Majority carrier type inversion in the FeSe family and a ‘doped semimetal’ scheme in iron-based superconductors

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Abstract
The field and temperature dependencies of the longitudinal and Hall components of resistivity have been studied for high-quality FeSe1-xSx (x up to 0.14) single crystals. A quasiclassical analysis of the experimental data indicates a strong variation of electron and hole concentrations under the studied isovalent substitution and a clear trend towards the majority carrier type inversion. On this basis, we propose a ‘doped semimetal’ scheme for the superconducting phase diagram of the FeSe family, which can probably be applied to other iron-based superconductors. In this scheme, the two local maxima of the superconducting temperature can be associated with the Van Hove singularities of a simplified semi-metallic electronic structure. A multcarrier analysis of the experimental data also reveals the presence of a tiny and highly mobile electron band for all the samples studied. Substitution for sulfur in the studied range leads to one order decreasing in the density of highly mobile electrons, from 3% to 0.2% of the total carrier concentration. The mobility of these carriers does not depend on impurities, which may indicate an enhanced electron–phonon interaction and allows us to consider the highly mobile carriers as a possible source of unusual acoustic properties of FeSe.

Supplementary material for this article is available online

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(Some figures may appear in colour only in the online journal)
1. Introduction

The energy of the superconducting pairing depends on the density of interacting electrons. Therefore, possible enhancement of superconductivity by increasing the electron density in the case where the Fermi level is near Van Hove singularities has been studied starting with $V_3X$ type compounds [1]. Possible enhancement of superconductivity due to changes in the pairing mechanism at these singular points [2] has also been studied for a long time.

The discovery of cuprate superconductors motivated an in-depth study of the Van Hove scenario [3–5] for high-temperature superconductivity (HTSC). Because of continued support by new experimental facts, the Van Hove scenario remains relevant to HTSC for many years [6, 7]. For iron-based superconductors (IBS), it has been suggested that density waves or their fluctuations, which are considered responsible for superconductivity in many families of IBS, can be a consequence of tuning to the nearest Van Hove instability in multiband materials [8].

Among IBS, iron selenide possesses superconductivity in an almost stoichiometric form [9, 10], giving an excellent possibility to study the electronic properties of IBS on structurally perfect crystals. For this material, there were discovered several interesting phenomena related to the carrier properties near singular points of the electronic structure or in small pockets of the Fermi surface. Perhaps one of the most interesting phenomena is the absorption of the $C_{11}$ acoustic mode at a record level for metals [11]. This can be considered as an experimental detection of a giant electron–phonon interaction for some small electron or hole pockets. It is also interesting that the angle-resolved photoemission (ARPES) study of the substituted FeSe showed a significant change in the superconducting gap between Fermi surface pockets [12]. These results may suggest the existence of small pockets of carriers with ‘enhanced’ superconducting properties.

Here we present the results of a quasiclassical multicarrier analysis of the experimental magnetotransport data for high-quality FeSe$_{1-x}$S$_x$ crystals. The analysis reveals a minority highly mobile band in all studied crystals. The carrier concentration in this band does not exceed a few percent of the total and rapidly decreases with increasing substitution or impurity level. The carrier mobility in this band does not depend on the impurity level which may indicate an enhanced electron–phonon interaction and explain the detected record values in acoustic properties.

The multicarrier analysis also found unexpectedly large changes in both the total carrier concentration and in the difference between electron and hole concentration in the main bands of the studied series. Thus, a chemical pressure probably produces the changes in electronic properties of the studied compounds which are partially equivalent to doping. This assumption allows considering a model of ‘doped semimetal’ for a phase diagram of the IBS by analogy with the model of ‘doped Mott insulator’ for superconducting phase diagrams of cuprates. As a result, both phase diagrams of HTSC can be built on a single assumption that the principal factor is the position of the Fermi level relative to the bands’ extrema.

2. Experiment

The crystals of FeSe$_{1-x}$S$_x$ were prepared using conventional KCl/AlCl$_3$ flux technique [13, 14]. The energy dispersive microanalysis confirms a good chemical homogeneity of the grown crystals. The chemical composition was studied at three points for four average size crystals from each growth batch, which provided the statistical error in sulfur content lower than 5% for all batches.

