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Physica B 315 (2002) 171–178

PHYSICA B

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Magnetic nanoparticles between electrodes of tunnel junction: anomalous tunnel conductance

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Received 9 July 2001; received in revised form 15 October 2001

Abstract

Magnetic particles of microscopic size can be created in the process of Ni, Fe and Co mechanically controllable break junctions fabrication and trapped between the electrodes by magnetic dipole forces. Tunneling between the protruding nanoparticle and the sample electrode shows clear distinctions from the usual junctions: heavy deviation of the current–distance $I(z)$ dependence from the expected exponential behavior at electrode separations z below 4.0–4.5 Å and on numerous occasions a sudden jump-like decrease of the tunnel current at $z \approx 1.5$–2.0 Å. Possible mechanisms behind observed anomalies including the short-range magnetic exchange coupling are discussed.

PACS: 73.40.Gk; 75.30.Et

Keywords: Electron tunneling; Exchange interaction; Nanoparticles

1. Introduction

At standard scanning tunneling microscopy (STM) tip–sample separations the tunnel current can be well described by the Tersoff and Hamann independent electrode approach [1]. However, at smaller spacings electrodes can no longer be treated independently due to an increasing overlap of the wave functions. The influence of electrode interaction on electronic structure of materials and eventually on the possibility to achieve atomic resolution is one of the most long-standing problems in a STM and is not yet understood adequately. That is why studies of the transition from tunneling to the ballistic regime of conductivity have drawn considerable attention since the first experiments of Gimzewski and Möller [2]. For junctions with ferromagnetic electrodes this issue is of particular interest because of additional phenomena involved:

(i) The short-range interaction between electronic states of atoms with a permanent magnetic

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0921-4526/02/$ - see front matter
PII: S0921-4526(01)01462-4

moment. The forces associated with an exchange coupling are one order of magnitude smaller than metallic adhesion forces and are probably insufficient to produce any detectable effect on the electrode surfaces. At the same time the interaction between ferromagnetic electrodes causes perceptible changes in the local density of states (LDOS) around the Fermi level and therefore, affects the tunnel current–distance dependence [3].

(ii) The distance dependence of spin-polarized tunneling. The thickness of the tunnel barrier can influence the degree of spin polarization and hence results in a deviation of the junction resistance from the simple exponential decrease with diminution of electrode separation [4].

The inherent rigidness and high stability features of the mechanically controllable break junctions (MCBJ) technique permits precise and highly reproducible measurements of the tunnel current–distance dependencies $I(z)$ and an accurate tunneling spectroscopy of LDOS in a wide range of electrode separations including distances at which the short-range forces, stemming from the overlapping of electron densities, become of crucial significance.

Earlier we reported the observation of metallic adhesion force influence on $I(z)$ curves (at $z<3$Å) for Pt as well as a corrugation enhancement in the 6–3 Å range for Al and Au MCBJ [5]. In this article we are presenting results of similar experiments for ferromagnetic materials with particular emphasis on the intermediate (2–5 Å) range of electrode separation. We found that for common tunnel junctions there is not much difference between $I(z)$ dependencies for Ni, Fe, Co and non-magnetic 3d-Pt and Pd. At the same time a part of the characteristics show anomalous behavior which we could explain by the presence of small magnetic particles produced in the process of the breaking and trapped between the electrodes. This has also been verified by transmission electron microscopy (TEM) observations. Since the electronic and magnetic properties of metallic nanoparticles are currently yet another intriguing subject of STM research, we conducted a more extensive investigation of such tunnel systems.

2. Experimental

The principle behind the MCBJ technique proposed originally by Moreland and Ekin [6] and developed to the present state by Muller and co-workers [7] is basically quite simple and can be briefly described as following. The sample mounting (Fig. 1a) consists of a thin filament glued onto a phosphor–bronze bending beam (covered with a layer of capton foil) using two small drops of a hard epoxy (Stycast 2850FT). The wire is then cut in the midpoint of the glued section for about 80–90% of its diameter. For ferromagnetic materials special precautions must be taken to keep the produced notch free of magnetic sawdust (particles of cut metal and broken fragments of the steel razor blade used for notching). It can be completely dislodged by a brush and/or high-pressure blast of air. After mounting in the experimental setup (described elsewhere [8]) and cooling to 4.2 K the sample was broken in a high vacuum surrounding by bending the substrate against the counter support (C) achieved by applying a coarse force at the center of the beam. After that the electrodes can be brought together and the contact resistance fine tuned by adjusting the beam deflection with a piezodriver.

