Observation of negative magnetoresistance in granular materials with nearest-neighbour hopping conduction

1993 J. Phys.: Condens. Matter 5 5313

(http://iopscience.iop.org/0953-8984/5/30/011)

J. Phys.: Condens. Matter 5 (1993) 5313–5324. Printed in the UK

Observation of negative magnetoresistance in granular materials with nearest-neighbour hopping conduction

A B Pakhomov†‡, D S McLachlan‡, I I Oblakova†‡ and A M Virnik§

† Ioffe Physical Technical Institute, Russian Academy of Sciences, Saint Petersburg 194021, Russia

‡ Physics Department, University of the Witwatersrand, PO Wits, 2050, Johannesburg, South Africa

§ Institute for High Temperatures, Russian Academy of Sciences, Moscow 127412, Russia

Received 9 February 1993, in final form 31 March 1993

Abstract. Quasi-critical percolation systems are prepared from conducting metal–insulator granular composite samples by subjecting them to high-density current pulses. This treatment drastically reduces the room-temperature conductivity of the mixture, due to the explosion of a fraction of the metallic grains in percolation channels. Provided that the pulse current density is high enough, the samples show the hopping conductivity characteristic of an insulator.

Abnormal dielectric properties of quasi-critical percolation systems have been previously investigated, and the objective of the present work is to study the transport and magnetotransport phenomena. Two distinctly different nearest-neighbour hopping (NNH) conduction regimes, which depend on the sample preparation conditions, are observed in the quasi-critical samples. The first type of conduction is dominated by hopping between adjacent metallic grains embedded in a dielectric host medium. The grain diameter, evaluated from the resistance versus temperature data, is found to be several nanometres. Negative orbital magnetoresistance (NMR) with a quasi-linear field dependence, is observed at both 77 and 300 K. In the sample of the second type (those which have been subjected to higher-current pulses or to several sequential pulses of the same amplitude), conduction is also found to be dominated by NNH between conducting sites in the host medium, but an evaluation of the 'grain' size shows them to be of atomic dimensions. Positive magnetoresistance (PMR) is now observed. The non-applicability of the familiar model of NMR in variable-range hopping (VRH) systems to the samples of the first type is discussed.

1. Introduction

Measurements of resistivity and magnetoresistance are both necessary for a complete investigation of the electrical transport in inhomogeneous media. Interest in these phenomena has increased considerably during the last decade, due to the development of theoretical models for the change in conductivity and magnetoresistance arising from both electron–electron interactions and weak localization on the metallic side of the metal–insulator transition. In particular, it has become possible to explain negative orbital magnetoresistance in disordered metals. The understanding of variable-range hopping (VRH) in the insulating region has also improved considerably. More recently negative magnetoresistance (NMR) has been observed and described theoretically in both doped semiconductors and granular metals, in the VRH conduction regime.

It is worth noting that theoretical models of NMR in doped semiconductors [1–6] and in granular metals [7–9] are based on similar assumptions, as are (with some particular exceptions) the models for their conduction mechanisms (compare [9–11] and [12]). In this

0953-8984/93/305313+12$07.50

section a brief review of the theoretical investigations of hopping transport in disordered systems, with the main emphasis on NMR models, is given. In the second section the preparation of quasi-critical samples is described, as this is important for an understanding of the difference between the present samples and those that are usually investigated in granular metal experiments. The description of the experimental methods is also given. In the third section it is shown that the quasi-critical samples have a nearest-neighbour hopping (NNH) type of conduction, characterized by a simple exponential resistance versus temperature dependence. It is found that, depending on the preparation conditions, the magnetoresistance may be either positive or negative at room temperature. Section 4 contains our conclusions.

1.1. Hopping conduction

Historically the first model of hopping conduction in granular metals is that of Neugebauer and Webb [13], in which electrons transfer between nearest-neighbouring metal granules by tunnelling. The electrons which tunnel between grains are thermally activated, the activation energy being equal to the charging energy of the granule with one extra electron placed on it. This model gives that

$$R \propto \exp[2\chi S + V/kT] \tag{1}$$

where R is the effective resistance between the two grains, S the distance between them, χ the tunnelling constant (generally of the order of $1/\xi$, where ξ is the localization length), V the charging energy, T the temperature and k the Boltzmann constant. Assuming that the grains are spherical, the authors of [13] suggested the following formula for V:

