Theoretical and experimental investigation of magnetotransport in iron chalcogenides

Federico Cagliarisi, Fabio Ricci, Gianrico Lamura, Albert Martinelli, A Palenzona, Ilaria Pallecchi, Alberto Sala, Gianni Profeta and Marina Putti

1 CNR-SPIN-Genova corso Perrone 24, 16152, Genova, Italy
2 CNR-SPIN and Department of Physical and Chemical Sciences, University of L’Aquila, Via Vetoio 1, 67100 L’Aquila, Italy
3 Chemistry and Industrial Chemistry Department, University of Genova, via Dodecaneso 31, I-16146 Genova, Italy
4 Physics Department, University of Genova, via Dodecaneso 33, 16146 Genova, Italy

E-mail: putti@fisica.unige.it

Received 17 September 2012
Accepted for publication 23 October 2012
Published 26 November 2012
Online at stacks.iop.org/STAM/13/054402

Abstract
We explore the electronic, transport and thermoelectric properties of Fe\(_{1+y}\)Se\(_x\)Te\(_{1-x}\) compounds to clarify the mechanisms of superconductivity in Fe-based compounds. We carry out first-principles density functional theory (DFT) calculations of structural, electronic, magnetic and transport properties and measure resistivity, Hall resistance and Seebeck effect curves. All the transport properties exhibit signatures of the structural/magnetic transitions, such as discontinuities and sign changes of the Seebeck coefficient and of the Hall resistance. These features are reproduced by calculations provided that antiferromagnetic correlations are taken into account and experimental values of lattice constants are considered in DFT calculations. On the other hand, the temperature dependences of the transport properties can not be fully reproduced, and to improve the agreement between experiment and DFT calculations it is necessary to go beyond the constant relaxation time approximation and take into account correlation effects.

Keywords: Fe based superconductors, Fe\(_{1+y}\)Se\(_x\)Te\(_{1-x}\), magnetotransport properties, thermoelectric properties, first-principles density functional theory calculations

1. Introduction
The discovery of high-temperature superconductivity in iron pnictides (FePn) [1, 2] raised a renewed interest in searching for new superconducting materials that contain Fe and share common structural features. Among these, superconductivity was found in the iron chalcogenide FeTe when Te was partially substituted by Se [3]. The Fe\(_{1+y}\)Se\(_x\)Te\(_{1-x}\) family exhibits lower transition temperatures, as compared to those of FePn, but a simpler crystal structure. This structure is characterized by layers of square lattice of Fe ions that are tetrahedrally coordinating the chalcogen ions (Ch), and is a prototype system to investigate the fundamental aspects of superconductivity in Fe-based superconductors.

In common with the other Fe-based superconductors, FeCh materials present a similar Fermi surface topology [4] and commensurate antiferromagnetic (AFM) order in the parent compound FeTe (\(x = 0\)) at temperatures below about 70 K [5]. The ground state in FeTe is thought to be crucial for understanding the superconductivity mechanisms. In FeTe, as predicted theoretically [6] and proven experimentally by neutron diffraction [7–9], the Fe moments align according to a bccollinear AFM arrangement with magnetic wave vector \((\pi, 0)\), in contrast with the commensurate spin
density-wave (SDW) order at the nesting wave vector \((\pi, \pi)\) of FePn materials. Interestingly, only short-range incommensurate magnetism survives and eventually coexists with superconductivity in Se-doped samples as indicated by muon spectroscopy studies \([10–12]\). All these aspects point toward a peculiar nature of magnetism in FeCh that does not support a nesting Fermi surface mechanism for the superconductivity. Moreover, superconductivity is induced by isovalent substitution of Se and/or S at the Te site of FeTe, which does not significantly unbalance the nesting condition.

However, it was shown that by varying the Se/Te ratio \([13]\) and also the excess Fe \([11]\), the magnetic properties of the Fe\(_{1+y}\)Se\(_x\)Te\(_{1−x}\) can be tuned, suppressing the \((\pi, 0)\) AFM order in favor of spin fluctuations with magnetic vector of \((\pi, \pi)\), thus reconciling a common magnetic origin for superconductivity in FeCh and FePn superconductors \([14]\).

