Conductance regimes of W-based granular metals prepared by electron beam induced deposition

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Abstract. We prepared a series of W-based granular metals by means of electron beam induced deposition from the carbonyl precursor W(CO)$_6$. For samples with W-contents of 31.8(±1.4), 34.0(±1.7) and 36.9(±1.8) at%, we observed a modified power law dependence $\sigma = \sigma_0 + bT^\beta$ of the electrical conductivity with $\beta = 0.47–0.58$, which we found to be approximately fulfilled over the temperature range from about 2 to 265 K. Deviations from this modified power law are discussed. Existing theoretical approaches that can, in principle, account for power-law dependencies in $\sigma(T)$ for homogeneously disordered or granular metals are reviewed and their relevance for explaining our data is critically examined. Firstly, if a percolating path is formed by touching metallic particles, the formation of a pseudo-gap at the Fermi level that follows a $T^{1/2}$ temperature dependence according to Altshuler and Aronov may explain our data. However, the Altshuler–Aronov result is valid for weak Coulomb coupling and represents a small, low-temperature correction. Its applicability close to a metal–insulator transition is questionable. Secondly, we analyze whether an alternative transport mechanism may be at work that is based on the onset of large-scale coherent electron motion along a tunnel-percolation path in the limit of large inter-grain tunneling. Again, this approach cannot be unambiguously applied to explain our experimental findings.
1. Introduction

Granular metals are well suited for studying the interplay of four major aspects in solid-state physics: quantum size effects, electronic correlations, dimensionality and disorder (for a recent review, see [1]). Depending on the preparation technique, one or several of these aspects can be tuned. Studying these materials’ electronic transport properties, which are dominated by inter-grain tunneling, yields important insights into the underlying physics. This is so because the tunnel process is strongly influenced by correlation effects, such as the Coulomb blockade in the limit of weak inter-grain coupling, which has a direct bearing on the conductivity.

We prepared a series of tungsten granular metal samples with different metal contents covering the range from insulating to nearly metallic behavior and measured the temperature dependence of the electrical conductivity $\sigma(T)$. We first analyze this behavior for the different samples based on a model-independent approach to identify the samples that are close to the metal–insulator transition (MIT), either being still on the insulating side or being metallic in the sense that they fulfill the criterion $\sigma(T \to 0) > 0$ [2]. We then focus on the $\sigma(T)$ behavior for these samples, which have the largest fractional metal volume occupation. The $\sigma(T)$ behavior can be approximately described by a modified power law of the form $\sigma \simeq \sigma_0 + bT^{\beta}$ with $\beta \simeq 1/2$ within the temperature range accessible to us from about 2 K to about 265 K. Deviations from this modified power law behavior are critically discussed. We then turn to comparing our results with existing theoretical models that lead to such a temperature dependence of the conductivity. Firstly, we discuss the applicability of the Altshuler–Aronov correction of the temperature-dependent conductivity for disordered metals with weakly interacting electrons in the presence of static disorder [3]. Secondly, we speculate on whether an alternative scenario based on a tunnel-percolation model and the onset of large-scale coherent electron tunneling may be of relevance for explaining our data. This analysis refers to recent theoretical work on the conductivity of a lattice model of granular metals in the limit of large inter-grain tunneling [4].

2. Experimental

In figure 1, we show a scanning electron microscopy (SEM) image of a representative sample prepared by electron beam induced deposition (EBID) and used in our transport measurements. The EBID technique is based on rastering an electron beam over a substrate surface that is covered by adsorbed metal-containing precursor molecules supplied by a gas injection system.
Molecule dissociation occurs in the focus of the electron beam [5]. For suitable deposition conditions, the dissociation product is a permanent deposit consisting of a disordered array of crystalline metallic nanoparticles with diameters ranging from about 1 nm to 5 nm embedded in an insulating matrix. The metal content, i.e. average particle size and interparticle distance, can be varied by choosing appropriate deposition conditions [6]. Details concerning electron beam induced processes (deposition and etching) can be found in a very recent review by Utke et al [7]. From the established metal precursors for EBID we chose the W-precursor W(CO)$_6$ for a particular reason. The W metal content in the deposits can be widely varied so that it is possible to cover the full range from insulating to nearly metallic behavior. We tested for possible aging effects of the EBID structures by in situ resistance measurement during venting of the electron microscope. We found the aging effect to be small. In ambient conditions, we observed a decrease in the samples’ conductivity by 2–4% over 1 h. After 4 days, the conductivity reduction was found to be below 15%. Details concerning these aging effects on the timescale from seconds to several days can be found in [8]. From our preliminary data it is not yet clear whether EBID structures can be prepared from alternative metal precursors, such as MeCpPt(CH$_3$)$_3$, so that they have sufficient metal content to be in the metallic regime beyond the MIT. We discuss this point briefly in the ‘outlook’ section.