$$V = 2e^2/\epsilon d \tag{2}$$

where e is the electron charge, d the diameter of the metal grains (all assumed to be equal in this simple model) and ϵ the effective dielectric constant of the surrounding media. The validity of equations (1) and (2) was first confirmed by the measurements of resistance versus temperature dependence for planar granular metal films on the insulating side of the percolation threshold [13]. However, in the majority of experiments with granular metal films the simple activation temperature dependence, characteristic of nearest-neighbour hopping, is not observed. More often the following behaviour [9, 11, 14] is found to occur *on the insulating side of the metal–insulator transition:*

$$R = R_0 \exp[T_0/T]^n \tag{3}$$

where T_0 is a constant, and the exponent n has a fractional value, $n \simeq 0.5$ being the typical value. The 'fractional temperature dependence' is explained within the framework of the concept of VRH first introduced by Mott [15]. The essence of Mott's argument may be explained as follows. Assuming that tunnelling is possible between all the grains (now not necessarily all of the same size) and not only between nearest neighbours, then at a given temperature there exists an optimal conduction path which consists of a series of resistances, each characterized by both the individual hopping distance S_{ij} and the individual activation energy V_{ij}. The resistance between sites i and j is now given by

$$R_{ij} \propto \exp(2\chi S_{ij} + V_{ij}/kT) \tag{4}$$

with

$$V_{ij} = \tfrac{1}{2}(|V_i| + |V_j| + |V_i - V_j|)$$

where V_i, V_j are the charging energies of the two granules. Optimization can be achieved by minimizing the resistance of a network of individual bonds R_{ij}, with subject to both the hop length and the activation energy (see [9, 12]). This may be performed by the critical path method and, assuming a uniform density of states, one obtains $n = \frac{1}{4}$ in three dimensions [15]. This behaviour is often observed in amorphous semiconductors, but with a value of n that usually differs from $\frac{1}{4}$ in both doped semiconductors and granular metals. Abeles [14] suggests that $n = \frac{1}{2}$ is the universal behaviour in granular metal films.

Shklovskii and Efros [12] showed, for atomically doped semiconductors, that the Coulomb interaction results in a correlation Coulomb gap near the Fermi level which gives rise to the often observed result that $n = \frac{1}{2}$. Attempts have also been made to extend the idea of the Coulomb correlation gap to the case of granular metals [10], but there are strong objections to this treatment from both the experimental [11] and theoretical [19] points of view.

Alternatively the result $n = \frac{1}{2}$ has been obtained for granular metals in computer simulations [9, 16], without involving the Efros–Shklovskii correlation gap. The authors of [9, 16] use a realistic log-normal distribution of the charging energies [17] and also take into account the effect of 'random potentials' in the material [18]. In this model [9, 16] the result $n = \frac{1}{2}$ arises not as a result of a special conduction mechanism, but as the behaviour in an intermediate temperature range between that at high temperatures where one has NNH ($n = 1$) and at low temperatures where Mott's VRH ($n = \frac{1}{4}$) occurs. This prediction has been experimentally confirmed for granular metal films in [19].

Although a consensus has not yet been reached on which, if any, of the models correctly describes VRH in granular metals we have adopted the point of view that, in granular hopping conductivity, an n of 1 indicates NNH [9].

1.2. Negative magnetoresistance in the variable-range hopping conduction regime

To the best of the authors knowledge no observations of NMR in granular metals or doped semiconductors, where there is NNH conduction, have as yet been reported. On the other hand, NMR in the VRH regime is observed in both doped semiconductors [20–24] and in granular metals [7, 8, 25]. As no theoretical models for NMR where the conduction is by NNH exist, one can only examine the models for NMR that apply to VRH.

There are two alternative theoretical models of NMR in the VRH hopping regime. The authors of [3] extend a concept, similar to that used to explain the magnetoresistance due to the magnetic field dependence of weak localization in disordered metals [1, 2], to VRH-type conduction. The field dependence of resistance in this model is obtained using the argument [3] that the increase of localization due to the closed loops causes a shift in the mobility edge x_c [26] and has the form

$$\ln \rho(T, H)/\rho(T, 0) \propto -|H|^{1/2\nu} T^{-1/2} \tag{5}$$

where ρ is the resistivity, H is the magnetic field, ν is the critical index of the localization length and T is the temperature. In experiments on films of granular copper, which have been oxidized during the evaporation process [7], it was shown that the magnetoresistance data for intermediate fields fitted equation (5) with $\nu = 1$. The shift of the metal–insulator

transition predicted in [3] and [26] has been confirmed in the experiments on granular aluminium [8, 25]. In both cases the samples showed VRH and were close to the percolation threshold.