To investigate the above issues, we clarify the role of Se substitution in determining the evolution of the electronic properties and magnetic ground state of Fe\(_{1+y}\)Se\(_x\)Te\(_{1−x}\), which play a major role in the superconducting mechanisms. More specifically, by carrying out both theoretical and experimental analyses, we focus on the normal-state magnetotransport and thermoelectric properties, which are powerful probes of the band structure at the Fermi level, the excitations coupled with charge carriers and the main coupling mechanisms. The comparison between theoretical predictions and experimental data guides the theoretical studies and clarifies the complex behavior of experimental magnetotransport and thermoelectric curves. Hence, the objectives of our study are (i) presenting a complete set of experimental results of resistivity, Hall effect and Seebeck effect in Fe\(_{1+y}\)Se\(_x\)Te\(_{1−x}\), (ii) performing extensive first-principles density functional theory (DFT) calculations of structural, electronic, magnetic and transport properties of these compounds, and (iii) testing the level of agreement between these theoretical predictions and experimental data, discussing the likely reasons for deviations and suggesting the route to improve the agreement. In this respect, we note that many reported \textit{ab initio} calculations consider, as a starting point, the experimental lattice parameters and usually use the relaxed internal \(z\) coordinates of chalcogen atoms (Se and/or Te) to obtain the total energy minimum. This approach, although justifiable, limits the predictive power of first-principles DFT calculations, in particular in predicting new and promising superconducting materials.

2. Experimental results

2.1. Structural parameters

Fe\(_{1.05}\)Te and Fe(Se\(_{0.5}\)Te\(_{0.5}\)) samples were prepared by solid-state synthesis as described elsewhere \([15]\). FeSe\(_{0.95}\) was produced by a multistep technique based on melting and subsequent annealing as described in \([16]\). The Fe\(_{1.05}\)Te sample was characterized by neutron powder diffraction (NPD) \([9]\). Although the samples were prepared with nominal \(y = 0\), NPD detected a certain excess Fe, which gradually disappeared with increasing Se content \([9]\). Some parameters of the studied samples are listed in Table 1.

| Composition       | \(a\) (Å) | \(c\) (Å) | \(h_{cb}\) (Å) | \(T_N\) (K) | \(T_c\) (K) |
|-------------------|------------|------------|----------------|------------|------------|
| Fe\(_{1.05}\)Te   | 3.8219(1)  | 6.2851(1)  | 1.7548(1)      | 70.2       |            |
| Fe(Se\(_{0.5}\)Te\(_{0.5}\)) | 3.801(1)  | 6.043(1)   | 1.636(1)       | 14         |            |
| FeSe\(_{0.95}\)   | 3.770(1)   | 5.522(1)   | 1.488(1)       | 8          |            |

2.2. Magnetic characterization

Dc susceptibility measurements were performed with a magnetic properties measurement system (MPMS, by Quantum Design) to define the magnetic and the superconducting transition temperatures. Figure 1(a) shows the dc susceptibility of the Fe\(_{1.05}\)Te sample. The onset of the antiferromagnetic magnetic order (Néel temperature, \(T_N\)) is clearly seen at about 70 K. Figure 1(b) shows the low-field dc susceptibility of Fe(Se\(_{0.5}\)Te\(_{0.5}\)) and FeSe\(_{0.95}\) samples. The Fe(Se\(_{0.5}\)Te\(_{0.5}\)) sample exhibits a broadened two-step transition, related to the granularity of the sample; nevertheless, a full shielding is achieved at low temperature. The FeSe\(_{0.95}\) sample exhibits a wide transition with an onset of about 7.7 K and a maximum shielding volume of 60% at low temperatures.

2.3. Magnetotransport characterization

Transport properties measurements were carried out with a physical properties measurement system (PPMS, Quantum Design) in the temperature range 5–300 K and in magnetic fields up to \(B = 9\) T. Hall coefficients \((R_H)\) were determined by measuring the transverse resistivity at selected fixed temperatures, sweeping the field from \(-9\) to \(9\) T. The Seebeck (S) effect was measured with the PPMS thermal transport option in continuous scanning mode at a 0.2 K min\(^{-1}\) cooling rate.

Figure 2(a) shows resistivity curves of all the studied Fe\(_{1+y}\)Te\(_{1-x}\)Se\(_x\) samples; whereas their absolute values are quite similar, their temperature behaviors are substantially different. The resistivity of the \(x = 0\) sample shows the usual negative temperature dependence above the magnetic transition which occurs around \(T_N = 70\) K. At the transition, the resistivity abruptly decreases and then exhibits metallic behavior down to the lowest temperatures. The magnetic transition is not detectable by resistivity in the Fe(Se\(_{0.5}\)Te\(_{0.5}\)) and FeSe\(_{0.95}\) samples. Instead, the onset of superconductivity appears at about 14 and 10 K, respectively. The FeSe\(_{0.95}\) sample exhibits a metallic behavior whereas the Fe(Se\(_{0.5}\)Te\(_{0.5}\)) sample shows a broad peak at about 200 K, followed by a progressive decrease down to the superconducting transition.