In our experiments, we utilized a dual-beam system (FEI, Nova Nanolab 600) with a Schottky-type electron emitter and an ultimate resolution of 1 nm. This system allows for a continuous variation of the beam energy at several pre-defined fixed beam current settings. The precursor gas was supplied by a dedicated gas injection module, which delivered the gas via a 0.5 mm diameter capillary in close proximity to the electron beam focus on the substrate surface. We used p-doped silicon as substrate material insulated via a 300 nm thick thermally grown SiO$_2$ layer on which about 100 nm thick aluminum or gold/chromium contacts had been previously patterned by standard lithography techniques. The rectangular-shaped samples were written by repeatedly looping the same electron beam raster pattern with a pitch of 20 nm and a dwell time per pixel of 100 µs. The primary electron energy was fixed at 5 keV for all samples except sample 1, with the lowest metal content, for which 10 keV was employed. For samples 2–6, the metal content was varied by changing the beam current. Only beam currents at three
Table 1. Selected properties of the EBID samples as used for the transport measurements. Beam parameters (energy and current) and sample geometries \((l \times w \times h)\): samples 1 (10 keV; 2.5 nA; 5.40 \(\mu\)m \(\times\) 1.38 \(\mu\)m \(\times\) 215 nm), 2 (5 keV; 3.3 nA; 5.40 \(\mu\)m \(\times\) 2.09 \(\mu\)m \(\times\) 104 nm), 3 (5 keV; 1.2 nA; 7.05 \(\mu\)m \(\times\) 1.66 \(\mu\)m \(\times\) 236 nm), 4 (5 keV; 3.7 nA; 14.93 \(\mu\)m \(\times\) 1.63 \(\mu\)m \(\times\) 192 nm), 5 (5 keV, 6.6 nA; 5.37 \(\mu\)m \(\times\) 2.57 \(\mu\)m \(\times\) 212 nm) and 6 (5 keV, 3.9 nA; 9.12 \(\mu\)m \(\times\) 1.48 \(\mu\)m \(\times\) 145 nm).

| Sample | \(x\) = W (at%) | C (at%) | O (at%) | \(y_{\text{min}}\) (vol%) | \(y_{\text{max}}\) (vol%) |
|--------|-----------------|--------|--------|-----------------|-----------------|
| 1      | 19.0            | 67.1   | 13.8   | 24.1            | 38.2            |
| 2      | 22.6            | 56.0   | 21.4   | 27.8            | 42.8            |
| 3      | 27.5            | 50.4   | 22.1   | 33.0            | 49.3            |
| 4      | 31.8            | 44.4   | 23.8   | 37.4            | 53.8            |
| 5      | 34.0            | 44.3   | 21.7   | 40.4            | 56.9            |
| 6      | 36.9            | 35.6   | 27.5   | 37.1            | 53.4            |

Pre-defined values in the nanoampere (nA) range were employed and checked by Faraday cup measurements (see Table 1 for values). We did not succeed in preparing samples with metal content above 37 at% due to inherent limitations of the EBID process at the fixed beam energy of 5 keV.

The samples’ composition was determined in situ by energy dispersive x-ray (EDX) analysis at 5 keV electron beam energy. The low beam energy was chosen so that no undesired x-ray fluorescence was excited in the substrate material. This was verified by Monte Carlo simulations of the electron trajectories for the given sample thicknesses and compositions [9]. We checked the influence of carbon deposition from the residual gas on the derived element composition during spectrum acquisition by repeatedly taking spectra from the same sample area. We found that the systematic overestimation of the carbon concentration is smaller than 1%. The EDX-specific error from the limited statistics and the employed ZAF correction can only be estimated to about ±5%. The resulting error in the W content given, as given in Table 1, thus varies from about ±1.2 at% for sample 1 to about ±1.8 at% for sample 6.

