

**Temperature-dependent correlations in covalent insulators: Dynamical mean-field approximation**J. Kuneš<sup>1,\*</sup> and V. I. Anisimov<sup>2</sup><sup>1</sup>*Theoretical Physics III, Center for Electronic Correlations and Magnetism, Institute of Physics, University of Augsburg, Augsburg 86135, Germany*<sup>2</sup>*Institute of Metal Physics, Russian Academy of Sciences-Ural Division, 620041 Yekaterinburg GSP-170, Russia*  
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Motivated by the peculiar behavior of FeSi and FeSb<sub>2</sub>, we study the effect of local electronic correlations on magnetic, transport, and optical properties in a specific type of band insulator, namely a covalent insulator. Investigating a minimum model of covalent insulator within a single-site dynamical mean-field approximation, we are able to obtain the crossover from low-temperature nonmagnetic insulator to high-temperature paramagnetic metal with parameters realistic for FeSi and FeSb<sub>2</sub> systems. Our results show that the behavior of FeSi does not imply microscopic description in terms of Kondo insulator (periodic Anderson model) as can be often found in the literature, but in fact reflects generic properties of a broader class of materials.

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The effect of local electronic correlations turning metals into Mott insulators has been one of the major themes of condensed-matter theory. Electronic correlations in band insulators have received much less attention and were largely limited to investigation of Kondo insulators (KI) described by the periodic Anderson model at half filling. The possibility of a transition from a band insulator (BI) to a Mott insulator (MI) in the ionic Hubbard model<sup>1</sup> attracted new attention to the correlated BIs. Among the correlated BIs FeSi,<sup>2</sup> and more recently FeSb<sub>2</sub>,<sup>3</sup> have been subject of a particular interest as they are the only known 3*d* materials exhibiting behavior similar to Kondo insulators. At low temperatures the electrical resistivity  $\rho(T)$  and magnetic susceptibility  $\chi(T)$  correspond to thermally activated narrow gap semiconductor. However, at higher temperatures ( $T \geq 300$  K) the slope of  $\rho(T)$  changes sign and becomes positive as in a metal.<sup>4</sup> The metal-insulator crossover is consistent with the optical measurements where the gap in the low- $T$  absorption spectrum starts getting filled with increasing temperature, with no trace of the gap observed<sup>4-6</sup> any more at  $T \geq 300$  K. The magnetic susceptibility  $\chi(T)$  vanishes at low  $T$ , passes through a maximum near 500 K, and obeys a Curie-Weiss law at higher temperatures.<sup>2,4</sup> Low electron doping by substituting Fe by Co ( $\approx 10\%$ ), or the substitution of Si by Ge ( $\approx 30\%$ ) yield a ferromagnetic metal.<sup>7</sup> Recently a colossal Seebeck coefficient was reported in FeSb<sub>2</sub>.<sup>8</sup>

The band-structure calculations within local density approximation (LDA) predict FeSi to be a nonmagnetic semiconductor<sup>9</sup> in agreement with the low-temperature experimental data. Interestingly, contrary to the usual underestimation of the gap by LDA, the calculated value  $\approx 100$  meV is two to three times larger than the estimate from optical and photoemission measurements.<sup>4-6</sup> Using the LDA+ $U$  approach to mimic the effect of on-site Coulomb repulsion, Anisimov *et al.*<sup>10</sup> found a ferromagnetic metallic phase very close by in energy. This approach has also allowed to describe transition from nonmagnetic insulator to ferromagnetic metal with substitution Ge for Si in isoelectron series FeSi<sub>1-x</sub>Ge<sub>x</sub>,<sup>11</sup> and the semiconductor-metal transition in FeSb<sub>2</sub>.<sup>12</sup> Nevertheless, current band structure theory itself cannot explain the temperature dependence of physical properties.