In figure 2(b), the Hall resistance is plotted as a function of temperature for three samples. The Hall coefficient \(R_H\) is rather small, namely few times \(10^{-8}\) m\(^3\) C\(^{-1}\), and it changes sign with temperature, reflecting the nearly compensated |
Figure 1. (a) Zero-field cooling (ZFC) dc susceptibility of the Fe$_{1.05}$Te sample taken in an external magnetic field of 3 T; the peak of the corresponding derivative $d\chi/dT$ has been used to define the magnetic transition temperature. (b) ZFC dc susceptibility in an external magnetic field of 1 mT for Fe(Se$_{0.5}$Te$_{0.5}$) and FeSe$_{0.95}$ samples. The arrows indicate the onset of superconductivity determined from the intersect of linear fitting curves above and below the transition. All the samples showed a positive offset which was removed for presentation purposes.

The multiband nature of this family. In the parent compound Fe$_{1.05}$Te, $R_H$ is positive at room temperature and shows a slight increase with decreasing temperature from $3 \times 10^{-9}$ to $6 \times 10^{-9}$ m$^3$/C. At the transition it undergoes an abrupt jump to negative values of approximately $-2 \times 10^{-9}$ m$^3$/C. Contrary to the FePn case, there is no evidence of exponential drop of carrier concentration below $T_N$ [15].

In the Fe(Se$_{0.5}$Te$_{0.5}$) sample $R_H$ changes sign from positive ($\sim 50$ K). Also $R_H$ of the FeSe$_{0.95}$ Sample is negative at low temperature, becomes positive at 60–90 K, and then turns again negative at higher temperatures.

In figure 2(c) the Seebeck coefficient $S$ of three samples is plotted as a function of temperature. The Fe$_{1.05}$Te sample reaches a steady negative value of approximately $-6 \mu$V K$^{-1}$ at high temperatures. Such saturation of $S$ at high temperatures was first pointed out in [17] as a feature of the 11 family, in contrast to other Fe-based pnictides, and is typical of narrow-band materials. Indeed, in such materials, at sufficiently high temperatures the kinetic terms contributing to $S$ can be neglected and the value of $S$ can be calculated by simple combinatorial arguments, considering only the density of carriers, as described by the Heikes law [18–20]. At 70 K, an abrupt change occurs in parallel with the magnetic transition of Fe$_{1+y}$Te, similarly to what observed in the Hall resistance of the same sample. Upon further cooling, $S$ progressively vanishes as $T$ approaches zero, owing to vanishing entropy. In the Fe(Se$_{0.5}$Te$_{0.5}$) sample, $S$ is almost zero at high temperatures; it exhibits a large negative peak around 25 K, which is possibly a signature of a drag mechanism related to the exchange of momentum between charge carriers and magnetic fluctuations, and drops to zero at $T_c$. The Seebeck coefficient of the FeSe$_{0.95}$ sample is very similar to the one measured by Song et al [21], namely it is positive at high temperatures, $S \approx 10 \mu$V K$^{-1}$, then decreases with decreasing temperature and undergoes multiple sign changes down to the lowest temperatures. A clear change of slope is observed in correspondence with the structural transition at 70 K. The vanishing $S$ and $R_H$ values of the Fe(Se$_{0.5}$Te$_{0.5}$) and FeSe$_{0.95}$ samples indicate that transport occurs just at the crossover between hole-type and electron-type behavior and suggest that these samples are almost compensated. Another proof of the compensated multiband nature of these systems comes from the lack of
trivial correspondence between the sign of the Hall resistance and the sign of the Seebeck coefficient.

