# Magnetic correlations on the insulating side of the metal-insulator transition in amorphous $Si_{1-x}Mn_x$

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We have investigated the low-temperature conductivity and magnetoresistance of amorphous $Si_{1-x}Mn_x$ films on the insulating side of the metal-insulator transition after annealing at room temperature for eight years. As temperature is reduced, we find a crossover from an $\exp[-(T_0/T)^{1/2}]$ form for variable-range-hopping conduction in a Coulomb gap to a simply activated law, $\exp(-\Delta E/kT)$. Application of a magnetic field results in a linear decrease of the activation energy $\Delta E$. This behavior is attributed to the presence of a "hard" magnetic gap caused by the *s-d* exchange interaction between the hopping electrons and localized spins on clusters of Mn atoms with the formation of magnetic polarons.

The transport properties of highly disordered systems are strongly affected by electronic correlations of Coulombic origin. Long-range Coulomb interaction causes a depletion of the single-particle density of states near the Fermi energy,[1,2] referred to as the Coulomb gap.[2] Efros and Shklovskii[2] (ES), stabilizing the ground state against one-electron excitations and allowing no relaxation, found that on the insulating side of the metal-insulator transition inside this gap, the density of states vanishes smoothly in accordance with a parabolic law making it a "soft" gap. Within such a gap, the temperature dependence of conductivity arising from variable-range hopping (VRH) is described by $\sigma(T) = \sigma_0 \exp[-(T_0/T)^{1/2}]$. This form has been found in many systems[3] including as-prepared amorphous $Si_{i-x}Mn_x$ films.[4-6]

There is recent experimental evidence for the existence of "hard" gaps at very low temperatures in some materials,[7-13] which manifest themselves as a crossover from a conductivity of the ES form, given above, to a simple-activation law (SA) $\sigma = \sigma_0 \exp(-\Delta E/kT)$, when temperature is reduced. Vinzelberg *et al.*[10] have attributed the SA form, found in amorphous Cr-$SiO_2$ films, to a stronger than parabolic decrease in the density of states, which was predicted by several authors who took into account many-electron transitions and electron-hole correlations when stabilizing the ground state.[14-16] Strong temperature dependence observed at low temperatures in amorphous $Ge_{1-x}Cr_x$,[7] irradiated polymer films,[8] and insulating SiB (Ref. 11) was explained by the presence of a finite hard magnetic gap caused by spin-spin exchange interaction after spin-glass ordering. Similar behavior has been observed by Terry, Penney, and Von Molnar[12] in the dilute magnetic material $Cd_{1-x}Mn_xTe$:In and was interpreted in terms of the orientation of Mn spins by hopping carriers due to the *s-d* exchange interaction [the formation of magnetic polarons (MP)]. The present work demonstrates the appearance of the low-temperature crossover from the $\exp[-(T_0/T)^{1/2}]$ form to an $\exp(-\Delta E/kT)$ form in amorphous $Si_{1-x}Mn_x$ films after eight years storage (1986–1994) of the samples at room temperature. The result is explained by antiferromagnetic ordering in small clusters of manganese atoms formed during the room-temperature annealing and the formation of magnetic polarons through electron-induced ferromagnetic Mn spin alignment.

The layers of *a*-Si were prepared by electron-beam evaporation of crystalline Si on to quartz substrates at room temperature. The *a*-Si doping was carried out by implantation of Mn ions in an accelerator. A homogeneous distribution of the Mn across the film thickness ($d = 0.3\ \mu$m) was ensured by varying the ion energy. The resistance of samples was measured between 100 and 1.6 K for four different concentrations of manganese, $x = 7$, 9, 11, and 12 at. %, all of which are on the insulating side of the transition, and with magnetic fields of up to 4.5 T. The resistivity measurements were obtained using four-terminal dc techniques to avoid problems from any contact resistance. However, simultaneous two-terminal

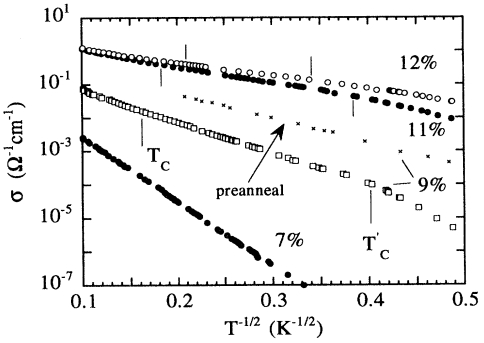


FIG. 1. Conductivity as a function of $T^{-1/2}$ for all samples in the interval 100–4.2 K. Variable-range hoping in a Coulomb gap is present in the range $T'_C < T < T_C$. Also shown, for comparison, are the preanneal results for the 9% sample.