An alternative treatment of the problem is suggested in [4–6]. Here the authors consider the role of interference among the various possible waves corresponding to various trajectories of an electron tunnelling from site i to site j. The applied magnetic field changes the phases of the wave-functions along different trajectories and hence the localization length and the conductance between the two electron sites. It may be shown by logarithmic averaging over an ensemble of sites [4, 5] and by a first-principles percolation critical path calculation [6], that the orbital magnetoresistance of the macroscopic system does not average out, but has instead a finite negative value in intermediate and high fields. According to this model, in intermediate fields quasi-linear behaviour is observed:

$$\Delta\rho/\rho \propto -|H|/H_c \tag{6}$$

where H_c depends on the optimal hopping distance and the localization length. The predictions of this theory are in general agreement with experiments [8, 20, 21, 24], involving different VRH systems.

Experiments with hopping systems with very small concentrations of grains, where one can expect the NNH behaviour at high temperatures, are limited due to the very high resistivity of such samples and it has been pointed out in [8] that measurements of magnetoresistance in this extreme case are probably not feasible experimentally. Magnetoresistance data are presented in [8] for granular Al samples which have zero-field resistances $R(0) \simeq 10^{11}\ \Omega$ at $T = 1.3$ K and show a VRH type of conductance. The author of [8] estimates for these samples that the hopping distance $S_m \simeq 1000$ Å, while the intergrain separation is about 30 Å. One can expect that at lower concentrations of metallic grains, a crossover to the NNH regime must be observed at high temperatures, as the contribution of the next-nearest hops becomes exponentially small. No theoretical predictions of NMR in this regime exist.

Both theories, [3] and [4–6], use the fact that in the VRH regime the optimal hopping distance is greater than the typical inter-impurity (inter-granular) separation. In both theories application of magnetic field changes the interference conditions, which may lead to a decrease of the resistance of a macroscopic sample. As in NNH the hopping or tunnelling distance is equal to the intergranular distance it is hard to see how the above theories will apply to this case.

2. Experimental method

The quasi-critical system described here was originally developed to obtain granular percolation systems, at a metal–insulator transition, for dielectric measurements [27, 28]. The samples are prepared by first plasma spraying Al and Al_2O_3 powders, so as to produce a system just on the conducting side of the percolation threshold. Typical granular sizes are 20 or 50 μm and the samples are 1–2 mm thick. The sample is then exposed to a single high-density current pulse or a series of pulses, all of which have a duration of about 10 μs. The pulses are generated by the high-voltage capacitor bank. The current causes explosive evaporation of the metal granules in the percolation channels, which link the large metal clusters. When the charging voltage is in the range 5–40 kV the resistance increases from its original value by between nine and 13 orders of magnitude to between

10^7 and 10^{11} Ω at room temperature. These samples are labelled type H (high-resistance). However, if the charging voltage is between 0.5 and 3 kV the resistance increases by only 5–7 orders of magnitude to between 10^3 and 10^5 Ω at room temperature and exhibits a D.C. hopping conductivity. These are labelled type M (medium-resistance) samples. In the intermediate voltage range 3–5 kV one cannot be certain if a type M or a type H will be obtained. A sample subjected to a series of low-voltage (0.5–3 kV) pulses may first undergo a metal–insulator transition to type M and then cross over to the type H behaviour.

Samples in this paper are labelled N-P (M or H) where N is the sample number, P is the number of pulses and M or H indicates the type of sample.

The DC resistance of the samples, with room temperature resistances of 10^7 Ω or more, are measured with a Keithley 617 electrometer in the two-probe V/I mode, using constant voltages of 0.1, 1 and 10 V, between 330 K and the temperature where the resistance exceeds 10^{12}, 10^{13} and 10^{14} Ω with 0.1, 1 and 10 V respectively. Medium-resistance measurements are made using the standard four-probe technique with a scanned digital voltmeter and standard resistance. Resistance is measured between 300 K and the temperature where R reaches 10^6 or 10^8—the maximum measurable value of R for the experimental apparatus. In both cases the electrical contacts are made with silver paste. The temperature variation is obtained by lowering the samples into a helium or nitrogen storage vessel and is measured using an RhFe thermometer. A computer-controlled data acquisition system monitors the measurements continuously and records a point every time the temperature has changed by 1 K or more, or when the value of the resistance has changed by 1%.