3. First-principles DFT calculations

3.1. Computational details

The calculations were performed using the VASP package [22, 23] within the generalized gradient approximation [24] (GGA) to the DFT. This approximation is optimal for calculating structural properties; meanwhile, as pointed out by Shi et al [25] the local spin density approximation (LSDA) does not predict the right magnetic symmetry of FeSe and FeTe [26]. We used projected augmented-wave (PAW) pseudopotentials [27] for all the atomic species involved. To achieve a satisfactory degree of convergence (especially for cell relaxations) the 3p⁵ states of Fe, 4s²⁴p⁴ of Se and 5s²⁵p⁴ states of Te were treated as valence states with an energy cutoff of 550 eV. The Perdew, Burke and Ernzerhof (PBE) [28] functional was used to calculate the exchange-correlation potential. Integration over the Brillouin zone was performed considering different shells depending on lattices considered: by default we used 20 × 20 × 20, 13 × 13 × 9 and 14 × 7 × 9 sets in a uniform grid in the Monkhorst and Pack [29] scheme, for tetragonal (T), orthorhombic (O) and monoclinic (M) crystal structures, respectively. Structural optimization was performed by minimizing the stress tensor and internal forces on atoms. The quality of pseudopotentials was tested by comparing the pseudopotential band structure with that obtained with the all-electron full-potential linearized augmented plane waves (FLAPW; within the same computational setup). The band structure of paramagnetic FeTe calculated using the two different methods showed a satisfactory agreement.

We tested various computational approaches predicting electronic, magnetic and transport properties using both experimental and theoretical lattice parameters obtained considering both magnetic and non-magnetic ground states (mimicking the observed high-temperature paramagnetic (PM) state).

3.2. Structural parameters and electronic structure of FeTe

The calculated ground state for FeTe is the bccollinear monoclinic phase (AFM2), with an energy gain of $\Delta E = 0.477$ eV per unit-cell over the stripe-collinear order (AFM1).

We further investigated the magnetic order of Fe atoms along the c-axis and found a stabilization energy of 6.74 meV for the AFM phase between FeTe planes over the FM phase.

The experimental structure parameters evaluated at room temperature are listed in table 1. In table 2 we report lattice constants calculated for non-magnetic (PM) and magnetic (AFM2) phases, considering both experimental (EF) and theoretical lattice parameters (internal parameter relaxed (IR) and fully relaxed (FR)). The distance between Te atoms and the Fe plane ($h_{\text{CH}}$) plays a crucial role in determining the electronic and magnetic properties of FeTe (and its alloys) because it directly affects the p-d hybridization and the energy position of Fe d-orbitals at the Fermi energy ($E_{\text{F}}$) [30, 31]. Thus the prediction of this last value is particularly important. While many theoretical works used the experimental lattice parameters and the relaxed $h_{\text{CH}}$ values to describe the electronic structure [32–34] this procedure is not always justified (see below). As shown in table 2, the theoretical and experimental lattice parameters agree within a few percent. The worst agreement is found for the out-of-plane lattice constant $c$, which is overestimated by $\sim 4\%$ in the PM phase and by $\sim 8\%$ in the AFM2 phase. This behavior is peculiar for 11 compounds. It was shown previously that calculations of 122 and 1111 FePn compounds can correctly reproduce the experimental lattice parameters if the right antiferromagnetic order on Fe atoms is considered [35, 36].

On the other hand, the prediction of the internal degree of freedom ($h_{\text{CH}}$) both in the high-temperature and low-temperature phases requires the inclusion of antiferromagnetic correlations. Calculations considering relaxation in the non-magnetic phase predict $h_{\text{CH}}$ 10% lower than experiments. This result is not a computational artifact; it indirectly reveals the presence of antiferromagnetic correlations even above the Néel temperature, as observed in recent experiments [37].

Table 2. Experimental lattice constants (EF), experimental lattice constants relaxing the chalcogen height $h_{\text{CH}}$, (IR) and the fully relaxed crystal cell (FR). Experimental lattice parameters in high-temperature (PM phase) and low-temperature (AFM2) phase are taken from [9]. The first three rows are related to P4/nmm PM phases ($a \times a \times c$ cell) and the last two rows correspond to the bccollinear monoclinic FeTe P2₁/m phases: $2a \times b \times c$ cell with ferromagnetic order along the c-axis (AFM2) and $2a \times b \times 2c$ with antiferromagnetic order along the c-axis (AFM2*).

|            | a (Å) | b (Å) | c (Å) | $h_{\text{CH}}$ (Å) | $\mu_{\text{Fe}}$ (µB) | Figure |
|------------|-------|-------|-------|--------------------|------------------------|--------|
| PM         | 3.82  | 3.82  | 6.29  | 90.00              | 1.75                   | 3      | EF    |
| PM         | 3.82  | 3.82  | 6.29  | 90.00              | 1.58                   | 3      | IR    |
| PM         | 3.81  | 3.81  | 6.52  | 90.00              | 1.59                   | 3      | FR    |
| AFM2       | 3.83  | 3.78  | 6.26  | 89.17              | 1.75                   | 2.3    | 4      | EF    |
| AFM2       | 3.86  | 3.66  | 6.82  | 87.76              | 1.78                   | 2.4    | 4      | FR    |
| AFM2*      | 3.84  | 3.67  | 6.76  | 88.16              | 1.78                   | 2.2    |        |
Figure 3. Band structures of non-magnetic FeTe calculated using the experimental high-temperature lattice constants (left panel), the experimental lattice constants while relaxing the chalcogen height $h_{Ch}$ (central panel), and the simulated crystal cell (right panel). These band structures are related to the cell parameters shown in table 2.

