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Pressure-induced insulator-metal transition of localized states in $\mathbf{FeSi_{1-x}Ge_x}$

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Resistivity measurements have been carried out in $FeSi_{1-x}Ge_x$ ($x=0.0$, 0.05, and 0.20) in the 4–300 K range under the application of pressure up to 6.4 GPa. The resistivity data between 100 and 200 K fit an activated behavior yielding the measured transport gap Δ. The trends in the pressure variation of Δ seems to depend on the measured resistivity ratio $R(4.2\text{ K})/R(300\text{ K})$ at ambient pressure. The observed behavior of Δ with increase in pressure is argued to arise from two competing factors that contribute to Δ, a decrease due to shift in the mobility edge E_μ toward E_F and an increase due to changes in the electronic structure of the bulk. A remarkable feature of the experimental results, however, is the drastic change in the temperature dependence of conductivity $\sigma(T)$ in the 4–50 K range. In this temperature range, while $\sigma(T)$ fits the variable range hopping transport mechanism in pristine FeSi, significant deviation from such a fit is seen with Ge substitution and under the application of pressure. The data in these cases fit better to power laws. A plot of the logarithmic derivative $w=d\ln\sigma/d\ln T$ as a function of $T^{1/2}$ for various external pressures reveals that w is a decreasing function of temperature for low pressure and gradually becomes an increasing function of temperature at higher pressures, in both FeSi and $FeSi_{0.95}Ge_{0.05}$. These results indicate that the localized states in the gap delocalize, giving rise to an insulator to metal transition as a function of pressure. From the nature of the temperature dependence of w across the transition, it can be surmised that the insulator to metal transition in FeSi is possibly continuous as in doped semiconductors.

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I. INTRODUCTION

The metal-insulator transition (MIT) due to Anderson localization of electrons in disordered solids has been a subject of intense research for several decades.[1,2] It is now agreed that metallicity is implied by the observation of finite conductivity as T approaches zero.[3] Mott postulated that on the metallic side the system should have a minimum metallic conductivity,[4,5] and in this picture the metal-insulator transition approached from the metallic side is discontinuous. In contrast, the scaling theory of localization,[6] predicts that the conductivity should decrease continuously to zero, approached from the metallic side, according to $\sigma=\sigma_0(x-x_c)^\nu$, where x_c is the critical value of the control parameter and ν is the critical exponent.[6,7] The control parameter x that drives the transition can be carrier concentration, external pressure, or external magnetic field[7–9] as was shown in P-doped Si. This phenomenon has also been observed in three dimensions in other doped semiconductors, viz., Si:As and Si:B.[10,11] In experiments that suggest that the transition is continuous, the magnitude of the exponent is still a matter of debate.[12] The extrapolation schemes employed to obtain σ as T tends to zero are modified as more refined experiments are performed at lower and lower temperatures. Such studies and controversies also exist in resistivity studies on amorphous alloys of $Si_{1-x}Ni_x$, $Si_{1-x}Cr_x$, $Mo_{1-x}Ge_x$, and $Mo_{1-x}Si_x$.[13–15]

It has been demonstrated[15] that the nature of the metal-insulator transition and the critical concentration at which this occurs can be determined from a plot of $w=d\ln\sigma/d\ln T$ with respect to temperature. This is based on the fact that the temperature dependence of σ on the insulating side of the transition is of the variable range hopping type, viz., $\sigma=\sigma_0\exp[-(T_0/T)^{1/4}]$ and on the metallic side σ has a power law dependence on temperature. This results in w being a decreasing function of temperature on the insulating side and an increasing function of temperature on the metallic side. Further, from the variation of w with temperature across the transition, the discontinuous/continuous nature of the transition can be discerned. Such an analysis in the amorphous $Si_{1-x}Ni_x$ system has shown that the transition is possibly discontinuous, reiterating the validity of Mott's minimum metallic conductivity concept.

There is now enough evidence to believe that FeSi belongs to the class of correlated electron systems termed Kondo insulators. These systems are characterized by a small gap in the density of states and have a nonmagnetic ground state.[17–19] While band structure calculations predict the magnitude of the gap correctly,[20] the presence of the sharp features at the valence and conduction band edges seen in the experiments implies that electron-electron correlations are important.[21] The high temperature conductivity (100–200 K) in FeSi is governed by activated transport across the gap from which the magnitude of the Kondo insulating gap can be extracted. Another interesting feature of the transport properties in FeSi is that the resistivity behavior is of the variable range hopping type in the 5-40 K temperature regime, implying the presence of defect states in the gap. These states have been attributed to off-stoichiometry,[22] antisite disorder,[23] or the presence of distinct isomeric phases.[24] There is reason to believe that defects in FeSi are intrinsic, unlike in doped semiconductors,[7] as the literature indicates that the variable range hopping transport is still present in purer samples. In this study we point out the similarity of the transport properties in the FeSi system to those of amorphous semiconductors, as regards chemical substitution and the application of pressure. As in the amorphous semiconductors, the temperature dependence, which is of the variable range

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hopping type in pristine FeSi, significantly deviates from it with chemical substitution and application of pressure. It would therefore be interesting to enquire if there is an insulator-metal transition of the Anderson type in this system under the application of pressure as in the doped/amorphous semiconductors. With this in mind we have carried out an analysis of the conductivity data in the 5–40 K regime in FeSi and Ge-substituted FeSi for several external pressures, in line with studies reported in amorphous and doped semiconductors.[16] Our present results in FeSi and $FeSi_{0.95}Ge_{0.05}$ indicate that there is an insulator to metal transition and that it is possibly continuous.