DC magnetoresistance measurements are performed using a water-cooled Cu coil magnet with pole pieces having a diameter of 10 cm. The magnitude of the magnetic field is measured with a calibrated Hall sensor. These measurements are performed at room temperature and at 77 K, the latter with the sample in a small nitrogen Dewar. Since the resistance of the samples is very sensitive to temperature drift, after having applied the DC test current we had to wait for several hours before thermal equilibrium is achieved. Resistance at a given value of the magnetic field is measured for both directions of the field. The zero-field resistance is measured after every measurement in the magnetic field in order to take into account possible resistance drift due to the temperature variation. Our attempts to observe the Hall effect in the quasi-critical samples have not been successful.

3. Results and discussion

As figure 1 shows, prior to the current pulses the plasma-sprayed samples have a temperature-dependent resistivity typical of a dirty metal. The large residual resistance is thought to be due to tunnelling in the oxide films that separate the Al grains. The samples do not become superconducting, since the lowest temperature reached is only 4.5 K.

The plots of the resistance of the type M and type H samples versus temperature indicate behaviour typical of hopping conduction. In order to unambiguously obtain the temperature dependence (n in equation (3)) for the resistivity of the type M and H samples, the data for these samples were, following [29], plotted in the form $\mathrm{d}\ln(1/R)/\mathrm{d}\ln T$ against $\ln(1/R)$, the data for this graph being determined from the numerical derivative of a set of shape-preserving cubic splines that were fitted to the original numerical resistivity data. As shown in figure 2 for sample 1-1M, if the data obey equation (3), they will appear as a straight line with a slope of $-n$. This procedure showed that all the type M samples had an n of one. The $\mathrm{d}\ln(1/R)/\mathrm{d}\ln T$ against $\ln(1/R)$ data for the type H were very noisy due to the very high resistances, and in only one case was it possible to clearly establish that n

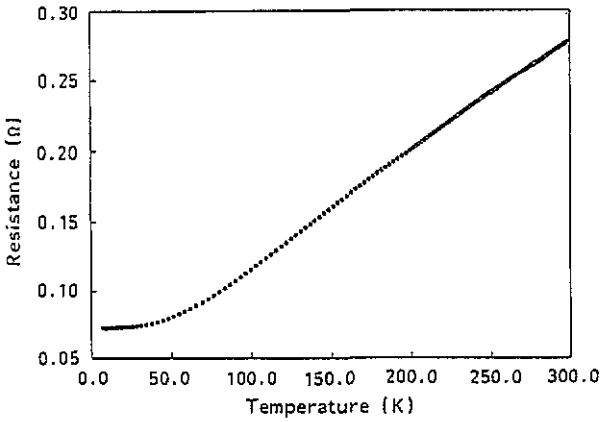

Figure 1. Plot of resistance versus temperature for a Al–Al_2O_3 sample, prepared by plasma spraying with a mean grain size 20 μm.

was equal to 1. However, as the statistical deviation between the experimental results for these samples and fits to equation (3) were also better for $n = 1$ than $n = \frac{1}{2}$ for all these very-high-resistivity samples, it was concluded that n was also equal to one for this class of samples. Because, as discussed in the first section, VRH gives rise to an n of $\frac{1}{4}$ or $\frac{1}{2}$ in three dimensions it must be concluded that both the medium- and high-resistivity samples are exhibiting NNH as $n = 1$.

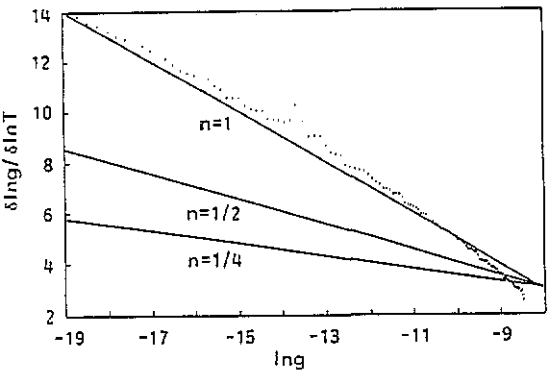

Figure 2. The logarithmic temperature derivative of $\ln g$ as a function of $\ln g$ (points), where $g = 1/R$ is the conductance for sample 1-1M. Straight lines indicate the slopes obtained with $n = 1$, $n = \frac{1}{2}$ and $n = \frac{1}{4}$ from equation (3).