From EDX no information can be gained about the distribution of W, C and O in the samples. Hoyle et al studied the microstructure of EBID patterns prepared with the W(CO)\(_6\) precursor for beam energies in the range of 2–20 keV by means of transmission electron microscopy (TEM) [10]. Applying the Scherrer formula to the electron diffraction patterns, which they obtained from deposits made with a total dose of 5000 C m\(^{-2}\), they estimated the size of W-containing nanocrystals to be smaller than 3 nm. Additionally, they found the structure of the nanocrystallites to be consistent with the high-temperature beta phase of tungsten carbide (\(\beta\)-WC\(_{1-x}\), with \(x\) depending on composition). For smaller total doses, e.g. 500 C m\(^{-2}\), they found only amorphous material. A more recent account on the microstructure of W-containing EBID deposits seems to support these findings [11], but its relevance to the present work is not clear since a different precursor (WF\(_6\)) was used. In our experiments, the total dose for each sample was at least 25 000 C m\(^{-2}\). We therefore assume, based on the findings of Hoyle et al, that the microstructure of our samples is that of a granular metal of \(\beta\)-WC\(_{1-x}\) nanocrystals embedded in a carbonaceous matrix.
The lateral dimensions of the samples and the contact positions were determined by direct inspection in the SEM after deposition. From these measurements the sample lengths $l$, relevant for transport measurements, are known to an accuracy of better than $\pm 5\%$. We furthermore performed atomic force microscopy measurements in non-contact mode to accurately determine the samples’ width $w$ and height $h$. These dimensions are known to an accuracy of better than $\pm 15\%$. The corresponding maximum geometry-dependent error for the conductivity data amounts to about 35%. For sample 3, we observed a strongly reduced conductivity, which we attribute to a defect at one of the inner voltage probes causing a reduction of the effective sample cross section. Nevertheless, the temperature dependence follows the systematic evolution of the conductivity with metal content.

Table 1 lists a selection of relevant sample properties. The fractional volume, $y$, occupied by the metal particles for a given integral metal content, $x$, depends on the density and molar mass ratios of the metal and the insulating matrix. For the insulating matrix, the density is not well known. Depending on the degree of $sp^2$ to $sp^3$ hybridization of the carbon atoms the matrix can be diamond- or graphite-like. Furthermore, the oxygen content needs to be taken into account. In table 1, we give a lower and upper limit for $y$ corresponding to a density range from $1.8 \text{ g cm}^{-3}$ (graphite-like, amorphous) to $3.5 \text{ g cm}^{-3}$ (diamond-like) using an averaged molar mass corresponding to the carbon-to-oxygen ratio for the given sample.

Conductivity measurements were performed in a variable temperature insert (VTI) mounted on a $^4\text{He}$ cryostat equipped with a 9 T superconducting solenoid. The voltage was chosen such that the corresponding electric field for samples 4–6 did not exceed $18 \text{ V cm}^{-1}$ for the conductivity measurements, so that $\sigma(T)$ was measured in the linear regime. For these samples, we observed linear $I(V)$ characteristics at small bias voltages down to the lowest temperature (see figure 4). For the low-conductivity samples 1–3, the applied electric field was chosen between 50 and $100 \text{ V cm}^{-1}$ in order to follow the strong $\sigma(T)$ reduction to as low a temperature as possible. The SiO$_2$ layer on top of the Si substrates in conjunction with our experimental set-up resulted in an isolation resistance of about $45 \text{ G} \Omega$. Due to this value of the isolation resistance we were not able to measure the conductivity of our low-metal content samples to the lowest temperatures while keeping the low excitation voltage. Accordingly, the $\sigma(T)$ data for sample 1 ends at about 20 K. The isolation resistance also had to be taken into account for the $I(V)$ characteristics of this sample at low temperatures. Moreover, in order to avoid irreversible switching in the $I(V)$ characteristic at enhanced bias voltage, which typically occurs at 2–5 V depending on the sample’s metal content, we used a current limit in our measurements. The measurements were performed in two- or four-probe geometry as shown in figure 1. We analyzed transfer resistance contributions by complementary three- and four-probe measurements on comb-like EBID structures over the accessible temperature range and found them to be smaller than 2%.