Yet another aspect of the present investigation is the study of the effect of external pressure on the Kondo insulating (KI) gap. The application of pressure is known to have varied effects on the measured gap in KI systems. In the classic *f*-electron Kondo insulator $Ce_3Bi_4Pt_3$, the application of pressure results in an increase in the magnitude of the gap, in accordance with the expectations of the hybridization gap model.[25] In SmB_6,[26] the gap decreases with pressure, whereas CeNiSn,[27] a KI with small gap,[28] metallizes with increase in pressure. In FeSi, Bauer *et al.*[29] report from their resistivity measurements an increase in the value of Δ with external pressure; temperature dependent magnetic susceptibity measurements using a superconducting quantum interference device (SQUID) magnetometer reveal that Δ increases as a function of pressure.[30] In this paper we present the pressure dependence of the KI gap in samples with different Ge concentrations, which is known to alter the Δ values at ambient pressure.[31] These results point out that defect states in the gap play a major role in giving rise to the disparate behavior of Δ with pressure in FeSi and Ge-substituted FeSi.

The paper is organized as follows. In Sec. II, we describe the experimental details. In Sec. III, we present the results of the effect of pressure on the KI gap as measured by the temperature dependence of resistivity $\rho(T)$ in the 100–200 K temperature range, and establish that its variation is correlated to the magnitude of the resistivity ratio $[R(4.2\ \mathrm{K})/R(300\ \mathrm{K})]$ (RR) at ambient pressure. In Sec. IV, we concentrate on the behavior of conductivity as a function of temperature in the 5–40 K regime for various pressures, and present evidence for the occurrence of the insulator-metal transition as a function of pressure based on the behavior of the logarithmic derivative. In Sec. V we present a discussion of the results and propose a schematic model for the electronic structure of this system, taking the input from the present resistivity measurements, in conjunction with what is already known in this system. Section VI provides the summary and conclusions.

II. EXPERIMENT

The $FeSi_{1-x}Ge_x$ samples were arc melted from stoichiometric quantities of the constituents in argon atomosphere and subsequently homogenized at 1000 °C for a week. X-ray characterization indicated single phase formation in the $P2_13$ structure.[31] The samples were subsequently cut using a diamond wheel, after which the resistivity measurements were performed in the four-probe geometry. The high pressure measurements were carried out in an opposed anvil pressure locked cell. A small piece of Pb mounted alongside the sample but electrically isolated from it was used as an internal pressure calibrant. The variation of the superconducting transition temperature of Pb with pressure is well documented.[32] Details of the sample assembly can be found in Ref. 33. The temperature of the sample was measured using a calibrated Si-diode thermometer and Rh-Fe thermometer and the Pb T_c was measured using a Ge resistance thermometer. A very good agreement was obtained in the temperatures read from all the thermometers. The experiment is carried out as follows. The pressure locked cell is first lowered into a liquid He cryostat and just enough He is transferred into the Dewar to lower the temperature to 4.2 K. The system is then allowed to warm up, while the Pb T_c is measured to obtain the pressure locked in. Then liquid He is transferred again into the Dewar to decrease the sample temperature to 4.2 K. The resistivity of the sample is measured in the 4.2 and 300 K temperature range as the cryostat warms up to room temperature over a period of 2–3 days. Parasitic thermal emf's are eliminated by current reversal and by taking the average of the voltage readings. The data acquisition is carried out through a personal computer using an IEEE interface card. The pressure inhomogeneity estimated from the Pb transitions is ~0.05 GPa. In addition, the resistivity of Pb at 300 K is pressure dependent, from which the decrease in pressure after thermal cycling from 300 to 4 K and back is estimated to be 0.2 GPa.

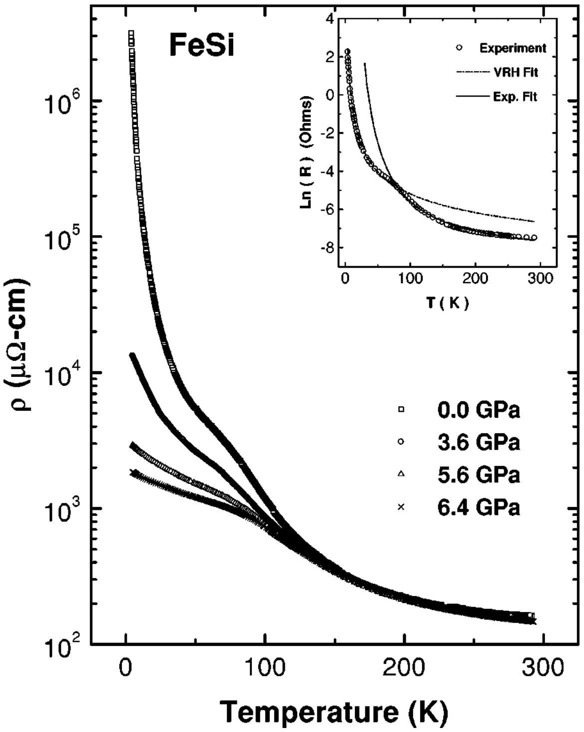

FIG. 1. Variation of $\rho(T)$ for the various pressures indicated in pristine FeSi (RR of 20 000). VRH and activated behavior fits in the 5–40 and 100–200 K temperature regimes are shown in the inset for the ambient pressure data.