Figure 3 shows a plot of the resistance on a log scale against $1/T$:

(i) Where sample 2 has been exposed to two pulses with charging voltages of 1 kV and 0.5 kV and the room temperature resistance $R(300)$ is 2.9 kΩ, i.e. sample 2-2M. The activation energy V is found to be 8.2×10^{-2} eV.

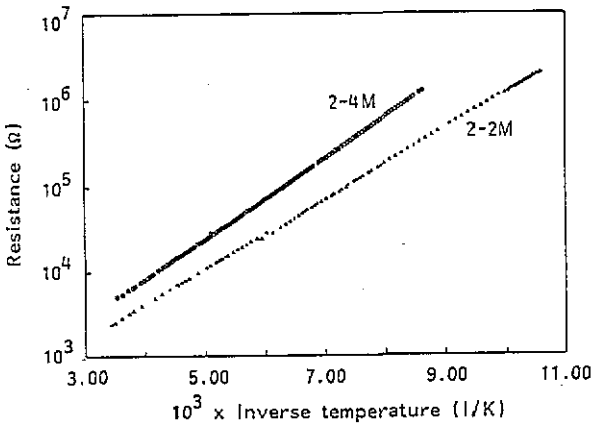

Figure 3. This figure shows the resistivity on a logarithmic scale against the inverse temperature for the samples 2-2M and 2-4M.

(ii) Where sample 2 has been exposed to two subsequent pulses with a charging voltage of 0.5 kV and $R(300)$ is 5.77 kΩ, i.e. sample 2-4M. The activation energy is now 9.4×10^{-2} eV.

Based on the method of sample preparation, which involves the explosive evaporation of Al grains into the dielectric, one may assume that the hops occur between the small metallic granules that have condensed into the dielectric host medium. Then, assuming that the granules all have a similar size, the mean diameter d can be calculated from equation (2) using the measured activation energy, if ϵ is known.

The value of ϵ in equation (2) needs special consideration. In the VRH region [9–12], an electron tunnelling between two localization centres traverses close to other electron sites (granules) because the hopping length is greater than the separation between the nearest-neighbour sites (granules). Therefore the electron tunnels through an effective medium, where the effective dielectric constant is greater than that of the host insulator [11]. The effective dielectric constant ϵ_{eff} may be evaluated using percolation [30] or effective medium [31] theories. However, if, as previously stated, the assumption is made that in both the M-type and H-type samples the scale of the hopping process is of the order of intergranular separation, the above theories cannot be expected to hold. When the hopping is between nearest neighbours one can in principle use the mean dielectric constant of the insulator phase, the latter to be defined taking into account the geometrical arrangement of air, Al_2O_3 and Al grains in the hopping channels.

We assume that when a metallic (Al) 'bond' that has a length of the order of the size of the grains in the initial percolating system, i.e. 20 μm or 50 μm, explodes due to the high-density current the tiny metal particles condense on the surface and in the pores of the surrounding Al_2O_3 grains. It must therefore be assumed that the majority of Al granules condense into a tubular array on the Al_2O_3 surface surrounding the exploded grains. On a macroscopic scale these hopping arrays are located in fractal 'cracks' or the insulating interlayers separating the macroscopic metallic percolation cluster [32]. Inside the fractal-shaped interlayers the tubular hopping arrays form a kind of a parallel resistor circuit between adjacent clusters. Note that this paper has and will primarily discuss resistance- and geometric-factor-independent quantities such as the activation energy since the true

geometric factor is that of a series of arrays of tubular 'blow holes' arranged in fractal 'cracks'.

Therefore, again assuming that the tunnelling is between nearest-neighbour grains, we conclude that the effective dielectric constant, to be used in the estimate of the granular diameter d from the above results, has a value intermediate between the values for pure alumina ($\epsilon \simeq 10$) and air or vacuum ($\epsilon = 1$). (This assumption was also made by Neugebauer and Webb [13] in making an estimate of the dielectric constant of the medium surrounding evaporated metal granules on flat glass substrates.) However, as has been previously discussed, the dielectric constant may increase due to the presence of the nearby granules. Taking these factors into account we choose the value of ϵ to be close to that of pure alumina, i.e. $\epsilon \simeq 10$. Then, using the experimentally observed values of activation energy for type M samples, $V_i = V = 0.07$–0.10 eV, the diameters of granules are estimated from equation (2) and found to lie between about 30 and 45 Å for all samples of this class. Also note that we have neglected the possibility of a Coulomb gap [9]. The actual activation energies and corresponding grain sizes are shown for a number of type M samples in table 1. Note that when a sample is subjected to a series of current pulses, this leads to an increase in the activation energy V of conduction (figure 3) and a corresponding decrease in the average size of metal granules between which hopping occurs. If exposed to a sufficiently high current pulse or a series of smaller pulses, the resistance of the sample increases abruptly by several orders of magnitude to a type H sample, corresponding to an abrupt increase in activation energy.