In our experiments we used 250 μm diameter Ni, Fe or Co wires of 99.996% purity (as manufactured) chemically etched for a short time to remove the surface contaminations. The notch depth did not exceed 80% leaving 40–60 μm of the wire material intact. We discovered that the break of the non-annealed brittle wires almost inevitably resulted in chipping off of small particles of material. These particles remain confined within the break area attached to one of the electrodes because of the magnetic dipole interaction. Since the wires were magnetized along their axis, the splinters are aligned along the magnetic force lines trying to bridge the gap between the electrodes. Therefore, the probability that the distance between microparticle(s) and the opposite electrode will be the shortest one is very high. The size of the particles ranges from a few microns (they can be easily observed with a standard optical microscope) to 10–30 nm. In the latter case the images of the nanoparticle can be obtained with the

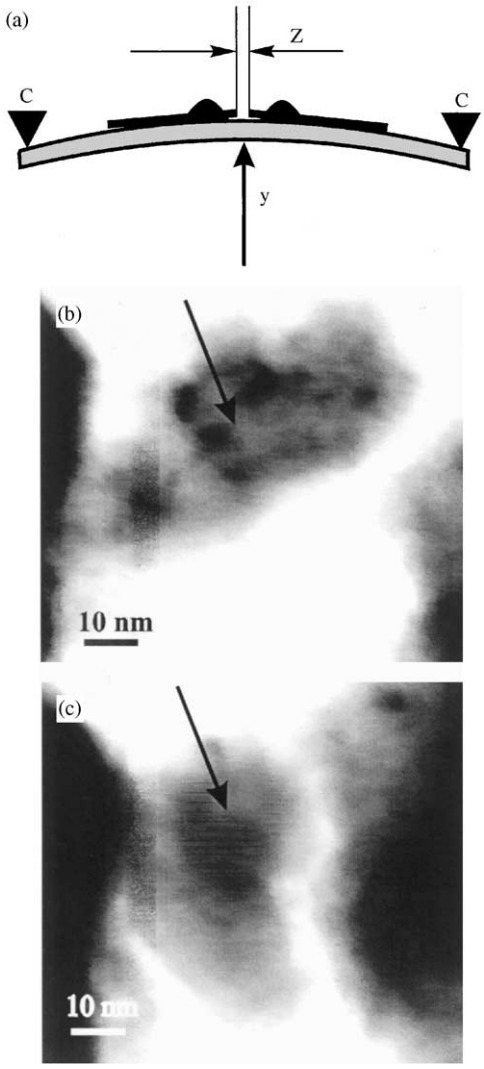

Fig. 1. (a) Design and principle of a mechanically controllable break junction. A bending force causes a vertical displacement y, which leads to a distance z between the electrodes. For clarity, all distances have been exaggerated. (b), (c) TEM image of Ni nanoparticle (indicated by an arrow) confined between electrodes of MCBJ.

combination of STM used for break-junction fabrication and transmission electron microscope (TEM) [9]. A typical TEM image is presented in Fig. 1b,c. Indications of the occurrence of even smaller particles $\sim$1–3 nm are mostly circumstantial and cannot be confirmed independently as their size is beyond the TEM resolution, which in the case of ferromagnetic materials is limited by the stray fields of the sample. The stability of a MCBJ with a magnetic nanoparticle trapped between the electrodes remains high and $I(z)$ curves can be reproduced very accurately.

As a rule, the break of Ni, Fe and Co well annealed (900–1000°C for 36–48 h), ductile and deeply notched 50 μm wires did not result in the creation of nanoparticles. (Hereafter, we will refer to the particle-free junctions as *usual* ones.) It is likely that the phenomenon of creating small particles during the breaking of brittle materials is more common and not restricted by ferromagnetic materials. However, as small as they are, these particles are unable to stay within the contact area only due to the short-range metallic adhesion and Van der Waals forces.

All measurements were done at 4.2 or 1.2 K under a stable temperature distribution in the insert and not before 5–6 h after the break to insure that the surface of the electrodes was relaxed [10]. To calibrate the distance between electrodes the field emission resonance (FER) spectra were measured in the Fowler–Nordheim region [11]. We found that the vast majority of measurements yielded work function ϕ values for Ni, Fe and Co rather close to the literature value [12] in the range 4.3 ± 0.3 eV. Therefore, one can use the simple formula for one-dimensional tunneling $I_T \propto V \exp(-2z/\hbar\sqrt{2m\phi})$ which gives us $z = 1.1 \pm 0.1$ Å per decade of tunnel current and is in a good agreement with calibration constants derived from the FER spectra. In accordance with Ref. [11] we placed the distance scale in such a way that a separation of 2 Å corresponds to a contact resistance of approximately 100 kΩ. The estimated error in the determination of the absolute vacuum gap in such a way is about ± 0.25 Å.

The data reported below are based on the careful analysis of a few hundreds of $I(z)$ dependencies which were converted for more clear presentation to plots of the tunnel resistance vs. electrode separation $R_T(z)$. Only those features, which were reproduced repeatedly for all materials and different samples are presented.

