W$ is the energy interval around which hopping proceeds at temperature $T$. For a locally linear $D(E)$ this yields

$$S = -\frac{k_B^2}{3e} C^2 (T_0 T)^{\frac{1}{2}} \left( \frac{d\ln D(E)}{dE} \right)_{E_F}$$

(2),

where $C$ is a constant. The sign of $S$ is thus dictated by $d\ln D(E)/dE$ at $E_F$, a situation thought to play an important role in the double sign reversal of $R_H$ and $S$ in $a$-Si and Ge.$^{48-53}$

The discussion above directly informs the interpretation of Regime II in Figures 2-4. First, the sign reversal of the 300 K $S$ in films exhibiting hopping at 300 K is not at all unexpected, without precedent, or without theoretical basis. The same can be said of the scatter in $S$ in Regime II (Figure 2(a)), as the magnitude and sign of $S$ become highly sensitive to the details of $D(E)$ near $E_F$. This is illustrated in the schematic DOS of a disordered semiconductor shown in Figure 5, where a donor band overlaps the conduction band. Here, $E_F$ located at $E_1$, deep in the conduction band, would result in diffusive transport, $R_H$ and $S$ being easily interpreted. $E_F$ in or around the donor band, however, is expected for hopping transport. As an illustration, we note that placing $E_F$ at positions $E_2$, $E_3$, $E_4$, or $E_5$ would result, based on equation (2), in positive, negligible, negative, and negligible $S$, respectively. Similar uncertainty in the sign of $S$ persists in the Efros-Shklovskii VRH regime of interest in light of Figure 4. As shown in the inset to Figure 5, and
also discussed in prior work, the sign of $S$ in that case, where $D(E)$ is coulomb-gapped, again arises only from DOS asymmetry (see equation (1)), and is thus variable.$^{51-53}$

In light of the above, the surprising feature in the data of Figure 2 is not that $S$ can reverse sign, but rather that $R_H$ remains apparently unaffected by hopping in Regime II, only inverting deep into the hopping regime at $\sim 0.01 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. One important observation here is that $R_H$ is a transport quantity, whereas thermopower is a thermodynamic one, measured under *open circuit conditions*. There are numerous scenarios where thermodynamic averages and transport results can be substantially different, and future theoretical work in this area specific to pyrite films would clearly be worthwhile. Two-band/channel conduction analysis explicitly including hopping could also be a fruitful avenue. In any case, the most important conclusion from Figures 2-4 is that, unlike the approach taken in much of the pyrite literature, $S$ is clearly not a reliable indicator of the majority carrier type in low $\mu$ pyrite films where $R_H$ is difficult to measure. Quite the opposite is evidenced in Regime II of Figure 2. In Regime III, where hopping transport dominates, eventually both $R_H$ and $S$ become inverted and small, the magnitudes reaching $\sim 10^{-3}$ cm$^3$C$^{-1}$ and $\sim 10 \mu \text{VK}^{-1}$. Based on the above, these small positive values, deep in the Efros-Shklovskii VRH regime, should clearly not be interpreted as $p$-type conduction.

Although it does not impact the general arguments made here, one additional important point is the exact nature of the hopping conduction observed in Regimes II and III. As briefly alluded to above, and discussed in detail in our prior work,$^{16,21}$ the $\rho = \rho_0 \exp(T_0/T)^{1/2}$ form is consistent not only with conventional Efros-Shklovskii VRH in a homogeneous doped semiconductor, but also intergranular hopping between nanoscopic conductive clusters in an insulating matrix. The latter mechanism was deduced in our earlier work on FeS$_2$ films in two distinct contexts,$^{16,21}$
highlighting the issue of local conductance variations in pyrite arising due to compositional fluctuations. A fuller discussion of the relation between the conventional Efros-Shklovskii mechanism and intergranular transport in pyrite was provided in Ref. 21. We note here simply that: (a) Regardless of the exact nature of the hopping conduction the general arguments above regarding the sign inversion and magnitude of $R_H$ and $S$ remain valid; and (b) Intergranular-type hopping may well play a role in at least some instances in the current work, potentially causing the quite large $T_0$ values and thus the existence of hopping transport up to 300 K.