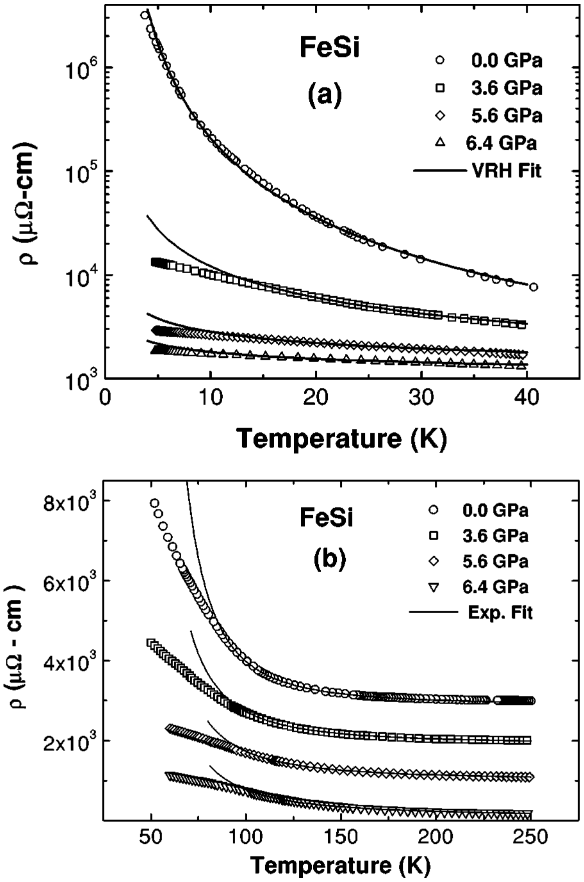

FIG. 2. (a) Variation of $\rho(T)$ in FeSi (RR 20 000) in the 4–40 K range; VRH formula fits are shown as solid curves. (b) Fits to show the activated behavior in these samples for various pressures in the 100–200 K range. Δ values have been extracted from fits in the 100–170 K region. The data at various pressures have been shifted along the ordinate axis for clarity.

III. RESULTS: PRESSURE DEPENDENCE OF Δ

In Fig. 1, the logarithm of resistivity $\rho(T)$ is plotted for various pressures for FeSi, as a function of temperature. It is clear from the figure that very large changes are seen in ρ in the low temperature region. Although not apparent from the figure, $\rho(T)$ at 300 K is found to decrease with increase in pressure. It can also be seen from Fig. 1 that the resistance ratio $R(4.2\text{ K})/R(300\text{ K})$ is drastically reduced by the application of pressure. The fits of the resistivity to the variable range hopping (VRH) formula $\rho=\rho_0\exp[(T_0/T)^{1/4}]$ in the 4.2–40 K range for all the pressures investigated in FeSi are shown in Fig. 2(a). It can also be seen from the figure that the fit to the VRH formula at ambient pressure is very good and the T_0 extracted from the fit is $\sim 1.56\times10^5$, very close to the earlier reported values.[22] For higher pressures the resistivity starts deviating from the VRH behavior for temperatures below 15 K and T_0 decreases to ~15 at a pressure of 6.4 GPa. In the higher temperature region, the resistivity data are fitted to an activated behavior $\rho=\rho_0\exp(\Delta/2kT)$ and the fits are shown in Fig. 2(b). A similar fit for $\text{FeSi}_{0.95}\text{Ge}_{0.05}$ using the VRH formula in the 4.2–40 K range for representative pressures is shown in Fig. 3(a) and that for the activated behavior in the 100–200 K regime is shown in Fig. 3(b). It can be seen from the figures that the VRH formula fits the data well down to the lowest temperature at ambient pressure, but deviates from it at low temperatures for large pressures.

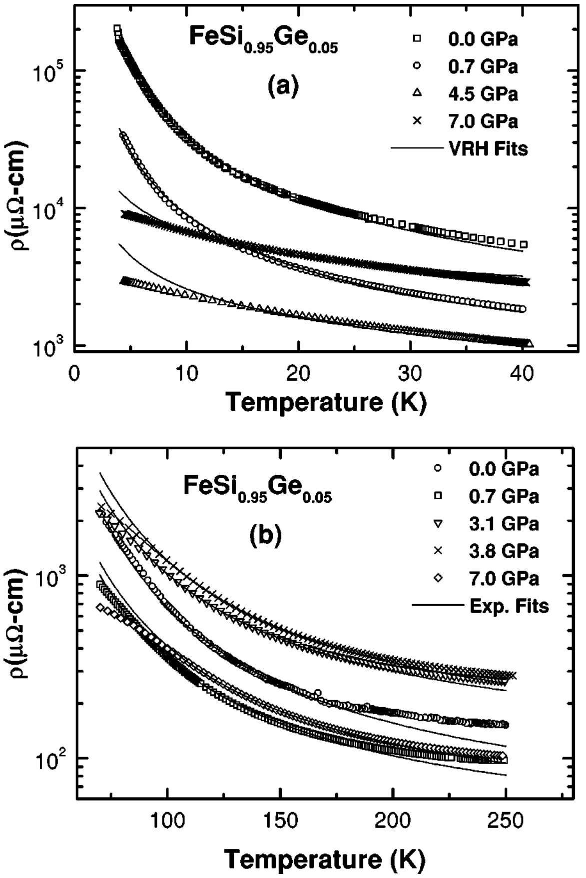

FIG. 3. (a) Variation of $\rho(T)$ in the 4–40 K range for a few pressures in $\text{FeSi}_{0.95}\text{Ge}_{0.05}$; VRH formula fits are shown as solid curves. (b) Fits to show the activated behavior in FeSi for various pressures in the range 100–200 K; the Δ values have been extracted from fits in the 100–170 K region.