Thermometry problems, e.g. thermometer/sample-hysteresis, can severely hinder a careful analysis of the $\sigma(T)$ behavior. The data were taken in temperature sweep mode during heating and cooling of the sample holder at a rate of about $\pm 1.2 \text{ K min}^{-1}$ for temperatures above about 15 K. In this temperature range, we did not observe thermometer/sample-hysteresis effects. Below about 15 K, the rate of temperature change decreased with a decrease in temperature. The crossover region of these two cooling regimes between about 10 and 15 K is most sensitive to possible thermometry problems. This is taken into account in the discussion section.
3. Results

In figure 2, an overview of the measured temperature-dependent conductivities for samples with different metal content is given. The conductivity data are shown normalized and in absolute values (inset) in log–log representation because the samples’ conductivities span a large range depending on the metal content. From this plot it appears evident that the samples can be classified into two categories. Samples 1–3 show a rapid decrease of conductivity as the temperature is lowered. In particular, the resistances of these samples grow to such large values that no reliable measurement is possible at small bias voltages, so that part of the low-temperature data is discarded. This is most relevant for sample 1, for which current flow at 4.2 K is observable only for bias voltages larger than 3 V and the resistance at 4 V amounts to about 10 GΩ. Samples 4–6 appear to show a finite conductivity in extrapolation to $T = 0$ K and would be considered ‘metallic’. However, such a low-temperature extrapolation can lead to erroneous conclusions, as was shown in systematic studies of the MIT in disordered solids [2]. The central point of this work is not to discuss the particularities of the MIT in the EBID structures, but to analyze the $\sigma(T)$ behavior of samples 4–6 in more detail with regard to correlation effects. Nevertheless, we need to check on which side of the MIT these samples are situated. This will be discussed in more detail in the following section.

We now turn to a selection of current–voltage characteristics taken on samples 1 and 4. In order to avoid irreversible switching in the current distribution in the samples, we limited the
maximum voltages to 5 and 1 V for samples 1 and 6, respectively. Figure 3 depicts $I(V)$ data for sample 1. The current values are normalized to the respective maximum current values at +5 V bias, so that the nonlinearity of the curves is visible at all temperatures. Two features are evident. At 4.2 K, current flow is detectable only for bias voltages beyond about 3 V. With an increase in temperature a clear nonlinearity remains for larger bias voltages. More importantly, in the low-bias region of the $I(V)$ characteristic, evidence for a Coulomb blockade effect can be seen (see the inset of figure 3). This feature is no longer visible at 100 K. We cannot exclude the possibility that part of the nonlinearity at larger bias voltages is caused by Joule heating.

Figure 4 shows $I(V)$ data for sample 4 up to 1 V and for small bias voltages (inset). This sample has the smallest metal content within the group of nearly metallic samples 4–6. For 4.2 and 10 K, a weak nonlinearity is visible. The $I(V)$ characteristic is weakly nonlinear at larger bias voltage at low temperatures but keeps a linear part for small bias. In this bias regime, the conductivity measurements were performed. At the lowest temperature, this corresponds to a current density of 64 A cm$^{-2}$. It should be noted that the current densities observed in this sample at 1 V bias at 300 K exceed 64 kA cm$^{-2}$. The $I(V)$ characteristics remain linear. At low temperature and larger bias, we cannot exclude heating as a possible cause for the observed weak nonlinearity.

4. Discussion

For the study of the MIT in three-dimensional disordered systems, the continuity behavior of the low-temperature conductivity $\sigma (T \to 0, x = x_0^+)$, as it is approached from the metallic side, is
still an undecided matter. For the granular metal samples presented here, the tuning parameter $x$ is the metal content. The key question is whether Mott’s prediction of a finite minimum metallic conductivity is correct [12]. In the present work, we want to analyze the $\sigma(T, x)$ behavior close to the MIT at $x \approx x_c$. In order to accomplish this, we must define a criterion whose application allows us to identify those samples that fulfill this criterion. A critical step in the analysis of the MIT is the determination of the limiting value $\sigma(0, x)$ for samples close to the transition. Simple extrapolation schemes can lead to erroneous conclusions, and a more general procedure based on the analysis of the logarithmic derivative $w = d \ln \sigma(T, x)/d \ln T$ as $x$ is varied was suggested [13]. For metallic samples, $w$ must vanish as $T = 0$ is approached. We follow this procedure here and we refer the reader, for a more detailed account, to [2].