Magnetoresistance (MR) and Hall effect measurements were done using the EDC option of MPMS 7XL with Keithley 2400 and Keithley 2182A. The dimensions of the crystals were measured using the AxioImager A1M optical microscope (Carl Zeiss). The critical temperatures of the superconducting and nematic transitions were determined from the temperature dependencies of $\rho_{xx}$ and $d\rho_{xx}/dT$ respectively.

3. Results

We studied crystals of FeSe$_{1-x}$S$_x$ with $x = 0, 0.037, 0.048, 0.09, 0.14$. The temperature dependencies of the resistivity $\rho_{xx}$ for one crystal from each studied batch are plotted in figure 1. The properties of the samples from the same batch were found to be very uniform. But the crystals from different batches with the almost same chemical composition could differ significantly, probably due to deviations in the growth conditions. For unsubstituted FeSe, we studied the crystals from two different batches. The MR at 15 K for these batches is six times different. Apparently, crystals with a lower MR (batch ‘B’) have much more defects [15]. Their critical temperature is also lower than the usual values for FeSe. Analyzing the properties of the low-quality composition we tried to reveal how the properties of carriers depending on the crystal quality. The batch with $x = 0$ and low MR is further referred to as ‘imperfect’ FeSe. On the graphs, the points
Hereinafter, we use the total carrier concentration \( n_C = n_{e1} + n_{h1} + n_{e2} \). The average mobility of the main bands \( \mu_{e1} + \mu_{h1} / 2 \) and deviations from the simple square law for MR. These features indicate the presence of carriers with significantly different mobilities. The nonlinear field dependence of the components of the conductivity tensor, measured at 15 K, with quasiclassical three-band expressions. Details of the method used have been described elsewhere [16, 17]. All the data obtained are summarized in table 1. Hereinafter, we use \( e1 \), \( h1 \), and \( e2 \) to denote the bands used in the analysis and the indices \( e1 \), \( h1 \), and \( e2 \) to indicate to which bands the extracted parameter (mobility or concentration) is related.

Figure 2 shows the parameters of the main electron \( e1 \) and hole \( h1 \) bands plotted as a function of sulfur content \( x \). The carrier mobility decreases rapidly with increasing degree of substitution, which can be explained by an increase in disorder. This is also confirmed by the low value of mobility in the ‘imperfect’ FeSe composition. The extracted values of mobility of the main electron and hole bands \( e1 \) and \( h1 \) differ only by a few percents, which is in agreement with the data obtained in pulsed magnetic fields up to 50 T for pure FeSe [16]. The observed increase in conductivity with increasing \( x \) (see figure 1) is provided by an increase in the concentration of the carriers shown in figure 2(a). Since the substitution is isovalent, the main reason for this increase is a change in the cell parameters. In turn, this means that the band structure of these compounds is highly sensitive to pressure. The observed changes in the conductivity of FeSe\(_{1-x}\)S\(_x\) series resemble a transition from bad to good metal in BaFe\(_2\)(As\(_{1-x}\)P\(_x\))\(_2\) induced by isovalent substitution [18].

Figure 3 represents the difference in carriers concentration between the main electron \( e1 \) and hole \( h1 \) bands as a function of sulfur content \( x \). In panel (a) we plot the difference \( n_{h1} - n_{e1} \) and their linear regression. Panel (b) shows that the ratio of this difference to the total concentration also noticeably increases with increasing \( x \), which indicates that the observed trend is not a consequence of changes in the total carrier concentration. The linear regression of the \( n_{h1} - n_{e1} \) dependence predicts a majority carrier type inversion at \( x = -0.037 \) which may be considered as a tellurium substitution for selenium. The deviation of ‘imperfect’ FeSe from the general trend can be explained by excessive doping with the defects contained in it.

Figures 4(a) and (b) show the properties of the highly mobile band \( e2 \) in FeSe\(_{1-x}\)S\(_x\) series as a function of \( x \). The figures show both the absolute values of concentration and mobility, as well as their ratio to the corresponding values of the main bands. In all the studied compositions, the concentration of highly mobile carriers does not exceed 3% of the total.