First we concentrate on the overall behavior of the high temperature part (100–200 K) of the resistivity with pressure and Ge substitution. We therefore plot the variation of Δ obtained from these fits as a function of pressure for all the samples investigated in Fig. 4. We notice that Δ at ambient pressure decreases with Ge substitution[31] and with decreasing RR of the sample. Further, it is seen from the figure that in FeSi (RR 20 000) Δ decreases from 700 K at 0 GPa to 480 K at 6.4 GPa. In the 5% Ge-substituted sample (RR 1400) Δ shows an initial decrease from 600 K at ambient pressure to 450 K at ~1 GPa, but with further increase in pressure up to ~7 GPa Δ increases to ~590 K. In the 20% Ge-substituted sample, which has a RR of 247, Δ shows an increase from 125 to 175 K from ambient pressure to 5.5 GPa. While at first sight the behavior of Δ seems disparate, taken in conjunction with the RR of the sample at ambient pressure, a systematics seems to emerge. For example, in FeSi with a large RR of 20 000 Δ decreases, in the 5% Ge sample with an intermediate RR of 1400 Δ decreases followed by an increase, and in the 20% Ge sample with RR of 247 Δ in-

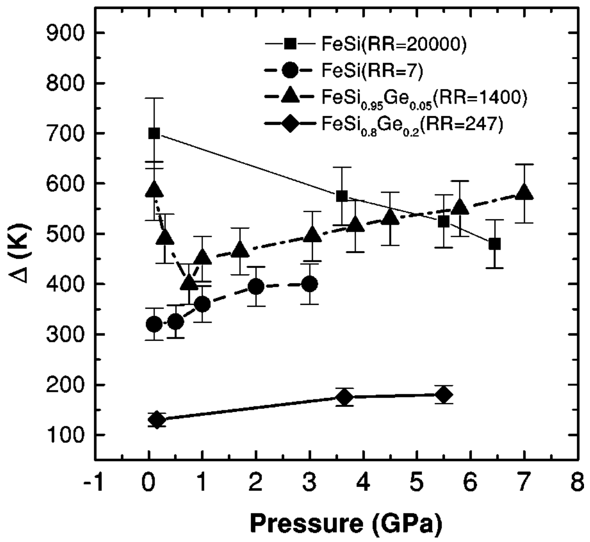

FIG. 4. Variation of Δ obtained from fits to activated behavior versus pressure in all the samples studied. The resistance ratio $R(4.2\ \mathrm{K})/R(300\ \mathrm{K})$ in each of the samples obtained at ambient pressure is also marked.

creases. Since we found a qualitatively different pressure dependence of Δ in pure FeSi from that of Bauer *et al.*,[29] and our results indicate differences in the pressure dependence of Δ dictated by the RR, we found it worthwhile to investigate an FeSi sample with a poor RR of 7. This sample was Fe deficient (Fe=49.9 at. %), whereas the sample with RR of 20 000 had Fe composition close to stoichiometry (50.02%). No differences could be discerned in either X-ray diffraction patterns or lattice parameter values between the two samples with different RR's. It can be seen from Fig. 4 that Δ for this sample increases from 320 K at ambient pressure to 400 K at 3.5 GPa. This trend of an increase in Δ with pressure in the FeSi sample with RR of 7 is in agreement with the results of Bauer *et al.*[29] It should be remarked that large variations in the experimentally observed RR in samples arise mainly due to great differences in the measured low temperature resistivity. This in FeSi is dictated by the presence of defect states in the gap; hence the RR is an index of the quality of the sample. From Fig. 4, it appears that the type of Δ variation with pressure is intimately related to the presence of defect states in the KI gap. It is therefore important to understand the nature of these defect states and their variation with pressure before interpreting the pressure variation of Δ, which we attempt in the next section.

IV. PRESSURE EFFECTS: LOCALIZED STATES

The temperature dependence of the measured conductivity $\sigma(T)$ in the 5–40 K range for various pressures investigated is compared in Fig. 5 for the FeSi sample. It is clear from the figure that as T tends to zero $\sigma(T)$ seems to approach zero at ambient pressure, as is expected for an insulator; since the present experiments terminate at 4.2 K we may not be fully justified in extrapolating and drawing conclusions about the behavior of σ as T tends to zero. In fact, measurements exist down to 30 mK and from these experiments the extrapolated value of $\sigma(T=0)$ is finite in FeSi,[34] and is $\sim 0.04\ \Omega^{-1}\,\mathrm{cm}^{-1}$, much smaller than the expected minimum metallic conductivity 37–74 $\Omega^{-1}\,\mathrm{cm}^{-1}$ in this system.[34] In contrast, for the FeSi sample under 3.6 GPa pressure (cf. Fig. 3), the extrapolated $\sigma(T=0)$ is unambiguously finite and is $\sim 50\ \Omega^{-1}\,\mathrm{cm}^{-1}$. It is also clear from Fig. 5 that with increase in pressure the magnitude of $\sigma(T=0)$ increases to $\sim 500\ \Omega^{-1}\,\mathrm{cm}^{-1}$, for a pressure of 6.4 GPa. From the present results it can be inferred that the system undergoes an insulator to metal transition at $T=0$, somewhere between ambient pressure and 3.6 GPa.

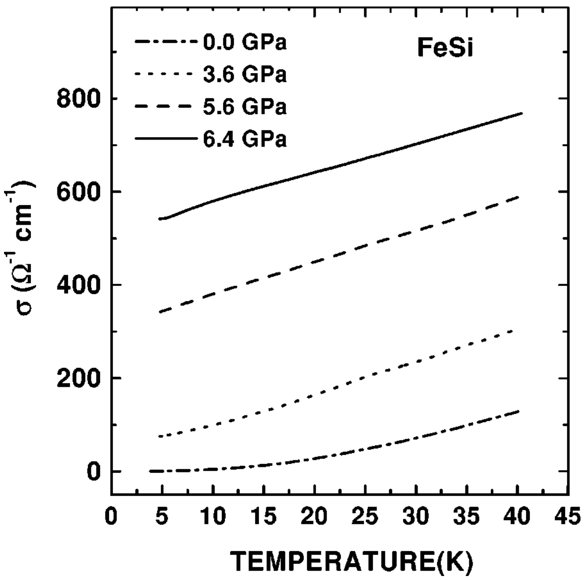

FIG. 5. The conductivity versus temperature in the 5–40 K temperature range for all pressures investigated in pristine FeSi (RR 20 000). Note that the extrapolated $\sigma(T=0)$ becomes larger with increasing pressure and the temperature dependence becomes more linear in character.