To describe the susceptibility and other thermodynamic quantities, Mandrus *et al.*<sup>13</sup> proposed a temperature independent model density of states with two very narrow ( $\approx 500$  K) peaks separated by a gap of ( $\approx 1000$  K). The origin of the narrow peaks was attributed to an extreme renormalization of the noninteracting bands similar to Ce-based Kondo insulators invoking localized states very weakly hybridizing with broad conduction band. However, the assumption of strongly renormalized peaks surviving up to high temperatures appears rather unlikely. Moreover, the Fe 3*d* states hybridize very strongly with *sp* bands: a large contribution of Fe 3*d*-orbitals character can be observed in  $\approx 8$  eV energy region.<sup>9,12</sup>

In this work we study a minimal model of correlated covalent insulator<sup>14</sup> within the dynamical mean-field approximation (DMFT). While the construction of the model is guided by the band structure of FeSi and FeSb<sub>2</sub>, we do not aspire to describe the physics of these materials in its full width. Our goal is to use simple model free of the complexity of a multiband low-symmetry system to capture semi-quantitatively the essential physics of FeSi/FeSb<sub>2</sub> and provide a well understood reference point for later multiband study.

In construction of the model we envision Hubbard Hamiltonian on a lattice with one orbital per site, but more than one site in the primitive cell. The DMFT approximation allows us to calculate important physical quantities, in particular the single-particle spectrum, from the knowledge of the noninteracting spectral density  $D(\omega)$  and the on-site repulsion  $U$ . We use  $U=1.5$  eV throughout this work, which yields semiquantitative agreement with experiment; the rather small value can be justified by a strong Fe-ligand hybridization. The key feature of  $D(\omega)$ , obtained by truncating the LDA density of states for FeSb<sub>2</sub> so that the low energy peak and gap structure is captured, is the presence of a gap between bands of the same orbital character. Fu and Doniach<sup>15</sup> studied a two-orbital model with an on-site hybridization, which leads to a gapped  $D(\omega)$ . Furmann *et al.*<sup>16</sup> calculated the single-particle and optical spectra of such model and addressed the question of interaction-driven BI to MI transition at high temperature.

In general, gapped local spectral function  $D(\omega)$  is charac-

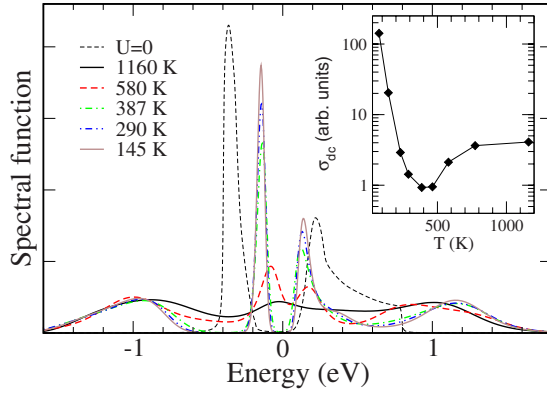


FIG. 1. (Color online) Single-particle spectral density at various temperatures. The noninteracting spectral function is marked with the dashed line. The inset shows the temperature dependence of dc conductivity.

teristic of covalent insulator, which is an instance of a band insulator. In contrast to ionic insulator, arising e.g., from staggered potential or crystal field, with the local orbitals either filled or empty, the local orbitals of covalent insulator are half (or in general partially) filled. The ground state of a covalent insulator is characterized by formation of nonlocal bonding combinations of orbitals, which are separated by a gap from the antibonding combinations. Introducing an on-site repulsion  $U$  leads to competition between electron localization and formation of nonlocal bonds. Large  $U$  makes the system a Mott insulator (MI).<sup>17</sup> The concept of BI to MI transitions driven by the on-site repulsion was recently studied in the context of the ionic Hubbard model.<sup>1</sup> While analogies can be drawn between the two cases there are also obvious differences which make the details BI-MI transitions in the correlated covalent insulator an interesting question. Here we focus on evolution of physical properties with temperature.