Isovalent substitution in FeSe\(_{1-x}\)S\(_x\) causes a rapid decrease in the concentration of the highly mobile carriers (see figure 4(a)). The variation of mobility in figure 4(b) can be interpreted in two ways. First, the ratio of mobilities increases with increasing \( x \) except for the case of ‘imperfect’ FeSe, for which it reaches its maximum. On the other hand, the absolute values of mobility do not show monotone changes, and the increase in the ratio is mainly due to a decrease in mobility in the main bands. A weak relationship between mobility and impurity level can indicate a high value of the electron–phonon interaction. Therefore it can be assumed that the highly mobile carriers can be responsible for a record acoustic absorption observed in ultrasonic experiments [11].

A successive decrease in the ratio of mobilities \( \mu_{e2}/(\mu_{e1} + \mu_{h1}) \) with the concentration of highly mobile carriers (see figure 5) can also be interpreted in two ways. First, this may reflect the carrier mass renormalization with a change in the volume of the corresponding pocket. On the other hand, if we suppose a strong electron–phonon interaction for the highly mobile carriers when the ratio of mobilities is proportional to the impurity level, then this dependence may be caused by a rapid decrease in the density of the highly mobile carriers with an increasing impurity level.

4. Discussion

Isovalent substitutions have the main influence on the cell volume and therefore can be considered as a chemical pressure. The significant variation in the carrier concentration...
with isovalent substitution observed in our samples is unusual. Besides, the method used also reveals significant changes in the ratio of electrons and holes. Nevertheless, these unexpected results are consistent with some already known properties of the FeSe family and other IBS.

A monotonic increase of the Fermi surface size of FeSe$_{1-x}$S$_x$ with increasing $x$ is detected by Shubnikov–de Haas quantum oscillation [19]. The ARPES spectroscopy of strained and strain-free FeSe [20] also reveals a marked change in the energy overlap between the hole and electron pockets and a strong variation in hole and electron concentration. Thus, variations in the concentration of the carriers in FeSe family are reliably confirmed by microscopic methods.

The observed change in the carrier doping level of the studied compounds is qualitatively agreed with reports on changes in the Hall coefficient. The relationship between the Hall coefficient and superconducting properties has been revealed in almost all reports where the Hall coefficient of IBS was measured. For example, a direct correlation between the Hall coefficient and the critical temperature was found for

Table 1. Summary of properties of the studied FeSe$_{1-x}$S$_x$ crystals: sulfur content $x$, thickness of the studied crystal $h$, superconducting critical temperature $T_c$, temperature of nematic transition $T_N$, MR at 15 K in 7 T, and parameters extracted from magnetotransport measurements at 15 K using three-band model.

| Sample | $x$ | $h$ (μm) | $T_c$ (K) | $T_N$ (K) | MR (10$^{-1}$ | $\mu_n$ | $n_n$ | $\mu_p$ | $n_p$ | $\mu_e$ | $n_e$ |
|--------|-----|----------|---------|---------|----------------|----------|------|----------|------|----------|------|
| A0#1   | 0   | 84       | 9.6     | 87       | 1.15           | 1470     | 5.6  | 1384     | 6.3  | 5871      | 0.24 |
| A0#2   | 0   | 93       | 9.5     | 86       | 1.02           | 1330     | 4.8  | 1300     | 5.5  | 4907      | 0.28 |
| B0#1   | 0   | 99       | 8.9     | 84       | 0.19           | 642      | 3.16 | 513      | 4.5  | 3687      | 0.03 |
| A4#1   | 0.037 | 37    | 10.3    | 83       | 0.50           | 998      | 4.6  | 950      | 5.0  | 4473      | 0.05 |
| A4#2   | 0.037 | 46    | 10.4    | 82       | 0.52           | 1011     | 10.2 | 915      | 12.9 | 4356      | 0.31 |
| A5#1   | 0.048 | 54    | 10.4    | 82       | 0.58           | 1070     | 8.2  | 1014     | 9.7  | 4939      | 0.13 |
| A9#1   | 0.09  | 45    | 10.3    | 76       | 0.44           | 987      | 10.7 | 889      | 14.9 | 5053      | 0.13 |
| A14#1  | 0.14  | 51    | 10.6    | 68       | 0.31           | 816      | 11.9 | 775      | 15.4 | 4636      | 0.05 |
| A14#2  | 0.14  | 48    | 10.4    | 67       | 0.28           | 763      | 11.5 | 731      | 14.7 | 4502      | 0.04 |

Figure 3. (a) Difference in carriers concentration between the main electron ($e_1$) and hole ($h_1$) bands in absolute (a) and relative (b) units as a function of sulfur content $x$. The dashed line is a linear regression. The diamond symbols are for ‘imperfect’ FeSe.