Another noteworthy feature of the results shown in Fig. 5 is that the temperature dependence of σ in the 5–40 K temperature range, which is of the variable range hopping type at ambient pressure, becomes more linear with increase in pressure. In fact $\sigma(T)$ fits the relation $\sigma=\sigma_0+\sigma_1 T^{1/2}+\sigma_2 T$, with the coefficient of the linear term showing a systematic increase with increase in pressure. Exponents of both 1/2 and 1 for the conductivity in the metallic regime were obtained earlier in other amorphous systems[14] and have been argued to arise due to electron-electron interaction and disorder effects[35] and the possible influence of phonons.[14]

In Fig. 6 is plotted $\sigma(T)$ versus T in the 5% Ge-substituted sample, for all the pressures investigated. From Fig. 6, it appears that the extrapolated $\sigma(T=0)$ tends to zero for pressures up to ~3 GPa, beyond which it extrapolates to finite values, indicating that the metal-insulator transition might occur at pressures greater than 3 GPa. Here again it is noticed that the temperature dependence of $\sigma(T)$ is more linear with increase in pressure. A plot of the $\sigma(T=0)$ obtained from a fit of the power law behavior $\sigma=\sigma_0+\sigma_1 T^{1/2}+\sigma_2 T$ is shown in Fig. 7, which shows an increase from values tending to zero at ambient pressure to $\sim 210\ \Omega^{-1}\,\mathrm{cm}^{-1}$ at ~5 GPa, beyond which the pressure de-

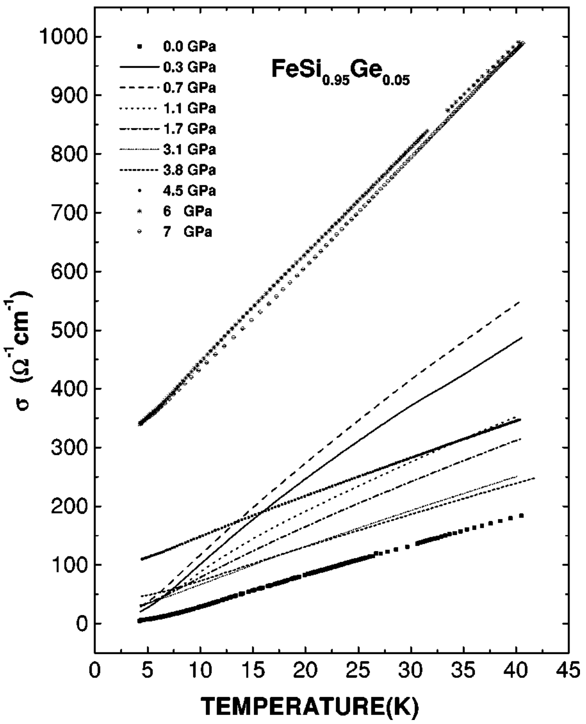

FIG. 6. The conductivity versus temperature in the 5–40 K temperature range, for all pressures investigated in $FeSi_{0.95}Ge_{0.05}$. Note that the extrapolated $\sigma(T=0)$ becomes larger with increasing pressure and the temperature dependence becomes linear in character.

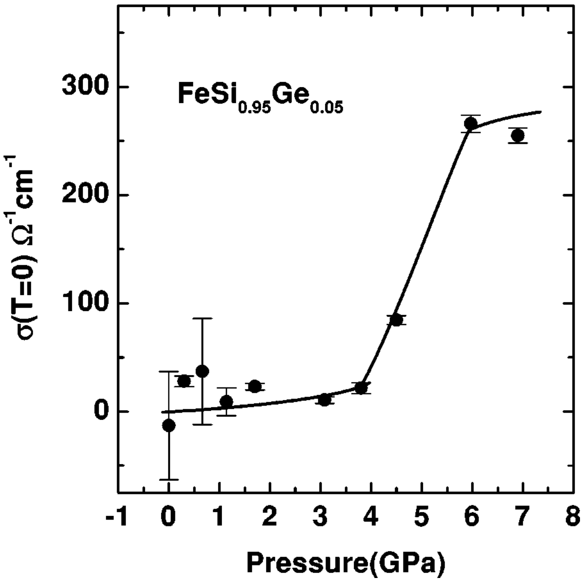

FIG. 7. The conductivity $\sigma(T=0)$ obtained from power law fits described in the text, as a function of pressure. The solid line is a guide to the eye.