The central quantity in the DMFT framework is the single-particle self-energy  $\Sigma(\omega)$  which is determined by the self-consistent solution of the equations:

$$G(i\omega_n) = \int d\nu \frac{D(\nu)}{i\omega_n + \mu - \nu - \Sigma(i\omega_n)} \quad (1)$$

$$G_0^{-1}(i\omega_n) = G^{-1}(i\omega_n) - \Sigma(i\omega_n), \quad (2)$$

where  $\Sigma[G_0(i\omega_n), U]$  is determined by solving of the auxiliary Anderson impurity problem, for which we employ the Hirsch-Fye quantum Monte Carlo algorithm.<sup>18</sup> In Fig. 1 we show the evolution of the single-particle spectral density with temperature  $T$ . At low  $T$  renormalized quasiparticle bands with reduced gap (relative to  $U=0$  case) and Hubbard bands are well distinguished. With increasing temperature the lifetime of the quasiparticles decreases (see the self-energy in Fig. 2) and the sharp peaks in the spectral density are smeared as observed in the photoemission experiment.<sup>6</sup> The system thus smoothly evolves from low- $T$  insulator to high- $T$  incoherent metal.

This behavior becomes apparent from the temperature dependence of dc conductivity  $\sigma(T)$  calculated according to<sup>19</sup>

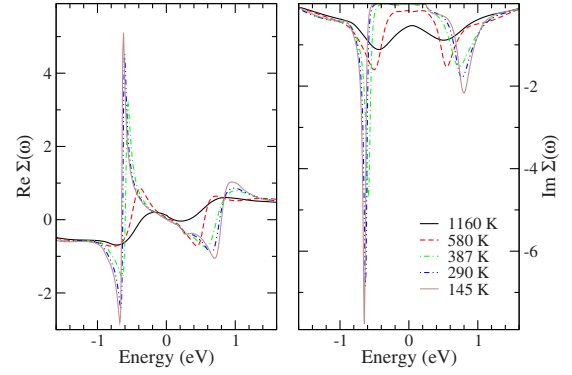


FIG. 2. (Color online) Single-particle self-energy  $\Sigma(\omega)$  for various temperatures.

$$\sigma(T) \propto \int d\epsilon d\omega \Phi(\epsilon) \rho^2(\epsilon, \omega; T) \frac{\partial f(\omega; T)}{\partial \omega} \quad (3)$$

$$\rho(\epsilon, \omega; T) = -\frac{1}{\pi} \text{Im} \left( \omega^+ - \epsilon - \Sigma(\omega; T) - \frac{i}{\tau} \right)^{-1} \quad (4)$$

$$\Phi(\epsilon) = \frac{1}{V} \sum_k \left( \frac{\partial \epsilon_k}{\partial k_x} \right)^2 \delta(\epsilon - \epsilon_k) \approx \left( \frac{\partial \epsilon_k}{\partial k_x} \right)^2 D(\epsilon). \quad (5)$$

Approximating the squared electron velocity  $\left( \frac{\partial \epsilon_k}{\partial k_x} \right)^2$  by its average value the transport density  $\Phi(\epsilon)$  reduces to the spectral density  $D(\epsilon)$  times a constant. Equation (3) is only valid if the quasiparticle lifetime is finite. To ensure this at all temperatures, we introduce a small constant contribution to the linewidth  $1/\tau = 0.015$  eV which can be thought of as arising from impurity scattering in real materials. Temperature enters formula (3) through the Fermi-Dirac distribution  $f(\omega; T)$  and the self-energy  $\Sigma(\omega; T)$ . The  $T$  dependence of resistivity  $\rho = \sigma^{-1}$  (see Fig. 1) is governed by the Fermi-Dirac distribution at low temperatures where the thermally activated behavior of band insulator is observed. At higher temperatures the increase of the number of thermally activated charge carriers is compensated by the decreasing quasiparticle lifetime, which eventually becomes dominant and the resistivity assumes the metallic  $T$  dependence with positive slope. This behavior of resistivity is observed in both FeSi (Ref. 4) and FeSb<sub>2</sub>.<sup>3</sup>