Figure 4. High-symmetry $k$-points of monoclinic Brillouin zone (left panel), bicollinear FeTe band structure calculated for the experimental low-temperature lattice constants (left panel) and the theoretical crystal cell (right panel), considering the FM alignment along the $c$-axis.

Fe d-band around 0.25 eV becomes degenerate with the two other bands at $\sim$0.13 eV, upon $h_{Ch}$ energy minimization; (ii) a similar behavior is found for the two split bands (the fourth and the fifth above $E_F$). The band structure corresponding to the theoretical ground state is shown in the right panel.

Speaking in terms of the Fermi surfaces (FS) we can see from the band structure that at $\Gamma$ point, for the simulation which considers the experimental values of the lattice constants, there are three hole-like non-degenerate surfaces: two of them are open cylinders, and one is a closed surface around this high symmetry point; at M point, there are two quasi-degenerate electron-like surfaces. When relaxing the chalcogen height $h_{Ch}$ or lattice constants, the FS shape changes at these two special points—although the topology remains the same, the radii of the cylinders change with $h_{Ch}$.

Figure 4 shows the band structures obtained for the bicollinear antiferromagnetic phase, considering the experimental and theoretical lattice constants. The band structures are very complex (due to the large size of the unit cell) and show some differences between the two structures. However, we found one hole-like and two electron-like Fermi surfaces (not shown) for both the considered structures.

In summary, we find that DFT calculations fail to predict the right crystal structures and internal degree of freedom in FeTe, when antiferromagnetic order is neglected.

Table 3. Tetragonal non-magnetic (PM) and collinear orthorhombic FeSe Cmme phase ($\sqrt{2}a \times \sqrt{2}b \times c$ cell); the data are shown for experimental fixed [40] (EF) and fully relaxed (FR) lattice parameters.

|     | $a$ (Å) | $b$ (Å) | $c$ (Å) | $h_{Ch}$ (Å) | $\mu_{Fe}$ ($\mu_B$) | Figure |
|-----|---------|---------|---------|--------------|----------------------|--------|
| PM  | 3.76    | 3.76    | 5.48    | 1.46         | 5                    | EF     |
| PM  | 3.69    | 3.69    | 6.06    | 1.38         |                      | FR     |
| AFM1| 3.76    | 3.75    | 5.48    | 1.46         | 2.1                  | 5      | EF     |
| AFM1| 3.75    | 3.71    | 6.11    | 1.45         | 1.8                  | FR     |
We demonstrate, on the other hand, that inclusion of antiferromagnetic correlations in the calculation allows to predict the experimentally observed crystal symmetry, chalcogen height $h_{Ch}$ and magnetic phase. While all these quantities are predicted with sufficient accuracy, we show that Fermi surfaces and band structure details around the Fermi level, which are crucial in predicting and understanding the superconducting properties, are sensitive to minute modifications of the crystal structure (in particular $h_{Ch}$).

### 3.3. Structural parameters and electronic structure of FeSe

According to the literature, superconducting FeSe$_x$ exhibits a structural transition around 70–90 K [38, 39], although the presence of a related magnetic transition has not been detected. Accordingly, the transport data on FeSe$_x$ do not exhibit clear signatures of magnetic transitions, in contrast to Fe$_{1+y}$Te. Also Mössbauer spectra show no peak splitting or other significant changes through the phase transition,
which would be expected for magnetic order [38]. Magnetic fluctuations observed in FeSe$_x$ must therefore be faster than the characteristic time scale of the M"ossbauer effect (typically $\sim 10^{-7}$ s) and thus cannot be the origin of the observed static structural phase transition in this compound. Disentangling the magnetic and structural behavior in the simple FeSe$_x$ system implies that the crystallographic phase transition and magnetic ordering are driven by different effects.