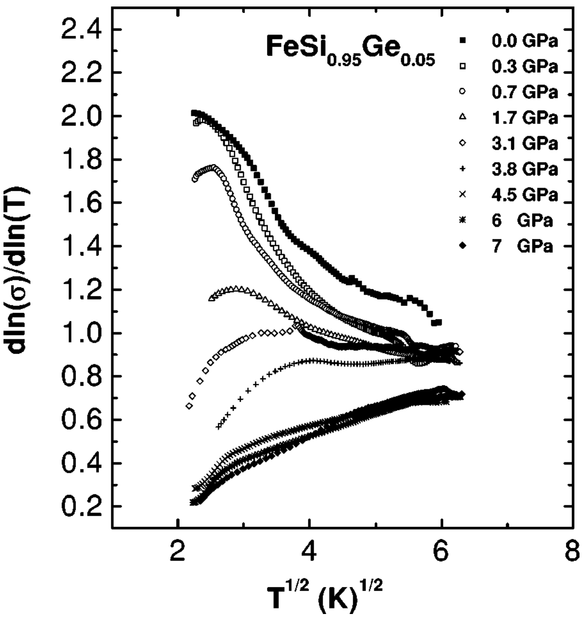

FIG. 8. The logarithmic derivative of conductivity (w) versus temperature in the 5–40 K temperature range, for all pressures investigated in the $FeSi_{0.95}Ge_{0.05}$ sample. Note that w increases with decreasing temperature for pressures upto 2 GPa, beyond which it shows a tendency to extrapolate to 0 as T tends to 0.

pendence of $\sigma(T=0)$ flattens out. In order to obtain the precise value of the critical pressure at which the MIT occurs[15] we plot the variation of w with temperature for different pressures for $FeSi_{0.95}Ge_{0.05}$ in Fig. 8. A careful look at Fig. 8 indicates that the temperature dependence of w changes gradually from having a negative to a positive temperature coefficient with increase in pressure. The change of sign of dw/dT occurs beyond ~1.7 GPa, implying that the insulator to metal transition occurs between ~1.7 GPa and ~3.1 GPa, close to that inferred from Fig. 6. In Fig. 9 we plot $w(T)$ plot for FeSi (RR 20 000), from which it is clear that w is a decreasing function of T as expected for an insulator at ambient pressure, but under 3.6 GPa external pressure shows a temperature dependence that is an increasing function of temperature, reinforcing that the MIT in FeSi occurs in the 0 to 3.6 GPa range. This is in agreement with the inference drawn from the $\sigma(T)$ data shown in Fig. 5 for FeSi for various pressures. It is worth pointing out that on the insulating side w, after showing an unambiguous increase with decrease in temperature, exhibits a downturn at the lowest of temperatures. This could possibly arise from the fact that the resistivity in FeSi and related systems becomes smaller than that predicted by the VRH formula and tends to saturate at very low temperatures, which has led to a suggestion that FeSi has a semimetallic ground state at $T=0$.[34]

It was shown by model calculations[15] that the discontinuous/continuous nature of the MIT can be discerned by a study of the behavior of $w(T)$ close to the MIT. Since in the plots of $w(T)$ vs T for both FeSi and 5% Ge-substituted FeSi (cf. Fig. 8 and Fig. 9) no minimum is seen as the pressure is varied, as was seen in Ref. 15 for a typical discontinuous MIT, it can be concluded that the insulator-metal transitions observed in the present investigation are possibly continuous.

In Fig. 10, we plot $\sigma(T)$ versus T for the 20% Ge-substituted sample. The $\sigma(T=0)$ obtained in this sample at ambient pressure is $\sim 55\ \Omega^{-1}\,\mathrm{cm}^{-1}$, a value well within the range of the minimum metallic conductivity obtained in these systems.[34] The $\sigma(T=0)$, however, shows an increase

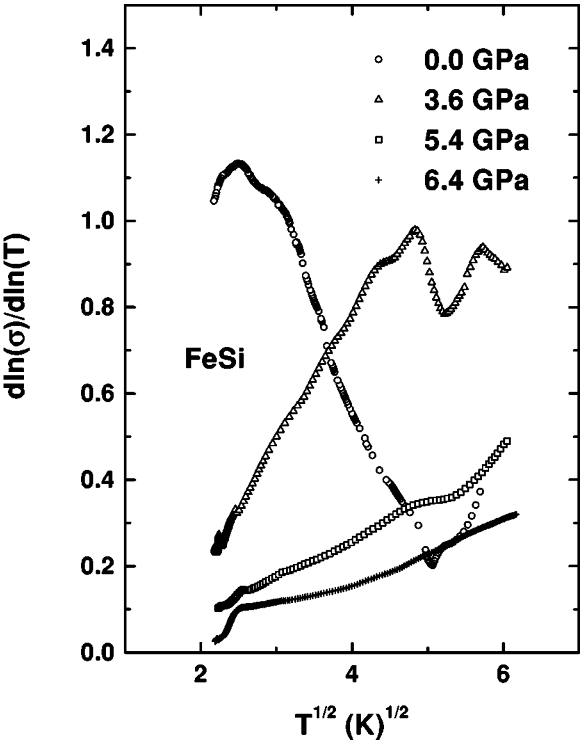

FIG. 9. The logarithmic derivative of conductivity (w) versus temperature in the 5–40 K temperature range, for all pressures investigated in the FeSi (RR 20 000) sample. Note that w increases with decreasing temperature at ambient pressure. For pressures greater than 3.6 GPa, w decreases with temperature, possibly extrapolating to 0 as T tends to 0.

with increase in pressure. The corresponding plot of w versus temperature indicated that w is an increasing function of temperature even at ambient pressure, which also implies that the sample is metallic at ambient pressure. From our results, it is clear that external pressure induces an insulator to metal transition in FeSi and in the 5% Ge-substituted sample. In the following we try to understand the results in the context of similar experimental data on doped and amorphous semiconductors.