In general, the conductivity consists of intraband and interband contribution. The intraband contribution is obtained from<sup>19</sup>

$$\sigma(\omega) \propto \int d\epsilon d\omega' \Phi(\epsilon) \rho(\epsilon, \omega') \rho(\epsilon, \omega' + \omega) \times \frac{f(\omega') - f(\omega' + \omega)}{\omega}. \quad (6)$$

To calculate the interband contribution the band dispersion is necessary. In the present case of a narrow-band semiconductor the behavior of the interband contribution can be understood by looking at a typical transition corresponding to a specific  $k$  point. We choose excitation from the valence-band

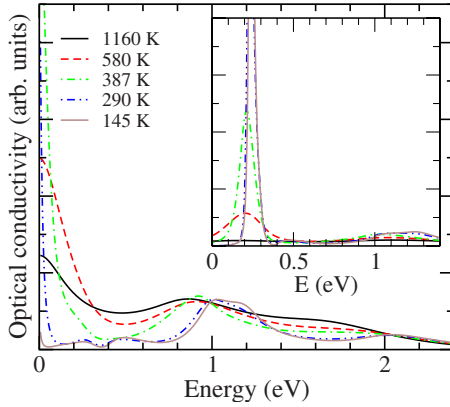


FIG. 3. (Color online) Intradband contribution to the optical conductivity at various temperatures. The inset shows the evolution of a typical interband contribution.

peak at  $\epsilon_1$  to conduction-band peak at  $\epsilon_2$  as the typical transition

$$\sigma_{IB}(\omega, k) \propto M_k \int d\omega' \rho(\epsilon_1, \omega') \rho(\epsilon_2, \omega' + \omega) \times \frac{f(\omega') - f(\omega' + \omega)}{\omega}. \quad (7)$$

The total interband conductivity  $\sigma_{IB}(\omega)$  would be obtained by summation over the  $k$  points weighted by the transition amplitude  $M_k$ , which results in some broadening due to the band dispersion. The  $T$  dependence of contributions from different  $k$  points follows the same pattern governed by the self-energy  $\Sigma(\omega; T)$  and the Fermi-Dirac function, and thus the typical transition provides a good idea about the behavior of total  $\sigma_{IB}(\omega)$ . The intradband contribution (6) is shown in Fig. 3. The main effect of decreasing the temperature consists in depletion the low-frequency region of spectral weight. Drude peak appears at intermediate temperatures, due to the thermally populated quasiparticle states, and disappears at lower temperatures. The appearance of the Drude peak is not a generic feature of the model, but depends on the relative size of the Kondo scale, given by the interaction parameter  $U$  and the overall bandwidth, and the semiconducting gap. The appearance of well defined quasiparticle states at low temperatures is also reflected by building up of a peak in  $\sigma_{inter}$  (inset of Fig. 3) above the energy of the single-particle gap. Absence of clear Drude peak at high temperatures, and spectral weight transfer from low-frequency region to above the single-particle gap upon cooling agrees well with the trend observed experimentally.<sup>4</sup>

Next we discuss the behavior of local and uniform magnetic susceptibilities, which are calculated by integrating the imaginary time-correlation function  $\langle m_z(\tau)m_z(0) \rangle$  and employing the formalism of Ref. 20, respectively. In Fig. 4, susceptibilities of the system without local interaction are compared with those of interacting and doped system.<sup>21</sup> At half filling the uniform susceptibility exhibits an exponential decrease at low  $T$ , while the local susceptibility saturates to a finite value, in both interacting and noninteracting system. The interaction, which favors formation of local moments,