Table 1. The activation energies V and grain sizes d for various type M and H samples. Note the complete absence of intermediate values.

	Sample								
	1–1M	2–2M	2–4M	3–3M	4–1M	5–1M	6–1M	7–1M	8–1M
Activation energy V (eV)	0.085	0.082	0.093	0.069	0.085	0.099	0.087	0079	0.073
Estimated d (Å)	35.00	35.00	30.50	45.40	33.90	29.00	33.00	36.36	39.26
	Sample								
	9–1H	10–1H	11–1H	12–1H	13–1H	14–1H	15–1H	16–1H	17–1H
Activation energy V (eV)	0.793	0.793	0.991	0.913	0.950	0.952	1.069	0.741	0.819
Estimated d (Å)	3.635	3.635	2.900	3.150	3.035	3.025	2.695	3.880	3.516

Figure 4 shows the results for the magnetoresistance $[R(H) - R(0)]/R(0)$ at room temperature of samples 2-1M, 2-2M, 2-3M and 2-4M for a magnetic field perpendicular to the sample plane, when the DC current is flowing in the plane. All these samples, which are different modifications of the basic sample 2, display an NMR, the magnitude of which decreases with the room temperature resistivity and hopping activation energy and eventually vanishes into the noise when $R(293\ \mathrm{K})$ is about 300 kΩ and $d \lesssim 30$ Å. If the magnetic field is parallel to the current, which is in the plane of the sample, the magnetoresistance decreases by approximately a factor of two. As shown in figure 5 for sample 3-3M the magnitude of the magnetoresistance increases by a factor of about 3.5 as the temperature drops from 293 K to 77 K. There are insufficient data to determine the exact temperature dependence of this NMR, as temperature stability requirements make these measurements very difficult.

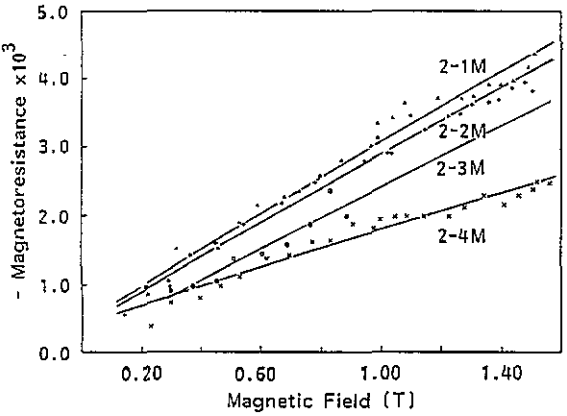

Figure 4. This figure shows the negative magnetoresistance $[R(H) - R(0)]/R(0)$ against the magnetic field for a sample which has been exposed to a series of current pulses: 2-1M, 2-2M, 2-3M and 2-4M. The straight lines are linear least-squares fits to the experimental data.

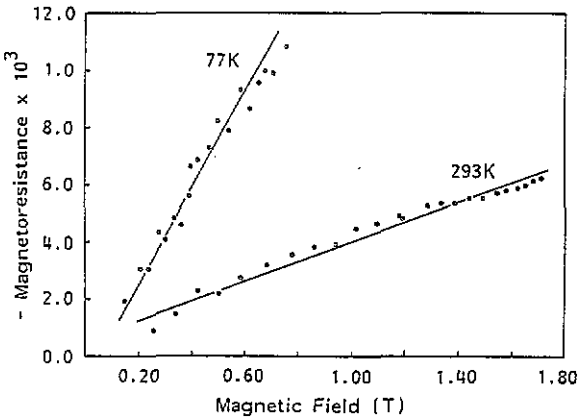

Figure 5. This figure shows the negative magnetoresistance $[R(H) - R(0)]/R(0)$ field for the sample 3-3M at $T = 293$ K and $T = 77$ K.