Within the DFT-GGA theory we predict a collinear stripe anti-ferromagnetic (AFM1) ground state with structural properties summarized in table 3. As we can see, even if the relaxed $c$ parameter significantly deviates ($\sim 10\%$) from the experimental one, the chalcogen height $h_{Ch}$ differs by less than 1%. The same agreement cannot be obtained if we consider the system to be non-magnetic. For the antiferromagnetic orthorhombic FR structure the Fe-Se distance is $\sim 2.362$ Å. Experiments show slightly different distances around 2.385 Å (this value refers to a sample of FeSe$_{0.92}$ stoichiometry) [38].

Figure 5 shows electronic band structures for high-temperature and low-temperature phases; they were calculated using the lattice parameters measured by neutron diffraction [40].

In the following section, guided by transport measurements, we simulate transport properties using a semiclassical Boltzmann approach and describe the system using both experimental and predicted crystal structures.

3.4. Calculated transport coefficients

Transport theory describes the flow of charges or heat through a solid material in external fields, such as an electric field and/or a temperature gradient, considering internal scattering processes between particles and (quasi)particles. Exchange of energy and momentum brings carriers far from equilibrium states, thus resulting in finite electric or thermal conductivity. The semiclassical Boltzmann transport theory [41] relates the rate of change of the equilibrium distribution function to diffusion, external fields and various scattering effects (described by relaxation times). Using first-principles eigenvalues we calculated the Seebeck and Hall coefficients within the semiclassical Boltzmann theory in the constant relaxation time approximation and assuming band-independent relaxation time [42]. This last assumption, which would not be reliable in a multiband system such as MgB$_2$ due to the different nature of bands involved in the transport [43], should not significantly affect iron-based materials. Comparison with experiments, although qualitatively (and in some cases quantitatively) possible, must consider the underlying approximations of the theory.

To compare with experiments, we simulate the transport properties as a function of chemical potential in a rigid-band approach, for either electron or hole doping.

Figure 6 shows the Seebeck and Hall coefficients calculated for FeTe within the EF lattice approach. The right and left panels present calculations for the AFM and PM case, respectively. Different curves correspond to the undoped (dashed line), electron doped (dotted line) and hole doped (solid line) conditions. The Fermi energy shift of about $\pm 0.04$ eV approximately corresponds to a $\pm (2-4)$% variation in Fe stoichiometry [44]. Note that while the Seebeck effect is always negative, the Hall effect is mainly negative in the AFM state and positive in the PM state. The shift of the Fermi energy does not produce a monotonic behavior; $R_H$ in the AFM state is negative and becomes positive upon electron doping. All these features result from the complex band structure and extremely compensated condition of these compounds.

Figure 7 shows the transport coefficients of undoped FeTe calculated within the EF approach. Experimentally, a clear discontinuity is observed at $T_N$ in all the transport coefficients, signifying the antiferromagnetic phase transition. The comparison of the calculated and measured Seebeck and Hall coefficients will thus consider the antiferromagnetic phase at low temperatures ($T < T_N$) and non-magnetic one at high temperatures ($T > T_N$).

The predicted Hall coefficient correctly changes its sign from negative to positive at the phase transition in agreement with the experimental data (figure 2(b)). The order of magnitude is correct in the AFM region, while in the PM phase the theoretical values are one order of magnitude lower than the experimental ones. The predicted Seebeck coefficient is always negative and exhibits a discontinuity at the transition, in agreement with experimental results. Nevertheless, the overall temperature dependence fails to reproduce the shape of the experimental curve, and the calculated $S$ is much smaller than the experimental value at $T < T_N$. Remarkably, using the FR structure, we were unable
to predict the correct sign for $R_H$ in the different temperature ranges.

Figure 8 shows the calculated $S$ and $R_H$ coefficients of undoped FeSe as a function of doping in the EF structure. The comparison with experiment is more difficult in this case. At high temperatures, experiments find a positive Seebeck coefficient, while calculations predict a small negative value. The result is robust with respect to Fermi level shift (simulating electron or hole doping) both in the LT and HT phases. Hole doping should change the sign of the Hall coefficient if the system keeps the AFM order, while the sign remains negative in the PM phase. The low-temperature phase is correctly predicted to have a negative sign, but the structures found in the experiments are not reproduced by the theory. These results are particularly interesting in view of the different superconducting behavior of FeTe and FeSe. The low-temperature transport properties have more different regimes in FeSe than FeTe. The theoretical description within the constant relaxation time approximation hardly describes the experimental structures.

4. Discussion

The presented theoretical and experimental results suggest that care should be taken in analyzing FeCh compounds. DFT calculations fail to predict the correct crystal structures and internal degrees of freedom in FeTe when antiferromagnetic correlations are neglected. Hence, we implement our approach starting from the experimental lattice constants (EF approach) and analyze the agreement between the different theoretical approaches and experimental data.