The derivation of $w$ from a data set is a nontrivial task, since this quantity very sensitively depends on the noise level. We applied the following procedure. First, we regularized our densely populated data sets by piecewise averaging $\sigma(T, x)$ over a temperature interval linearly growing with temperature. This resulted in a regularized data set $\sigma_r([T_i], x)$ with $T_i = T_{i-1} \cdot (1 + p)$. We chose $p = 0.03$. From this regularized data set, $w$ was derived by determining the slopes of piecewise linear regressions of $n$ sequential data points. We varied $n$ between 2 and 15 to find a suitable value for $n$ so that no systematic rounding of $w$ was introduced but a sufficiently smooth behavior of $w$ was obtained. We chose $n = 10$. The results for samples 1–6 appear in figure 5. From the figure, sample 6 would be considered to be metallic. For sample 5, this conclusion cannot be drawn. Since sample 4 does show an upturn at low temperatures, which indicates the onset of insulating behavior at very low temperatures, sample 5 might be considered as being closest to the MIT. For samples 1–3, insulating behavior at low temperatures is evident.

**Figure 4.** The $I(V)$ characteristic of sample 4 at various temperatures is indicated. The inset shows data at small bias for which a linear part in the $I(V)$ characteristics remains down to the lowest temperature measured.
The values for the logarithmic derivative at high temperatures are almost identical for samples 5 and 6, and the value for sample 4 is only slightly larger. This suggests that the transport mechanism is the same for these samples, and it is acting down to lower temperatures. Eventually, at low temperatures, the transport mechanism on the metallic and insulating side of the MIT would be considered different. This means that a fit of the $\sigma(T)$ behavior in accordance with one of the ‘pure’ models, such as thermally activated transport in the insulating regime or a (modified) power-law dependence in the metallic regime, would result in derived model parameters of questionable value [2]. A theoretical description of the transport close to the MIT would be needed, which is not available. Nevertheless, recent theoretical work on granular electronic systems approaching the MIT from the insulating side proposes a mechanism for the onset of coherent charge transport in the limit of strong tunnel coupling between the grains and suggests a universal temperature dependence of the conductivity in the vicinity of the MIT [14]. In order to proceed further we critically analyze our data with an emphasis on samples 4–6.

Several key parameters are relevant for the classification of the transport regimes in granular metals: one of the parameters is the dimensionless inter-grain conductance $g$ measured in units of the quantum conductance $e^2/h$. It is a measure of the transparency of the tunneling barrier between neighboring grains. Another parameter is the bare Coulomb charging energy $E_C = e^2/2C$ for a single grain of radius $r$ with capacitance $C \propto r$. This charging energy hinders charge transport in samples with small grain diameter (see the inset of figure 3). For samples in the metallic regime, $E_C$ is not as important. Another parameter is the average distance...
\[ \sigma(T) = \sigma_0 e^{-(T_0/T)^{1/2}} \]  

(1)

as is evident from figure 6, in which the data of samples 1 and 2 are plotted logarithmically versus \( T^{-1/2} \). Sample 2 follows this dependence only up to about 40 K followed by a crossover region to a possible Mott variable range hopping behavior with exponent 1/4, as is indicated by the dash-dotted line, at temperatures above 80 K. The temperature dependence according to equation (1) is well known for granular metals in the ‘low-conductance’ limit. It is attributed to co-tunneling in the presence of electrostatic disorder caused by trapped charges in the insulating matrix [4].

This behavior is not observed for samples 4–6. Instead \( \sigma(T) \) appears to follow a modified power-law behavior

\[ \sigma_B(T) = \sigma_0 + bT^\beta, \]  

(2)

with \( \beta \simeq 1/2 \) over the accessible temperature range in our experiment, as can be seen from figure 7. We performed a nonlinear curve fitting using the regularized data set \( \sigma_s(\{T_i\}, x) \), which was also employed for determining the logarithmic derivative of the conductivity.
Figure 7. Plot of $\sigma(T)$ versus $\sqrt{T}$ for samples 4–6. The dashed lines indicate fits according to equation (1). For fit parameters, see table 2.