The lines through the data in figures 4 and 5 are linear least-squares fits to the data at fields above 0.1 T. Linear fits were the best for the majority of the type M samples, but in some instances the magnetoresistance above 0.1 T was found to be more accurately described by an $H^{0.85-0.95}$ dependence. In some cases the data would appear to extrapolate to above the origin. Due to the noise, the field dependence below 0.1 T could not be determined. The origin of the resistivity noise in quasi-critical samples has not been investigated. We assume that it is due to charge fluctuations in finite-sized macroscopic percolation clusters [33].

Quasi-linear behaviour of the NMR for VRH is predicted by the theories given in [4–6], and this type of behaviour has been observed experimentally in doped semiconductors [20,21]. However, as it has been shown that in the type M quasi-critical samples nearest-neighbour intergranular hopping is occurring, application of this VRH theory to these NNH

results would not prove anything.

The resistivity and magnetoresistance of the type H samples, which also show a temperature dependence characteristic of NNH, are very different from those of the type M samples. Figure 6 shows plots of resistance, on a logarithmic scale, against $1/T$ for various type M and type H samples. Typical activation energies and corresponding 'grain' sizes are shown in table 1 for several type H samples. Since the 'granular' diameters calculated for the type H samples are comparable with atomic dimensions, we must assume that localization centres in the type H samples are single Al atoms, rather than Al granules. Note that no samples with activation energies between 0.099 and 0.713 eV or 'grain' sizes between 3.6 and 29 nm are observed. The reason for this is not known. Grains of this size may not be formed due to the extreme conditions during the electric explosion in which the grains are created. There is no reason to believe that Al grains smaller than 30 Å cannot be created or exist in other experimental situations. Indeed, nickel and copper metallic granules (clusters) consisting of several atoms have been produced and studied [34].

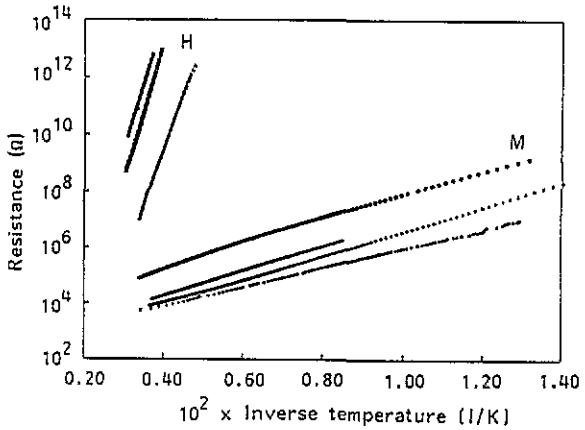

Figure 6. Plots of the resistance on a logarithmic scale against inverse temperature for various type M and type H samples.

It should also be noted that an activation energy of 0.7–1.1 eV does not preclude the presence of some grains with diameters of 30 Å or more. What it does imply is that these larger grains, with their lower charging energies, are on average too far apart to contribute significantly to the production process.

Due to the high resistance, the resulting noise, and the extreme sensitivity of the resistivity of the type H samples to small temperature variations, it proved very difficult to measure their magnetoresistivity. All that can be stated is that magnetoresistivity is positive for the type H samples and has a magnitude of about 10^{-3} when a magnetic field of 0.7 T is perpendicular to the plane of the sample and the current, and approximately a factor of two smaller when the field is parallel to the current. As the charge carrier sites in the type H samples are probably isolated atoms, one may consider applying theories designed for doped semiconductors. One such theory would lead to the conclusion that the increase in resistance with magnetic field could be due to the shrinkage of the wave functions of electrons localized on the 'impurity' states or 'atomic' Al sites [12].

4. Conclusions

The most important aspect of this paper is the observation of an NMR for a system in which the temperature dependence is $R(T) = R_0 \exp[V/kT]$, which is indicative of NNH. To the best of our knowledge this is the first time that an NMR has been observed for a system with this temperature dependence of the resistivity, and no theories exist to describe this phenomenon.

The second important observation is that two very distinct ranges of V (or d) occur. Furthermore it would appear that the abrupt crossover from a low activation energy to a high activation energy takes place as the energy released during the sample preparation is increased beyond some critical threshold.

The authors believe that the microstructure of the quasi-critical samples, which was discussed earlier, is unique and that this is the reason why an NMR, combined with a temperature dependence that indicates NNH, has been observed for the first time.

Acknowledgment

We wish to thank Professor T A Polyanskaya for her advice on making magnetoresistivity measurements.