Figure 4. (a) Concentration of the highly mobile carriers $n_{e2}$ and the ratio $[n_{e2}/n_{e1}]$ as a function of sulfur content $x$. (b) Mobility of the highly mobile carriers $\mu_{e2}$ and the ratio $[\mu_{e2}/\mu_{e1}]$ as a function of sulfur content $x$. The diamond symbols are for ‘imperfect’ FeSe.
pure FeSe.

Concentration of highly mobile carriers maximum is in the region of electron-type conductivity and the two maxima of the phase diagram means that one maximum is near the pure FeSe which also may be in this region.Muon spin rotation measurements indicate a Lifshitz transition in the low-temperature regime. Besides, the Van Hove singularity in the tetragonal phase. Furthermore, a similar small tensile stress, the ARPES study of strained BaFe$_{1-x}$Co$_x$As$_2$ thin films with a compressive and tensile in-plane strain in a wide range of Co doping [21]. The increase in the critical temperature of FeSe under pressure is also accompanied by changes in the Hall coefficient including the argument of the magnetotransport data measured in moderately high temperatures allows reliably extract the band parameters from high-quality crystals are available. Relatively high carrier mobility at low temperatures allows reliably extract the band parameters from the magnetotransport data measured in moderately high magnetic fields.

The data obtained by this analysis clearly indicate a trend towards an inversion of the carrier type in the region near $x \approx -0.037$. This point corresponds to FeSe under small tensile stress, which can be realized in FeSe$_{1-x}$Te$_x$ at a low content of tellurium. This is approximately the center of the combined phase diagram of the FeSe$_{1-x}$S$_x$ and FeSe$_{1-x}$Te$_x$ series, which has local maxima on both sides of this point. At a similar small tensile stress, the ARPES study of strained FeSe [20] indicates a Lifshitz transition in the low-temperature orthorhombic phase and proximity of the Fermi level to the Van Hove singularity in the tetragonal phase. Besides, the muon spin rotation measurements [24] find a quantum critical point near the pure FeSe which also may be in this region.

The inversion of the carrier type in the region between the two maxima of the phase diagram means that one maximum is in the region of electron-type conductivity and the second in the region of hole-type conductivity. It allows us to draw a direct analogy with cuprate high-temperature superconductors and consider carrier doping as a driving factor of the IBS phase diagram. This a ‘doped semimetal’ model for IBS in conjunction with a doped insulator model for cuprates allow us to draw a unified scheme for superconducting phase diagrams.

5. Conclusion

Our study has demonstrated that electron–phonon interaction for highly mobile carriers is strongly enhanced. At the same time, the density of the highly mobile carriers decreases rapidly with chemical substitutions, while the temperature of the superconducting transition does not decrease. This may suggest that the role of the mobile carriers in the superconductivity of FeSe$_{1-x}$S$_x$ series is insignificant. On the other hand, in this series the total carrier concentration increases almost three times indicating the absence of a simple linear relationship between the superconducting critical temperature and the density of carriers.

The quasiclassical multicarrier analysis of the electronic properties of FeSe$_{1-x}$S$_x$ has shown that the difference between the electron and hole concentrations or, in other words, the
level of carrier doping and the position of the Fermi level relative to the extrema of the electronic bands can be important for superconductivity. The Van Hove concept is the most natural way to bind a particular electronic band and a dome in a superconducting phase diagram although there is no experimental evidence that the maximum of the critical temperature is achieved when the position of the Fermi level and the singularity coincide. In the case of FeSe family, this is probably even impossible since the level of carrier doping in FeSe1-xSx does not exceed 20% of the total carrier concentration.

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