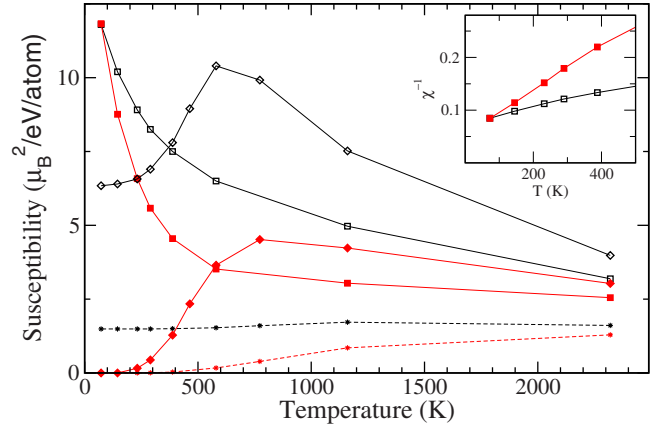


FIG. 4. (Color online) Temperature dependence of local (black) and uniform (red, dark gray) susceptibility for half-filled (diamonds) and doped (squares) system. The dashed lines mark the local (black) and uniform (red, dark gray) susceptibility of the non-interacting system.

strongly enhances both local and uniform susceptibility and results in appearance of Curie-Weiss tail at high  $T$ . Doping of 0.2 electron has a profound effect on the susceptibility. At this doping level the chemical potential is located close to the valence-band peak and thus a Stoner-like enhancement of the susceptibility can be expected. While the high  $T$  local moment is reduced due to departure from half filling, at low  $T$  both the uniform and local susceptibility show an increase characteristic for local-moment systems. Different slopes of the inverse local and uniform susceptibilities of the doped system (inset of Fig. 4) indicate that a simple Heisenberg model with rigid local moments does not provide the appropriate picture.

Taking the local dynamical correlations into account via DMFT method results in a satisfactory description of all major FeSi-FeSb<sub>2</sub> anomalies. The energy gap present in the single-particle spectrum at low temperatures, reduced by a factor of two from its LDA value, starts filling with increasing  $T$ , accompanied by smearing of the sharp peaks, so that above 600 K no trace of the gap is visible. Corresponding change from insulating to metallic character is observed in the resistivity and the optical conductivity. The uniform magnetic susceptibility increases exponentially from  $T=0$ , reaches maximum at  $\approx 600$  K and approaches Curie-Weiss law at higher temperatures. We find a moderate ( $Z \approx 0.5$ ) very weakly  $T$ -dependent quasiparticle renormalization below the room temperature implying that in this temperature range the  $T$  dependence of physical quantities such as conductivity or thermopower enters predominantly through the Fermi-Dirac distribution. This behavior is quite different from classical, e.g., Ce based, Kondo insulators and heavy-fermion compounds where a strong  $T$  dependence of the self-energy and thus the quasiparticle renormalization exists down to very low temperatures. Sharpening of the spectral features at low temperatures due to quasiparticle renormalization enhances the thermopower, proportional to the first moment of spectral density,<sup>19</sup> and thus qualitatively agrees with the experimental observation.<sup>8</sup>

In real materials with multiple bands, the orbital occupa-

tions deviate from half filling, e.g., due to crystal fields. Therefore the effect of competition between covalency and interaction-driven localization such as correlation enhancement of susceptibility is expected to be smaller than in the studied model. One can also imagine a situation with a staggered potential and a site dependent  $U$ , which can then describe materials with strong metal-ligand hybridization such as  $\text{LaCoO}_3$ . We believe that presented minimal model can provide a useful reference point for understanding such systems.

In conclusion we have investigated a minimal model of correlated covalent insulator to study the unusual temperature evolution of physical properties of  $\text{FeSi}$  and  $\text{FeSb}_2$ . The

model captures all the remarkable properties of these materials including the insulator to bad metal transition and the appearance of Curie-Weiss susceptibility at elevated temperatures.