While the above interpretation of the origin of the doping puzzle substantially elucidates a number of issues in unintentionally-doped FeS$_2$ films, we note that some outstanding questions nevertheless remain. First, it should be recalled that there are a handful of $p$-type thin film pyrite publications that have reported $\mu$ in the 2-80 cm$^2$V$^{-1}$s$^{-1}$ range,$^5,19,28,30$ one at 200 cm$^2$V$^{-1}$s$^{-1}$ (see Figure 1 and Table I).$^{27}$ Raw Hall data are often not provided in these cases, however (or are not measured to large $H$), making it difficult to assess the evidence for positive $R_H$. $\rho(T)$ data are also often not provided, making it difficult to assess the conduction mechanism. Nevertheless, hopping transport does not appear capable of explaining $p$-type behavior in cases with such high $\mu$. Further work to reproduce and verify these conclusions, and elucidate the possibility of a true $p$-type dopant, is imperative. Second, given the recent work that has demonstrated surface conduction, and even surface inversion in $n$-type FeS$_2$ crystals,$^{20}$ it is important to consider surface conduction as a possible origin of the behavior seen here. None of the key indicators of surface conduction are present in the films studied here, however. Prior work on bulk $n$-type crystals has demonstrated certain features in the temperature and thickness dependence of transport to be particularly useful for detecting surface conduction,$^{20,46}$ but no such features arise in our films. Moreover, consistent with our own bulk single crystal data,$^{46}$ and the arguments of
Limpinsel et al.\textsuperscript{20} and Caban-Acevedo et al.,\textsuperscript{18} surface inversion is increasingly unlikely as \textit{n}-doping becomes heavier, and surface band-bending is restricted. The apparent \textit{n} values in the films in this work range from $5 \times 10^{18}$ to $\sim 10^{21}$ \text{cm}^{-3}, much higher than in single crystals, rendering surface inversion an unlikely explanation for the apparent inversion in $R_H$ and $S$ in Figure 2. This remains true even for \textit{grain surface conduction}, another issue that must be considered here.

V. Summary

In conclusion, we have presented a comprehensive data set that encompasses Hall effect, thermopower, and resistivity measurements on a large set of bulk single crystal and polycrystalline pyrite FeS$_2$ films, aiming to clarify the puzzling observation that unintentionally-doped crystals are predominantly \textit{n}-type, whereas thin films are apparently \textit{p}-type. The results not only indicate unambiguously \textit{n}-type behavior in higher mobility films, but also show that the apparent \textit{p}-type behavior in lower mobility films can easily arise as an artifact of hopping conduction. This challenges the widespread belief in predominant \textit{p}-type conduction in pyrite films, underscoring the need to combine Hall effect and thermopower measurements of majority carrier type with temperature-dependent transport measurements to establish conduction mechanisms. These results are important both for interpretation of prior work, and for the design of future pyrite photovoltaic devices.

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References


31. Note that in the following citation the reported values of resistivity, carrier density, and mobility do not appear to be self-consistent. With the stated values of the resistivity and carrier density, a mobility of only 11 cm²V⁻¹s⁻¹ is obtained; the origin of the discrepancy with the 280 cm²V⁻¹s⁻¹ quoted in this paper is unknown. Takahashi, N., Nakatani, Y., Yatomi, T. & Nakamura,


40. See Supplemental Material at [URL] for additional information on structural/chemical characterization of single crystals and thin films; experimental details for thermopower measurements; electrical, impurity analysis, and characterization data on thin films; and correlations between hopping conduction and the Hall/Seebeck coefficient.


43. We note that nearest neighbor hopping also results in $m = 1$, albeit with different activation energy and doping dependence than a simple activation process.