V. DISCUSSION

A schematic diagram of the density of states of FeSi and related systems is shown in Fig. 11. The KI gap in the absence of disorder would be the energy difference between the positions of the sharp peaks residing at the conduction band edge (CBE) and the valence band edge (VBE). The Fermi level E_F lies in the middle of the gap. Disorder induces tails within the gap and the delocalized and localized states are separated by the mobility edge E_μ.[4,5] Since the nature of $w(T)$ at the insulator to metal transition implies that the transition is possibly continuous, we discuss the present results in terms of the scaling theory of localization.[1,2,4,5,36] According to this theory, as the transition is approached from the metallic side the zero temperature conductivity $\sigma(T=0)$ is expected to vanish continuously according to

$$\sigma(T=0)=C\|p-p_c\|^s, \tag{1}$$

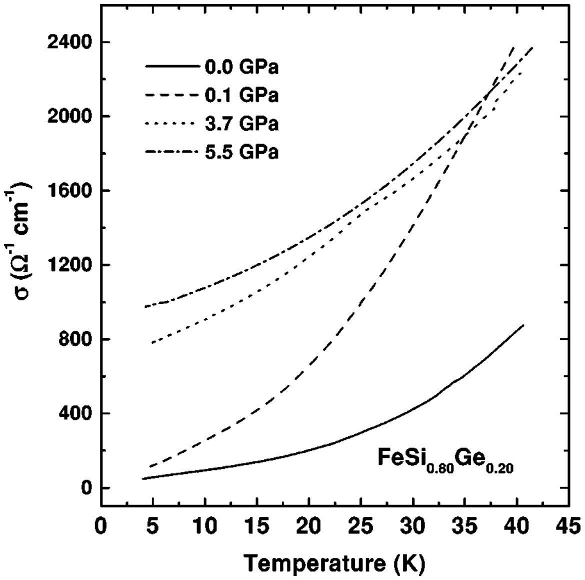

FIG. 10. The conductivity versus temperature in the 5–40 K temperature range for $FeSi_{0.80}Ge_{0.20}$.

where p is a control parameter, which is external pressure in the present experiments, C is a proportionality constant, p_c is the critical pressure at which the metal-insulator transition occurs, and s is the critical exponent. Approached from the insulating side of the transition, the localization length a varies as

$$a=a_0p_c/\|p-p_c\|^\nu, \tag{2}$$

where a_0 is the localization length far away from the transition; the localization length diverges as p tends to p_c with a critical exponent of ν; usually $\nu=s$.[2] When E_F lies in the energy regime in which electron states are localized, viz., between the mobility edges, E_μ (cf. Fig. 11), the system at zero temperature is in the insulating state with vanishing σ at $T=0$. When $\|E_\mu-E_F\|$ is small, the electronic states between E_μ and E_F becomes more delocalized and at $\|E_\mu-E_F\|=0$ the insulator to metal transition occurs. FeSi can be viewed as being on the insulating side of the insulator-metal transition. At pressures greater than ambient, although power law fits are better in the entire temperature range of 5–40 K, good fits to the variable range hopping transport mechanism can be obtained in the narrow temperature interval of 15–40 K. The hopping parameter T_0 extracted from these fits decreases by three to four orders of magnitude as the pressure is increased, as mentioned in Sec. III. Since T_0 varies as the cube of the localization length inverse, a decrease in the value of T_0 is consistent with the delocalization of gap states, or an increase in the localization length. This behavior is consistent with Eq. (2), viz., as the system moves away from the insulating regime the localization length diverges, and at a critical pressure the insulator to metal transition occurs. From Fig. 7, it is clear that, when viewed from the metallic regime, $\sigma(T=0)$ vanishes with decrease in pressure in accordance with Eq. (1). The quality of data did not permit the extraction of the critical parameters from the experimental results. From the ambient pressure data of Fig. 5,

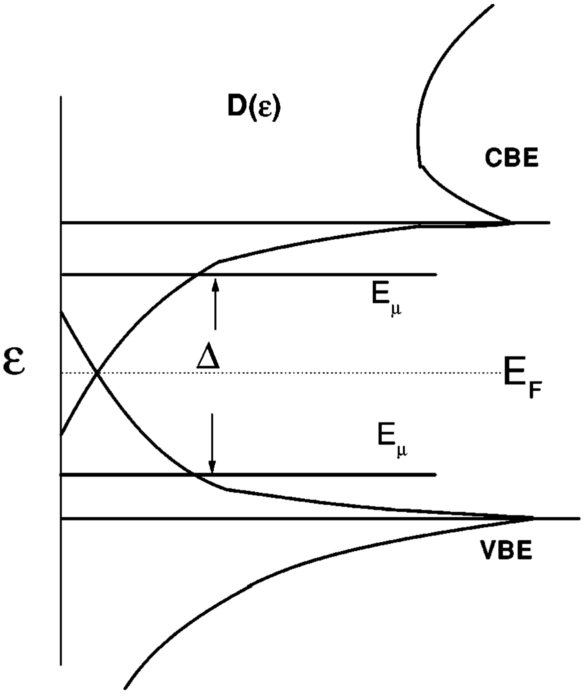

FIG. 11. A schematic representation of the density of states that can explain the properties of FeSi and Ge-substituted FeSi, as elaborated in the text.

Fig. 6, and Fig. 10, it appears that with increase in Ge concentration $\sigma(T=0)$ increases, possibly due to an increase in the density of states at E_F.[31] Recent band structure calculations also show that the density of states at E_F increases due to thermal and chemical disorder in FeSi.[37,38]

We now go back to understand the behavior of Δ versus pressure shown in Fig. 4. Conventionally the transport gap is the energy required for activation of electrons from the valence band to the conduction band. In the presence of disorder, the density of states can be modified as in Fig. 11. Thus the measured gap can be smaller than that predicted by the band structure (cf. Fig. 11) and is $\sim 2\|E_\mu - E_F\|$. Earlier we saw that with increase in pressure E_μ moves closer to E_F, as a consequence of which the measured gap decreases according to Fig. 11. The magnitude of this decrease with the application of external pressure will, however, depend on the extent of the band tail as well as the position of E_μ in the sample at ambient pressure, both of which depend on the degree of disorder in the sample, which cannot be very easily quantified.