Table 2. Optimal fitting parameters for samples 4–6. See the text for details.

| Sample | $\sigma_0$ ($\Omega^{-1} \text{ cm}^{-1}$) | $b$ ($\Omega^{-1} \text{ cm}^{-1} \text{ K}^{-\beta}$) | $\beta$ |
|--------|---------------------------------|---------------------------------|--------|
| 4      | 5.27                            | 4.08                            | 0.55   |
| 5      | 3.38                            | 7.81                            | 0.47   |
| 6      | 43.15                           | 6.45                            | 0.58   |

By using this set, we avoid systematic errors in the derived fitting parameters, which are due to clustering of data points in the low-temperature region. The obtained fitting parameters are shown in table 2. The corresponding fits are also presented as dashed lines in the inset of figure 5 showing the resulting $\nu(T)$ behavior. In this representation, it becomes evident that the modified power law does not provide a satisfying fit over the complete temperature range. The data for samples 5 and 6 show a broad maximum or shoulder, respectively, at about 10 K. We attribute this to thermometry problems, as indicated in the experimental section. Overall, we obtain better fits by assuming a weakly temperature-dependent coefficient $\beta$, which assumes the values of about 0.62 for temperatures above $\sim 25$ K and 0.45 for lower temperatures. However, we cannot provide a sound statement as to which physical mechanism may entail such a $\beta(T)$ behavior. More information concerning the estimate of the critical metal content $x_c$ for which the MIT occurs can be gained by comparing data taken again on sample 5 after 13 months have passed since the $\sigma(T)$ data presented so far were taken. This is shown in figure 8. Evidently, the character of the logarithmic derivative has changed and it is now indicating a thermally activated behavior at low temperatures. We conclude from this analysis so far that sample 6 may be on the metallic side of the transition, but sample 5, and certainly sample 4, are on the insulating side.
Figure 8. Comparison of the temperature-dependent conductivity of sample 5 as measured hours after deposition and after 13 months have passed, during which the sample was stored under ambient conditions. Inset: logarithmic derivative $w(T)$.

Even for sample 6 the issue cannot be unambiguously decided. What can be said is that these samples are close to the MIT and that a modified power law is observed, the validity of which down to low temperatures cannot be fully judged from our data.

To get an insight into possible reasons for the observed modified power law behavior, it must be determined to what degree percolation between the metallic crystallites needs to be taken into account. This may be relevant for sample 6. As a starting point, we have metallic particles of nanometer size randomly placed in space and the pores between them are filled by the insulating matrix. If there is no attractive force acting between the particles, and this is commonly assumed to be the case in solid composite materials [15], the system will exhibit percolation only in the limit of random close packing. For spherical particles, the fractional occupied volume at the percolation threshold is 64 vol%, and it will be smaller for ellipsoidal particles. 64 vol% can thus be considered as an upper limit for the percolation threshold. Based on our estimate of the occupied fractional volume, which depends on the actual density of the insulating matrix, it cannot be affirmatively stated whether any of the samples 4–6 is percolating. From the logarithmic derivative, which indicates the onset of insulating behavior at low temperatures for samples 4 and 5 (after aging), percolation can probably be ruled out for this sample. We now discuss for sample 6 whether a power law behavior may occur for a percolating system of metallic particles. For a homogeneously disordered metal, the interplay of electron–electron scattering and disorder was theoretically analyzed early-on by Altshuler and Aronov employing the model of a homogeneous electron gas with weak impurity scattering [3]. They found that a correlation-driven reduction of the density of states at the Fermi level occurs.
whose temperature dependence follows a $T^{1/2}$ behavior:

$$\frac{\delta D(x)}{D_0} = \frac{4\pi e^2}{\kappa^2} \frac{1}{2\sqrt{2\pi^2} (\hbar D)^{3/2}} \zeta(x),$$

(3)