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<th>S(300 K) [µVK⁻¹]</th>
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<th>Hall effect</th>
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Table I: Literature review of carrier types in unintentionally-doped FeS$_2$ from Hall effect and thermopower. The 300 K resistivity ($\rho$), 300 K Seebeck coefficient ($S$), carrier type from thermopower and Hall effect, and 300 K apparent Hall mobility ($\mu_H$) are shown for both films (yellow) and synthetic crystals (green).$^{5,9,12,18,19,20,22,23,26-39}$ The synthesis method and relevant citation are shown; CVD is chemical vapor deposition and CVT is chemical vapor transport. When a thermopower carrier type is listed, but with no corresponding $S$, this resulted from “qualitative thermopower”, or “hot point probe” measurements, where only the sign of $S$ is determined. The cases where carrier types are available from both thermopower (quantitative or qualitative) and Hall, are highlighted in color; purple indicates consistency between the two, orange inconsistency.
Figure Captions

Figure 1. Summary of the literature on carrier type in unintentionally-doped pyrite FeS$_2$ from Hall effect and thermopower. The room-temperature ($\sim$300 K) Hall coefficient ($R_H$) (a)$^{18,19,20,22,23,26-30}$ and Seebeck coefficient ($S$) (b)$^{26,28,29}$ are plotted vs. the reported Hall carrier mobility ($\mu$) for FeS$_2$ in various forms. The red/blue symbols indicate the apparent majority carrier type (hole/electron-like) based on the sign of $R_H$ and $S$. Explicitly, “hole-like” is associated with $R_H > 0$, $S > 0$, while “electron-like” is associated with $R_H < 0$, $S < 0$. Data are distinguished for thin films, synthetic single crystals and natural single crystals.

Figure 2. Hall effect, thermopower, and apparent carrier types in the unintentionally-doped FeS$_2$ films and crystals from this study. The room-temperature ($\sim$300 K) Hall coefficient ($R_H$) (a) and Seebeck coefficient ($S$) (b) are plotted vs. the apparent Hall carrier mobility ($\mu_H$) for the polycrystalline films and synthetic single crystals in the current study. Again, the red/blue symbols indicate the apparent carrier type (hole/electron-like) based on the sign of $R_H$ and $S$. Explicitly, “hole-like” is associated with $R_H > 0$, $S > 0$, while “electron-like” is associated with $R_H < 0$, $S < 0$. The arrows in panel (a) indicate upper bounds on $\mu_H$ and $R_H$, i.e. points at the limit of detection. The vertical dashed lines and markings “I”, “II” and “III” indicate the three regimes discussed in the text.

Figure 3. Representative raw data from Hall effect and thermopower measurements. The left panels show the magnetic field ($H$) dependence of the zero-field-background-subtracted Hall resistivity ($\rho_{xy}$) in regimes I (a), II (c) and III (e). The right panels show the temperature gradient (\(\Delta T\)) dependence of the negative thermoelectric voltage (\(-\Delta V\)) in regimes I (b), II (d) and III (f).
Note that $-\Delta V$ is plotted, to facilitate comparison to the Hall data. Dashed lines in all cases are straight line fits. Two samples are plotted in Region I (one crystal, one film), and two films are plotted in Region II (one where $R_H$ and $S$ agree on the sign of the majority carriers, one where they do not). In all cases the samples are labeled with their room temperature $\mu_H$. All data are at room temperature (~300 K).

**Figure 4. Temperature-dependent electronic transport measurements.** In the top panel the temperature ($T$) dependence of the resistivity ($\rho$) is shown in (a) Regime I, (b) Regime II, and (c) Regime III. The bottom panel shows $\ln W$ vs. $\ln T$ generated from the data in the top panel, where $W = -d\ln \rho/d\ln T$. Slopes of $m = \frac{1}{2}$ and 1 are shown, where $m$ is the exponent in $\rho = \rho_0 \exp (T_0/T)^m$. The room temperature (~300 K) apparent Hall mobility ($\mu_H$) for each sample is labelled.

Two samples are shown in Regime I (one crystal, one film), and three films are plotted in Regime II, illustrating the behaviors discussed in the text.

**Figure 5. Schematic density-of-states.** Schematic available density-of-states ($D(E)$) vs. energy ($E$) plot for the illustrative case of a Gaussian donor band (DB, blue) overlapping with a free-electron-like conduction band (CB, green). Five illustrative potential Fermi energy locations, $E_1$ through $E_5$, are indicated by the red dashed lines. The inset shows a density-of-states with a Coulomb gap of width $\Delta_C$ around a potential Fermi energy location $E_6$. 
Figure 1
Figure 2
Figure 3
Figure 4