Band structure calculations in FeSi indicate that with increase in pressure the band gap increases.[38] For the actual lattice constants expected under the application of external pressure,[39] band structure calculations were carried out in FeSi using the tight binding (TB) version of the linear muffin tin orbitals (LMTO) method in the atomic sphere approximation.[40] The band structure calculations were carried out for 1198 k points in the Brillouin zone. The total energy was evaluated to an accuracy of 0.000 001 Ry. The minimum gap is indirect and occurs between the valence band maximum along ΓR and the conduction band minimum along ΓX. Keeping all other parameters constant in the calculations excepting the lattice constant, a systematic but small increase was observed in the band gap as a function of a decrease in the lattice constant, as shown in Fig. 12. The lattice constants employed in the calculation were obtained from neutron diffraction measurements in the 0–8.4 GPa pressure range.[39] It can be seen from the figure that the magnitude of the gap is ~126 meV at a lattice constant of 4.484 Å, corresponding to that at ambient pressure, which is in good agreement with earlier calculations.[20,38] The band gap increases to 132 meV at 8.4 GPa, a mere 70 K increase. In the context of the results shown in Fig. 4, these calculations imply that the band edges (shown in Fig. 11) move apart with increase in pressure.[41] It is therefore clear that there could be a competition between a decrease of Δ due to movement of E_μ toward E_F and a band-structure-induced increase in Δ with pressure (cf. Fig. 12). This could be the origin of the varied behavior of Δ seen in the experiments (cf. Fig. 4).

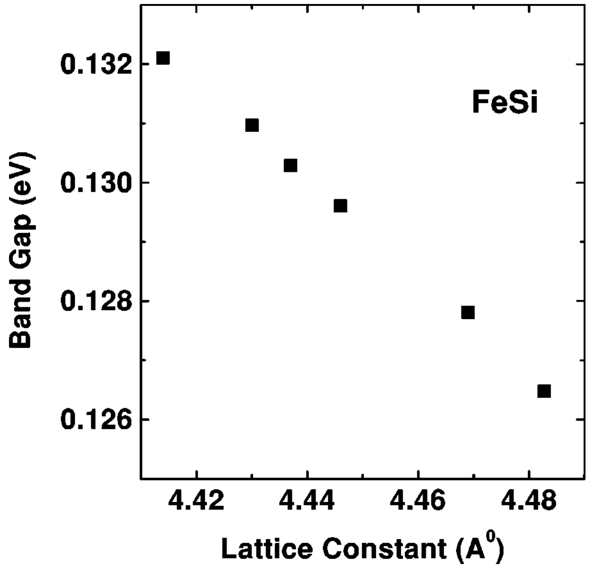

FIG. 12. The variation of the indirect band-gap obtained from the TB LMTO band structure calculations for lattice constants obtained from neutron diffraction as a function of pressure.

A comparison of the Δ values at ambient pressure in FeSi samples with RR of 20 000 (700 K) and RR of 7 (320 K) indicates that the latter is more disordered; the position of E_μ is closer to E_F (cf. Fig. 11). The increase in Δ with pressure in the latter sample could imply that only band structure effects are operative. The pressure-induced increase in Δ calculated from band structure is only ~70 K, which also tallies with the measured increase in FeSi (RR 7). In the sample with RR of 20 000, E_μ is possibly closer to the band edges and has a large range of energy over which it can shift with pressure. This dominates the change in Δ in comparison to the band-structure-induced increase, resulting in the observed decrease in Δ. The nonmonotonic variation of Δ seen in the 5% Ge-substituted sample (cf. Fig. 4) might arise as follows. Since the sample has an intermediate RR, it is plausible that E_μ is in the middle of the band tail. As pressure is increased, E_μ shifts closer to E_F [cf. Eqs. (1) and (2)]; simultaneously the band edges move apart due to band structure effects (cf. Fig. 12). Δ decreases with pressure until E_μ coincides with E_F, and with further increase in pressure band structure effects dominate the pressure dependence and Δ increases. The magnitude of the observed increase $\sim$120 K is also in reasonable agreement with that predicted by band structure. It is noteworthy that the variation of Δ with pressure in the 5% Ge-substituted sample changes direction at $\sim$1.7 GPa, which is very close to the pressure at which the logarithmic derivative of σ also changes sign (cf. Fig. 4 and Fig. 7).

VI. SUMMARY AND CONCLUSIONS

Electron transport in FeSi has two contributions (see Fig. 11), (a) activated electron hopping from valence band to conduction band responsible for the observed conductivity in the 100–200 K range and (b) electron conduction via defect states in the gap that contributes to conductivity in the 5–40 K temperature regime. External pressure affects both regimes of conduction in FeSi. In the low temperature regime, delocalization of electron states in the gap results in a shift in the mobility edge toward E_F, altering the zero temperature conductivity significantly. This gives rise to the observation of an insulator to metal transition as a function of pressure. The nature of the insulator to metal transition as inferred from the nature of the temperature dependence of w is possibly continuous as in doped semiconductors. The shift in the mobility edge also alters the measured gap, leading to a decrease in its magnitude with increase in pressure. The predicted gap behavior from band structure and calculations that include electron correlations[41] dictates that the band gap increases with increasing pressure. The observed pressure dependence of Δ has both these competing contributions. In fact, the behavior of Δ is a complicated outcome of the magnitude of the different contributions, viz., the number density of defect states, the shape of the band tails, and the position of the mobility edge, which differ widely from sample to sample.

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[41] A calculation by Fu and Doniach (Ref. 21), where they argue that the gap opening in FeSi arises from the hybridization of two correlated *d* bands parametrized by an on-site Coulomb repulsion *U*, also shows that the gap should increase with pressure.