All transport and thermoelectric measurements show discontinuities corresponding to the structural/magnetic transitions of the compounds. This is clearly seen for the Fe$_{1+y}$Te compound, which exhibits kinks in all the transport curves and a change in sign of the Hall effect below $T_N$. This behavior differs from the progressive decrease of carrier concentration in the FePn parent compounds [15], which is related to the opening of the SDW gap.

Theoretical calculations, which assume two different structural and magnetic phases below and above $T_N$, do reproduce such features. The EF approach, but not IR and FR approaches, also correctly reproduces the signs of $S$ and $R_H$, both above and below the transition temperature. This is an important indication that the EF structures must be chosen to improve the agreement with experiment. Structural relaxations (both for lattice parameters and internal coordinates) performed for a non-magnetic system do not allow reproducing the observed structures. On the other hand, the Fermi surface properties obtained with non-magnetic calculations improve the description of the high-temperature transport coefficients. The capability to reproduce (within a semiclassical theory) the observed kinks in the transport curves is important because it clarifies that the kinks and sign changes reflect the delicate balance between the hole and electron contributions to transport, due to the Fermi surface reconstruction [45], and it is not necessary to invoke changes in the scattering mechanisms and/or carrier localization across the transition.

Calculations also predict kinks for FeSe$_x$ across the structural transition. Experimental data show that even if resistivity appears smooth across the transition, the Hall effect changes sign and the Seebeck curve exhibits a clear change of slope around 70 K.

From our experimental results, we summarize the effect of Se substitution in Fe$_{1+y}$Se$_x$Te$_{1-x}$ as follows. The structural analysis confirms that with increasing Se content, the phase is stabilized by reducing the amount of excess Fe [9]. Excess Fe has multiple effects, namely (i) it dopes electrons into the system [44], (ii) it favors ($\pi,0$) magnetic fluctuations which
do not contribute to superconducting pairing [11, 13], and (iii) it induces weak charge localization via such magnetic fluctuations [13]. Indeed, the transport data are consistent with this framework. Resistivity curves show increasingly metallic behavior with increasing Se content because excess Fe suppresses charge localization. As for Hall and Seebeck coefficients, with increasing Se they become smaller and approach zero with multiple changes in sign as a function of temperature. This result suggests that Se substitution leads to charge compensation.

Calculations cannot reliably reproduce this trend, even in the EF structures, because band structure details around the Fermi level are too sensitive to minute modifications of the crystal structure (in particular $h_{\text{Ch}}$), as confirmed by the strong dependence of calculated curves on the position of the Fermi level (see figures 6 and 8).

As expected, the complex details of the transport and thermoelectric curves cannot be reproduced by the theory due to the use of constant relaxation time approximation, which neglects the energy/band/wavevector dependence of relaxation times. We tried to reproduce the room-temperature experimental values of $\rho$, $S$ and $R_H$ in a two-band picture, introducing band structure parameters in the free carrier expressions for $\rho$ and $R_H$ and Heikes relationship [18–20] for $S$. This attempt was unsuccessful and the predicted carrier concentrations did not agree with the experiment. This failure suggests that correlation effects should be taken into account to obtain a quantitative agreement between experiment and calculation in iron-based materials [46].

5. Concluding remarks

Semiclassical approach can provide quick and qualitative predictions on the transport properties of FeCh compounds, indicating interesting doping and structural dependences of transport coefficients. The comparison between theory and experiments is yet limited, and several issues need to be addressed for a better understanding of FeCh materials.

Acknowledgment

This work was supported by the FP7 European project SUPER-IRON (grant agreement No. 283204), by a CINECA-HPC ISCRA grant and by an HPC grant at CASPUR.