 

TABLE I. Fitting parameters for the variable-range-hopping conduction. The table shows the parameters obtained by least-squares fitting to the equation $\sigma=\sigma_0\exp[-(T_0/T)^n]$ in two different intervals of temperature, high ($\Delta T_h$) and low ($\Delta T_l$). $\Delta_c$ is the width of the Coulomb gap.

| Sample (%) | $\Delta T_h$/K | $\sigma_0/(\Omega\,\mathrm{cm})^{-1}$ | $T_0$/K | $n$ | $\Delta_c$/meV | $\Delta T_l$/K | $\sigma_0/(\Omega\,\mathrm{cm})^{-1}$ | $n$ | $\Delta E$/meV |
|---|---|---|---|---|---|---|---|---|---|
| 7% | 100–10 | 0.18 | 1900 | 0.49 | 25.3 | | | | |
| 9% | 40–6 | 0.35 | 445 | 0.49 | 5.7 | 6–3.1 | 0.12 | 1.05 | 3.8 |
| 11% | 35–7 | 2.33 | 107 | 0.51 | 2.6 | 7–1.6 | 0.49 | 1.1 | 1.7 |
| 12% | 18–8 | 2.08 | 60 | 0.49 | 1.3 | 8–1.8 | 0.47 | 0.95 | 0.9 |

measurements gave no evidence for significant resistance at the contacts, which were made with indium. A Keithley 602 electrometer was used as the dc current source and a Keithley 604 differential electrometer was used as a voltmeter to measure the four-terminal potential difference. Details of the sample preparation, characterization, and their properties were given in Refs. 4–6.

Measurements of $\sigma(T)$ in as-prepared $a$-$Si_{1-x}Mn_x$ films carried out in 1986 have showed a conductivity with temperature dependence of the ES form in the temperature range 90–4.2 K.[6] The $T^{-1/2}$ law was attributed to the presence of VRH with Coulomb correlations as originally proposed by Efros and Shklovskii.[2] The conductivity data for the same samples, measured after eight years in the temperature range 100–4.2 K are plotted versus $T^{-1/2}$ in Fig. 1 on a semilogarithmic scale. The figure shows clearly that the conductivity follows the ES law in the temperature range $T_C'<T<T_C$, denoted by markers. The identification is supported by direct least-squares fitting of the data to the form $\ln\sigma=\ln\sigma_0-(T_0/T)^n$, allowing all parameters to vary. It is possible to estimate the width of the Coulomb gap $\Delta_C$ as the hopping energy at $T=T_C$: $\Delta_C=0.5(T_0T_C)^{1/2}$. The value for $\Delta_C$ and the fitting parameters are listed in Table I. However, two unexpected features are revealed: (1) The magnitude of conductivity is less than that of the as-prepared samples (see Fig. 3 in Ref. 6); (2) at low temperatures ($T<T_C'$), a deviation from $T^{-1/2}$ dependence is observed in samples with $x=9$, 11, and 12 at. %. In these regions, $\sigma$ depends more strongly on the temperature, obeying an activation law with $n>\frac{1}{2}$.

The diminution of the magnetic gap with an increase of impurity content has been observed by Aleshin *et al.*[7] Such behavior was attributed to enhanced screening of the exchange interaction responsible for the magnetic reordering on approach to an insulator-metal transition.

Figure 2 shows data extended to lower temperatures (1.6 K) and plotted as a function of inverse temperature. Clearly, all curves exhibit a range of temperatures over which the SA law $\exp(-\Delta E/kT)$ is followed. The same result is given by the least-squares fitting at low temperatures (see Table I). Note that the hard gap $\Delta E$ is 65–70% of the soft Coulomb gap; the theoretically predicted hardening due to multielectron Coulombic correlations is only expected to produce $\Delta E=(0.1-0.2)\Delta_C$.[15,16]

The conductivity of the 11% sample in a magnetic field $B=4.5$ T is shown in Fig. 3. Zero-field data are included for comparison. The figure shows that the magnetic field leads to a decrease of the activation energy. The inset demonstrates that $\Delta E(B)$ dependence is linear. Magnetoresistance (MR) studies on the 11% sample have revealed a small positive MR at $T=3.1$ K (Fig. 4), which depends as $B^2$ on the magnetic field [Fig. 5(a)]. This is attributed to shrinkage of the wave functions by the magnetic field: The theory of positive MR in the VRH regime for low magnetic fields has been developed by Shklovskii and Efros.[17] For $l^2/a>d$, where $d$ is the mean distance between impurities, $l=(\hbar/eB)^{1/2}$ is a magnetic length, and $a$ is the localization length in zero field, they obtained the following relation for the magnetoresistance: $\Delta\rho(B)/\rho(0)=1.50\times10^{-3}(a/l)^4(T_0/T)^{3/2}$. The solid curve in Fig. 5(a) is the result of fitting experimental data to this form with $a$ as a free parameter. Setting