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- <sup>1</sup>A. Garg, H. R. Krishnamurthy, and M. Randeria, *Phys. Rev. Lett.* **97**, 046403 (2006); S. S. Kancharla and E. Dagotto, *ibid.* **98**, 016402 (2007); N. Paris, K. Bouadim, F. Hebert, G. G. Batrouni, and R. T. Scalettar, *ibid.* **98**, 046403 (2007).
- <sup>2</sup>V. Jaccarino, G. K. Wertheim, J. H. Wernick, L. R. Walker, and Sigurd Aarj, *Phys. Rev.* **160**, 476 (1967).
- <sup>3</sup>C. Petrovic, Y. Lee, T. Vogt, N. Dj. Lazarov, S. L. Budko, and P. C. Canfield, *Phys. Rev. B* **72**, 045103 (2005).
- <sup>4</sup>Z. Schlesinger, Z. Fisk, Hai-Tao Zhang, M. B. Maple, J. F. DiTusa, and G. Aeppli, *Phys. Rev. Lett.* **71**, 1748 (1993).
- <sup>5</sup>A. Damascelli, K. Schulte, D. van der Marel, and A. A. Menovsky, *Phys. Rev. B* **55**, R4863 (1997).
- <sup>6</sup>K. Ishizaka, T. Kiss, T. Shimojima, T. Yokoya, T. Togashi, S. Watanabe, C. Q. Zhang, C. T. Chen, Y. Onose, Y. Tokura, and S. Shin, *Phys. Rev. B* **72**, 233202 (2005); D. Zur, D. Menzel, I. Jursic, J. Schoenes, L. Patthey, M. Neef, K. Doll, and G. Zwirnagl, *ibid.* **75**, 165103 (2007).
- <sup>7</sup>N. Manyala, Y. Sidis, J. F. DiTusa, G. Aeppli, D. P. Young, and Z. Fisk, *Nature (London)* **404**, 581 (2000); M. A. Chernikov, L. Degiorgi, E. Felder, S. Paschen, A. D. Bianchi, H. R. Ott, J. L. Sarrao, Z. Fisk, and D. Mandrus, *Phys. Rev. B* **56**, 1366 (1997).
- <sup>8</sup>A. Bentien, S. Johnsen, G. K. H. Madsen, B. B. Iversen, and F. Steglich, *Europhys. Lett.* **80**, 17008 (2007).
- <sup>9</sup>L. F. Mattheiss and D. R. Hamann, *Phys. Rev. B* **47**, 13114 (1993); C. Fu, M. P. C. M. Krijn, and S. Doniach, *ibid.* **49**, 2219 (1994).
- <sup>10</sup>V. I. Anisimov, S. Yu. Ezhov, I. S. Elfimov, I. V. Solovyev, and T. M. Rice, *Phys. Rev. Lett.* **76**, 1735 (1996).
- <sup>11</sup>V. I. Anisimov, R. Hlubina, M. A. Korotin, V. V. Mazurenko, T. M. Rice, A. O. Shorikov, and M. Sgrist, *Phys. Rev. Lett.* **89**, 257203 (2002).
- <sup>12</sup>A. V. Lukoyanov, V. V. Mazurenko, V. I. Anisimov, M. Sgrist, and T. M. Rice, *Europhys. Lett.* **53**, 205 (2006).
- <sup>13</sup>D. Mandrus, J. L. Sarrao, A. Migliori, J. D. Thompson, and Z. Fisk, *Phys. Rev. B* **51**, 4763 (1995).
- <sup>14</sup>N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders, Philadelphia, 1976).
- <sup>15</sup>C. Fu and S. Doniach, *Phys. Rev. B* **51**, 17439 (1995).
- <sup>16</sup>A. Fuhrmann, D. Heilmann, and H. Monien, *Phys. Rev. B* **73**, 245118 (2006).
- <sup>17</sup>G. Moeller, V. Dobrosavljević, and A. E. Ruckenstein, *Phys. Rev. B* **59**, 6846 (1999).
- <sup>18</sup>J. E. Hirsch and R. M. Fye, *Phys. Rev. Lett.* **56**, 2521 (1986).
- <sup>19</sup>Th. Pruschke, M. Jarrell, and J. Freericks, *Adv. Phys.* **44**, 187 (1995); V. S. Oudovenko and G. Kotliar, *Phys. Rev. B* **65**, 075102 (2002).
- <sup>20</sup>M. Jarrell, *Phys. Rev. Lett.* **69**, 168 (1992).
- <sup>21</sup>A. Bentien, G. K. H. Madsen, S. Johnsen, and B. B. Iversen, *Phys. Rev. B* **74**, 205105 (2006).