References

[1] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 J. Am. Chem. Soc. 130 3296
[2] Ren ZX et al 2008 Chin. Phys. Lett. 25 2215
[3] Yeh K-W et al 2008 Eur. Phys. Lett. 84 37002
[4] Subedi A, Zhang L, Singh D-J and Du M-H 2008 Phys. Rev. B 78 134514
[5] Fruchart D, Convert P, Wolters P, Madar R, Senateur J-P and Fruchart R 1975 Mater. Res. Bull. 10 169
[6] Ma F, Ji W, Hu J, Lu Z-Y and Xiang T 2009 Phys. Rev. Lett. 102 177003
[7] Li S et al 2009 Phys. Rev. B 79 054503
[8] Bao W et al 2009 Phys. Rev. Lett. 102 247001
[9] Martineili A, Palenzona A, Tropeano M, Ferdeghini C, Putti M, Cimberle M R, Nguyen T D, Affronte M and Ritter C 2010 Phys. Rev. B 81 094115
[10] Khasanov R et al 2009 Phys. Rev. B 80 140511(R)
[11] Bendele M, Babkevich P, Katrych S, Gvashilaya S N, Ponomakushima E, Conder K, Roessli B, Boothroyd A T, Khasanov R and Keller H 2010 Phys. Rev. B 82 212504
[12] Lamura G et al 2012 Phys. Rev. B, submitted
[13] Liu T J et al 2010 Nature Mater. 9 716
[14] Han M J and Savrasov S Y 2009 Phys. Rev. Lett. 103 067001
[15] Tropeano M, Pallecchi I, Cimberle M R, Ferdeghini C, Lamura G, Vignolo M, Martinelli A, Palenzona A and Putti M 2010 Supercond. Sci. Technol. 23 054001
[16] Palenzona A et al 2012 Supercond. Sci. Technol. 25 115018
[17] Pallecchi I, Lamura G, Tropeano M, Putti M, Viennois R, Giannini E and Van der Mars D 2009 Phys. Rev. B 80 214511
[18] Heikes R R, Miller R C and Mazelsky R 1964 Physica 30 1600
[19] Heikes R R 1961 Thermoelectricity: Science and Engineering ed R R Heikes and R W Ure Jr. (New York: Interscience)
[20] Chaikin P M and Beni G 1976 Phys. Rev. B 13 647
[21] Song Y J, Hong J B, Min B H, Kwon Y S, Lee K J, Jung M H and Rhyee J-S 2011 J. Korean Phys. Soc. 59 312
[22] Kresse G and Furthmuller J 1996 Phys. Rev. B 54 11169
[23] Kresse G and Furthmuller J 1996 Comput. Mater. Sci. 6 15
[24] Kresse G and Joubert D 1999 Phys. Rev. B 59 1758
[25] Shi H, Huang Z, Tse J S and Lin H Q 2011 J. Appl. Phys. 110 043917
[26] Li S et al 2009 Phys. Rev. B 79 054503
[27] Bliöchl P E 1994 Phys. Rev. B 50 17953
[28] Perdew J, Burke K and Emzerhof M 1996 Phys. Rev. Lett. 77 3865
[29] Monkhorst H J and Pack J D 1976 Phys. Rev. B 13 5188
[30] Kuroki K, Usui H, Onari S, Arita R and Aoki H 2009 Phys. Rev. B 79 224511
[31] Kumar J, Auluk S, Ahluwalia P K and Awana V P S 2012 Supercond. Sci. Technol. 25 095002
[32] Subedi A, Zhang L, Singh D J and Du M H 2008 Phys. Rev. B 78 134514
[33] Singh P P 2010 J. Phys.: Condens. Matter 22 135501
[34] Shi H, Huang Z-B, Tse J S and Lin H-Q 2011 J. Appl. Phys. 110 043917
[35] Yildirim T 2009 Phys. Rev. Lett. 102 037003
[36] Colonna N, Profeta G, Continenza A and Massida S 2001 Phys. Rev. B 83 094529
[37] Vilmercati P et al 2012 Phys. Rev. B 85 220503(R)
[38] Margadonna S, Takabayashi Y, McDonald M T, Kasperkiewicz K, Mizuguchi Y, Takano Y, Fitch A N, Suard E and Prassides K 2008 Chem. Commun. 5607
[39] McQueen T M, Williams A J, Stephens P W, Tao Z, Zhu Y, Ksenofontov V, Casper F, Selcer C and Cava R J 2009 Phys. Rev. Lett. 103 057002
[40] Louca D et al 2010 Phys. Rev. B 81 134524
[41] Ziman J M 2001 Electrons and Phonons: The Theory of Transport Phenomena in Solids (New York: Oxford University Press)
[42] Madsen G K H and Singh D J 2006 Comput. Phys. Commun. 175 67
[43] Pallecchi I et al 2005 Phys. Rev. B 72 184512
[44] Zhang L, Singh D J and Du M-H 2009 Phys. Rev. B 79 012506
[45] Liu Y, Kremer R K and Lin C T 2011 Supercond. Sci. Technol. 24 035012
[46] Qazilbash M M, Hamlin J J, Baumbach R E, Zhang L, Singh D J, Maple M B and Basov D N 2009 Nat. Phys. 5 647