References

[1] Al'tshuler B L and Aronov A G 1985 *Electron–Electron Interaction in Disordered Systems* ed A L Efros and M Pollak (Amsterdam: North-Holland)
[2] Otsuka Y and Kawabata A 1985 *Progr. Phys. Suppl.* **84** 249
[3] Al'tshuler B L, Aronov A G and Khmelnitskii D E 1982 *JETP Lett.* **36** 195
[4] Nguen V I, Spivak B Z and Shklovskii B I 1985 *Sov. Phys.–JETP* **62** 1021
[5] Shklovskii B I and Spivak B Z 1991 *Hopping Transport in Solids* ed M Pollak and B Shklovskii (Amsterdam: Elsevier) p 271
[6] Entin-Wohlman O, Imry Y and Sivan U 1989 *Phys. Rev.* B **40** 8342
[7] Aronov A G, Gershenzon M E and Zhuravlev Yu E 1984 *Sov. Phys.–JETP* **60** 554
[8] McLean W L 1990 *Physical Phenomena in Granular Materials (Mater. Res. Soc. Symp. Proc. 195)* (Pittsburgh: Materials Research Society) p 117
[9] Sheng P 1992 *Phil. Mag* B **65** 357
[10] Entin-Wohlman O, Gefen Y and Shapira Y 1983 *J. Phys. C: Solid State Phys.* **16** 1161
[11] Adkins C J 1990 *Hopping and Related Phenomena* ed H Fritzshe and M Pollak (Singapore: World Scientific) p 93
[12] Shklovskii B I and Efros A L 1984 *Electronic Properties of Doped Semiconductors* (Berlin: Springer)
[13] Neugebauer C A and Webb M B 1962 *J. Appl. Phys.* **33** 74
[14] Abeles B 1976 *Applied Solid State Science* vol 6 (New York: Academic) p 1
[15] Mott N F 1968 *J. Non-Cryst. Solids* **1** 1
[16] Chen L F, Sheng P, Abeles B and Zhon M Y 1990 *Physical Phenomena in Granular Materials (Mater. Res. Soc. Symp. Proc. 195)* (Pittsburgh: Materials Research Society) p 187
[17] Granquist C G and Buhrman R A 1976 *J. Appl. Phys.* **47** 2200
[18] Adkins C J 1987 *J. Phys. C: Solid State Phys.* **20** 235
[19] McAlister S P, Inglis A D and Kroeker D R 1984 *J. Phys. C: Solid State Phys.* **17** L751
[20] Orlov V O and Savchenko A K 1986 *Pis. Zh. Exp. Teor. Fiz.* **49** 34
[21] Laiko E I, Orlov A O, Savchenko A K, Ilyichev E A and Poltoratsky E A 1987 *Sov. Phys.–JETP* **66** 1264
[22] Rentzsch R, Friedland K J and Ionov A N 1988 *Phys. Status Solidi* b **146** 199
[23] Ionov A N and Shlimak I S 1991 *Hopping Transport in Solids* ed M Pollak and B Shklovskii (Amsterdam: North-Holland) p 397

[24] Faran O and Ovadyahu Z 1988 *Phys. Rev.* B **38** 5457
[25] Sin M K, Lindenfeld P and McLean W L 1984 *Phys. Rev.* B **30** 4067
[26] Khmel'nitskii D E and Larkin A I 1981 *Solid State Commun.* **39** 1069
[27] Garanov V A, Kalachev A A, Karimov A M, Lagarkov A N, Matitsin S M, Pakhomov A B, Peregood B P, Sarychev A K, Vinogradov A P and Virnik A M 1991 *J. Phys.: Condens. Matter* **3** 3367
[28] Vinogradov A P, Virnik A M, Garanov V A, Kalachev A A, Lagarkov A N, Matitsin S M, Oblakova I I, Pakhomov A B and Sarychev A K 1992 *J. Tech. Phys. (St Petersburg)* N5 (in Russian)
[29] White H and McLachlan D S 1986 *J. Phys. C: Solid State Phys.* **19** 5415
[30] Efros A L and Shklovskii B I 1976 *Phys. Status Solidi* b **76** 475
[31] McLachlan D S, Priou A, Chenerie I, Isaac E and Henry F 1992 *J. Electromagn. Waves Applications* **6** 1099
[32] Pakhomov A B, Oblakova I I and Garanov V A 1992 unpublished
[33] Chen C C and Chou Y C 1985 *Phys. Rev. Lett.* **54** 2529
[34] Ramachandra Rao C N, Vijayakrishnan V, Sarma D D and Chainani A 1991 *Discuss. Faraday Soc.* **92** 147