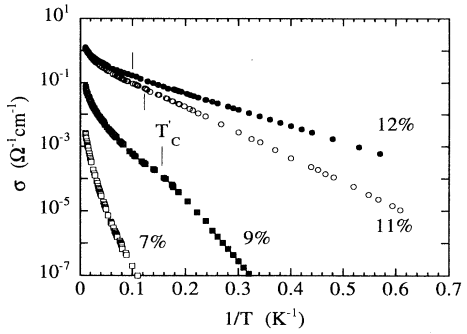


FIG. 2. Conductivity as a function of $T^{-1}$ extended to lower temperatures (down to 1.6 K).

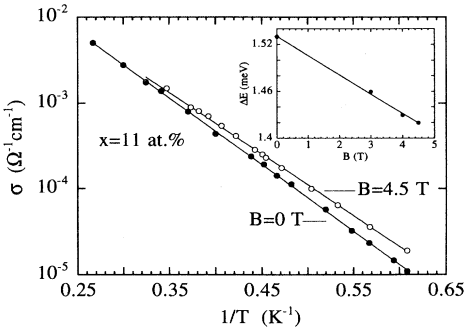


FIG. 3. Conductivity of the 11% samples at the magnetic field $B=4.5$ T as a function of $T^{-1}$. The data at $B=0$ T are included for comparison. Inset: dependence of the low-temperature activation energy on a magnetic field.

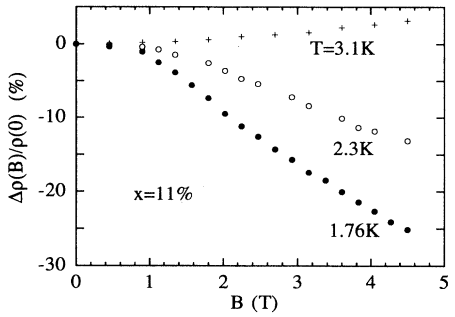


FIG. 4. Magnetoresistance of the 11% sample at different temperatures.

$T_0=107$ K, $T=3.1$ K produces $a=5.7$ nm this is a quite reasonable value for this sample.

We can also check the hopping model for the Coulomb-gap region and extract a value for $a$ by making a quantitative comparison with the Efros-Shklovskii theory. We do this for the 9% sample for which relative permittivity has been measured: $\varepsilon_r \approx 55$.[18] For the ES model to be valid, the model parameters have to satisfy the following conditions:[19]

(a) The temperature-dependent optimum hop energy of the variable-range tunneling process, $W_{\rm opt}=0.5k(T_0T)^{1/2}$ must satisfy $W_{\rm opt} \geq kT$. At $T=10$ K ($kT=0.86$ meV), we have $W_{\rm opt}=2.9$ meV, so this condition is satisfied.

(b) For variable-range tunneling to be occurring, the temperature-dependent optimum hop distance $R_{\rm opt}=0.25a\,(T_0/T)^{1/2}$ must be larger than the localization length $a$. This corresponds to $0.25(T_0/T)^{1/2}>1$. At $T=10$ K and with $T_0=445$ K, we have $0.25(T_0/T)^{1/2}=1.7$; therefore, this condition is also satisfied.

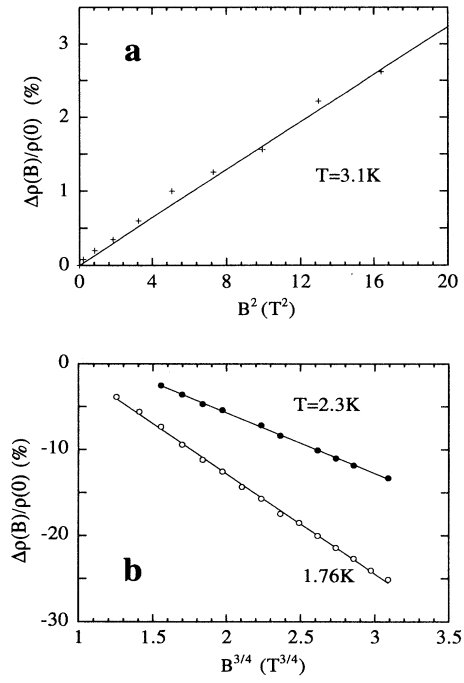


FIG. 5. Magnetoresistance of the 11% sample plotted against (a) $B^2$ and (b) $B^{3/4}$.