where $x = |E - E_F|/k_B T$, $D_0$ is the bare density of states at the Fermi level, $\kappa$ is the inverse Debye radius and $D$ is the diffusion coefficient due to impurity scattering. $\zeta(x)$ has two limiting functional forms: $\zeta(x \ll 1) = 1.07 + O(x^2)$, $\zeta(x \gg 1) = \sqrt{x}$. This result was later shown to be generalizable to strong static scatterers, albeit still in the limit of weak electron–electron scattering, within a tight-binding lattice approach using the coherent potential approximation [16]. It can thus be stated that the Altshuler–Aronov result is quite a general feature and does not depend on details of the band structure. We note, however, that its applicability close to the MIT is questionable and that it represents only a small correction to the diffusive background conductivity $\sigma_0$. Experimentally, the Altshuler–Aronov correction was observed in metal–amorphous semiconductor alloys [17, 18], disordered metals [19] and also granular metals [20] by means of low-temperature tunneling spectroscopy. The corresponding $\sigma \propto T^{1/2}$ behavior was found to be restricted to low temperatures. A more recent observation of this behavior was made in granular films of the Pd$_x$C$_{1-x}$ system [21]. For samples close to the MIT and presumably still on the insulating side, i.e. below the percolation threshold, $T^{1/2}$-behavior was found above $\sim 20$ K and extended to at least 100 K. At lower temperatures, deviations toward a more strongly decreasing conductivity were observed. Very recently, photoelectron emission spectroscopy on double perowskite Sr$_2$FeMoO$_6$ with controlled disorder revealed a $T^{1/2}$-behavior of the density of states at the Fermi level extending up to room temperature [22]. At present, whether the Altshuler–Aronov scenario is indeed applicable with regard to our observations and the observations made be Carl et al [21] or Kobayashi et al [22] appears questionable to us. We therefore discuss next an alternative theoretical model that approaches the $\sigma(T)$ behavior close to the MIT from the insulating side in the limit of strong tunnel coupling.

Microstructural details of the surface of the metallic crystallites are not known. As a consequence, it is in fact not clear whether a conducting path in this material can indeed be considered as a geometric percolation of metallic particles that directly touch. Considering the magnitude of the conductivity of the samples with metal content above $\sim 31$ at%, it is feasible that tunneling in the limit of strong inter-grain coupling provides the charge transport mechanism. It would then be appropriate to assume the existence of a tunnel-percolation path, a concept that has recently received support in conductance atomic force microscopy measurements on granular Ni in an SiO$_2$ matrix [23]. Recently, a theoretical study of correlation effects in ordered one-, two- and three-dimensional lattices of granular metals in the limit of large tunnel coupling, $g \gg 1$, was performed by Beloborodov et al [4]. They found two different conductance regimes. In the ‘high-energy’ or ‘high-temperature’ regime, the granular structure and the grain arrangement are important. In their lattice model, a temperature-dependent correction $\Delta \sigma_1(T)$ of the conductivity following a logarithmic dependence was obtained [4, 24]. It was later shown that this logarithmic temperature dependence is robust against disorder in the tunnel couplings [25]. These theoretical findings are believed to explain the experimental data obtained by several groups [26]–[28]. The ‘high-energy’ correction is expected to show saturation behavior before entering the ‘low-energy’ regime ($k_B T < g \delta$). In this regime, a dimension-dependent correction $\Delta \sigma_2(T)$ is predicted [4]. This correction does resemble the Altshuler–Aronov interaction correction for disordered metals at low temperature [3].

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It signifies an universal character of the large-scale behavior in the granular lattice model. Thus, it is assumed to be robust against disorder, but this has not yet seen rigorous theoretical proof. Beloborodov et al \[4\] predict for the ordered lattice in the low-temperature regime the following \(\sigma(T)\) behavior for 3D systems:

\[
\sigma(T) = \sigma_0 + \Delta\sigma_1(T) + \Delta\sigma_2(T) = \sigma_0 \left(1 - \frac{1}{6\pi g} \ln \frac{E_C}{\delta} + \frac{\alpha}{12\pi^2 g} \left( \frac{T}{g\delta} \right)^{1/2} + \mathcal{O} \right),
\]

(4)

with \(\sigma_0 = 2e^2 g / a\) (where \(a\) is the grain size) being the global sample conductivity in the Drude limit, \(\alpha \simeq 1.83\) and \(c\) is a temperature-independent constant of order \(\mathcal{O}(1/g)\). We suggest to associate the second-order correction \(\Delta\sigma_2(T) \propto T^{1/2}\) with our experimental findings. From our data (samples 4–6) we deduce the coefficients \(\sigma_0\) and \(b\) according to equation (2). By comparison with equation (4), the following relation is derived:

\[
g - \frac{\sigma_0}{b} \frac{\alpha}{12\pi^2 \delta^{1/2}} g^{1/2} = - \frac{1}{6\pi} \ln \frac{E_C}{\delta} + c' = 0
\]