The localization length is obtained from $T_0$ and the Coulomb-gap density of states, which depends only on $\varepsilon_r$. Using the forms given by Adkins,[19] we have $a=kT_0(\pi g_2)^{1/2}/10.5$, where $g_2=2.02\times10^3(\varepsilon_0\varepsilon_r/e^2)^3$. With $T_0=445$ K and $\varepsilon_r=55$, we obtain $a=2$ nm. This again is an acceptable result, and smaller than the value obtained for the 11% sample, as expected (although the values can only be considered rough estimates).

At low temperatures, MR becomes large in magnitude and negative in sign (Fig. 4). The sublinear dependence of the negative MR on $B$ at $B>1-1.5$ T rules out interpretation in terms of quantum interference in the VRH regime.[20,21] We attribute simply activated conduction and the presence of the hard gap to magnetic correlation between the spin of the hopping electron and magnetic moment of the impurity Mn atoms arising from the half-filled 3-$d$ shell, as had been done in case of $Cd_{0.91}Mn_{0.09}Te$:In.[12] It is well known that localized carriers tend to form within their localization length clusters of oriented ionic moments known collectively as bound magnetic polarons.[22,23] The direct demonstration of the existence of MP's was found in a dilute magnetic persistent photoconductor.[24] After eight years annealing, manganese atoms in our samples have precipitated into small inclusions with antiferromagnetic coupling. As a result, the average distance between the centers of localization is increased and the magnitude of hopping conductivity reduced. Localization of an electron on a cluster causes ferromagnetic Mn spin alignment to that cluster while others form an antiferromagnetic background. Each hopping electron locally lines up the manganese spins via the $s$-$d$ exchange interaction producing a net moment. The appearance of the hard gap is the result of the magnetic relaxation energy gained by formation of the MP at the site of the electron. This energy has to be provided for the electron to hop to another (antiferromagnetic) site.

Since the activation energy is now caused mostly by the magnetic ordering, it depends strongly on magnetic field. The magnetic part of the activation energy is determined by the difference between the magnetization in the ferromagnetic polaron and the antiferromagnetic background. This difference decreases upon application of $B$ because the background magnetization increases as $\chi B$, where $\chi$ is the susceptibility of antiferromagnetic manganese clusters. Since $c$ is nearly temperature independent, $\Delta E$ does not vary with temperature and depends linearly on the magnetic field. This is clearly demonstrated in the inset of Fig. 3.

The strong negative magnetoresistance at low temperatures is easily explained on the present picture. Applying a high magnetic field reduces the localization of bound electrons with respect to the zero-field situation due to alignment of all spins in the system and therefore

suppression of the magnetic relaxation. In this case, we can use theoretical results obtained by Altshuler, Aronov, and Khmelnitskii.[25] They calculated the field dependence of the negative MR arising from a negative shift of the mobility edge, which leads to a magnetic correction to the localization length. This effect produces $\Delta\rho(B)/\rho(0)\sim -B^{1/2\nu}$, where $\nu$ is the critical exponent of the localization length. Analysis of MR as a function of $B$ shows a dependence $B^{3/4}$ at $B>1$ T [Fig. 5(b)]. This implies $n=0.67$. This value is quite reasonable and comparable with the values of 0.6 found by Shafarman, Koon, and Castner[13] and of 0.7 found by Biskupski,[26] also extracted from MR data.

In summary, we have revealed the crossover at reduced temperatures from the ES form to simply activated conduction in the VRH regime in amorphous $Si_{1-x}Mn_x$ films after room temperature annealing for eight years. The low-temperature activation energy decreases linearly with an increase of a magnetic field. Our results imply that, in the absence of a magnetic field, there exists a hard gap due to *s-d* exchange interaction between the spins of the hopping electrons and the manganese atoms, precipitated into antiferromagnetic clusters. Application of a magnetic field assists alignment of Mn spins and, therefore, reduces the width of the hard gap. It is of interest that the value of activation energy $\Delta E$ at $T<T_C'$ is larger than the value of the hopping energy at $T=T_C'$ (see Fig. 2). Such behavior has not previously been seen. It means that $T_C'$ is the temperature of a phase transition: the antiferromagnetic ordering occurs at $T=T_C'$. The higher the Mn concentration in the Si, the larger the number of the Mn atoms in cluster and hence the larger the value of transition temperature (see Table I). Clearly, at the limit of pure metallic Mn, $T_C$ must tend to its bulk value. The sharpness of the magnetic transition is a curious feature, however, since it is supposed to occur within the (presumably very small) clusters of Mn atoms, in which case, one might expect it to be widened by the statistical spread of cluster sizes. Possibly the collective nature of the transition is mediated by the relatively extended states of the hopping electrons. This aspect deserves further investigation.

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