(5)

with \(c' = gc\). The variable \(c'\) is temperature independent and also does not depend on \(g\), because \(c = \mathcal{O}(1/g)\). For our samples, we find that \(\sigma_0/b = \mathcal{O}(1 K^{1/2})\). We can furthermore estimate the bare Coulomb charging energy \(E_C\) from an assumed grain diameter of 3 nm \[10\]. \(E_C\) then amounts to about 0.2 eV. The average energy level spacing for the tungsten particles is then about 5 meV. Inserting these numbers in equation (5), we see that the prefactor of the \(g^{1/2}\)-term is of the order of \(10^{-3}\), whereas the third term amounts to about 0.2. We can therefore approximate equation (5) and obtain

\[
g \simeq \frac{1}{6\pi} \ln \frac{E_C}{\delta} - c'.
\]

(6)

In [4], the constant \(c\) is not explicitly given, but it is a second-order correction, so that it is presumably negligible. We obtain

\[
g \simeq \frac{1}{6\pi} \ln \frac{E_C}{\delta} \simeq 0.2.
\]

(7)

Beloborodov et al \[4\] state that for a critical tunnel coupling \(g_C\), which coincides with our estimate equation (7), an MIT should occur. For \(g > g_C\), the granular lattice system would have a finite conductivity \(\sigma(T = 0)\), so it would be qualified as a metal. For \(g < g_C\), the system would be an insulator with \(\sigma(T = 0) = 0\). Since our estimate for \(g\) does coincide with \(g_C\), we are led to conclude that our samples are very close to the MIT with sample 6 possibly on the metallic side. Certainly, the most critical issue in associating our data with the model calculation is the high degree of disorder in our samples, which was not taken into account in the theoretical analysis. For example, for the \(\sigma_0/b\) values obtained from our data, no reasonable assumption for \(E_C\) and \(\delta\) will lead to \(g \gg 1\). It remains to be shown on theoretical grounds if the proper inclusion of disorder effects does indeed not destroy the coherent-motion contribution in the ‘low energy’ regime.

At this point we can only speculate that our observation and the observations in other works \[21, 22\] are due to the same conductance regime, which we have tentatively labeled
as the ‘tunnel percolation regime’. It remains to be shown whether the theoretical approach presented by Beloborodov et al [4] is relevant in this regard.

5. Conclusion and outlook

A satisfying association of the observed modified power law behavior of the temperature-dependent conductivity \( \sigma(T) \approx \sigma_0 + bT^\beta \) (where \( \beta = 0.47 \text{--} 0.58 \)) with either the Altshuler–Aronov correction or the coherent tunneling model is not possible. On the one hand, there is the ‘tempting’ explanation based on the Altshuler–Aronov correction for a percolating metallic conductance path. Yet, we cannot find a satisfying argument why this correction should be applicable close to the MIT and up to high temperatures even for the sample with the largest metal content. For samples still on the insulating side of the MIT, it cannot be applied. On the other hand, the suggested coherent large-scale electron motion along a tunnel-percolation path receives theoretical support only from a model calculation for a perfectly ordered granular metal. Our samples are highly disordered, which is a consequence of the preparation technique. It remains to be shown on theoretical grounds whether the proper inclusion of disorder effects does indeed not destroy the coherent motion regime. Experimentally it would be desirable to extend these studies to granular metals with a different metal species, such as Pt. This could help to clarify whether the observed behavior is a generic feature of granular metals prepared by the EBID technique. Work along these lines is in progress and we want to present preliminary results for EBID samples prepared with...
the Pt precursor MeCpPt(CH₃)₃. For this precursor, the formation of a granular structure of Pt nanocrystals in a carbon matrix is well established and the granular structure has been verified by TEM investigations [7]. On the other hand, in our attempts so far we did not succeed in reaching Pt contents larger than about 23 at% in our deposits. The results obtained for one representative sample are compiled in figure 9. With regard to the $\sigma(T)$ behavior and the $I(V)$ characteristics, a strong similarity to the results obtained for our W-sample 2 is evident (cf figures 3 and 6). Future work has to show whether it will be possible to extend these preliminary Pt-results for studying the MIT. A more detailed investigation of the microstructure of W-deposits, obtained from W(CO)₆, and their dependence on the beam parameters would also be very desirable. In particular, it must be determined what extent of influence is exerted by the matrix material, which may also contain W or may have graphite-like components that would contribute to $\sigma(T)$.

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