3. Results and discussion

The set of most frequently encountered $R_T(z)$ curves for the usual Ni MCBJ made of well-annealed 50 μm wire is presented in Fig. 2. The perfect exponential behavior over 5 orders of junction resistance (curve 1) is typical for the majority of $R_T(z)$ dependencies. Approximately 3–5% of all curves are bent upwards demonstrating *stronger than exponential* behavior (curve 2) [5,13] below 1 MΩ or ~3 Å. At these separations the attractive metallic adhesion forces between the foremost atoms are reaching a maximum and are pulling these atoms out of their equilibrium position thus reducing the vacuum gap width. The relatively small percentage of such curves can be explained by the fact that adhesion forces are pronounced mostly in a *flat surface-tip* configuration which is not common for MCBJ with rather irregular surface relief. A comparatively high percentage of $R_T(z)$ dependencies are bent downwards starting from $R_T \leqslant 10$ MΩ (or electrode separations of 4.0–4.5 Å) which means that the junction resistance decreases more slowly than expected (curve 3). This type of behavior is less frequent for non-magnetic materials and is usually was explained in the following way. When the normal axis of the tunneling area on the *blunt* electrode surface does not coincide with the shortest distance to the foremost atom of the more sharp electrode the site with the shortest distance changes as the tip is moved. This means that a surface scan is partially incorporated into the $R_T(z)$ curves (e.g. the tip is sliding along the slope at the surface of the opposite electrode when approaching it [10]). On very rare occasions the $R_T(z)$ dependence combined an initial downward bending with following upward bending (curve 4).

$R_T(z)$ characteristics of MCBJ with incorporated magnetic particles show two major differences from the usual ones. The first distinguishing feature is the heavy downward bending for the most part of $R_T(z)$ curves (Fig. 3). The relative number of *anomalous* curves and the magnitude of effect appear to increase in the succession Ni, Fe, Co.

We discuss several possible reasons for this type of behavior.

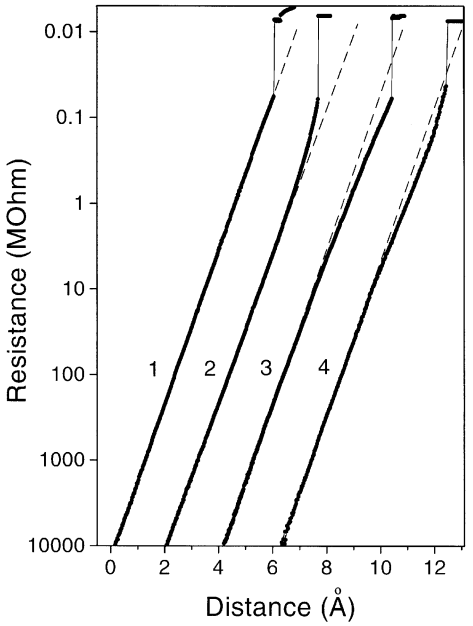

Fig. 2. The set of most common $R(z)$ dependencies for usual Ni MCBJ (see text).

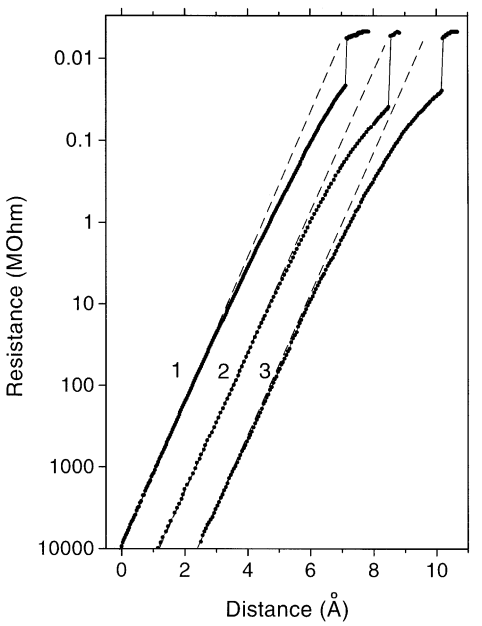

Fig. 3. Deviation of $R(z)$ curves from exponential behavior for MCBJ containing magnetic particles: 1.—Ni; 2.—Fe; 3.—Co.

(i) *Topological reasons*: For this we need to assume that the surface relief of particles is significantly different from that of usual electrodes which is unlikely. The main objection against this assumption is that deviation from exponential behavior always starts at approximately the same electrode separation whereas the irregularities of the surface relief are liable to cause such deviation at any distance as was observed in Ref. [10].

(ii) *Nanoparticle resistance in series*: Depending on particle size and the surface relief the electrical resistance of point contact(s) between the host electrode and the magnetic particle could range from a few Ohm to 2–3 kΩ. In the latter case the $R_T(z)$ dependence would deviate from exponential behavior, but this deviation becomes pronounced only at $R_T \lesssim 50$ kΩ.

(iii) *Spin-polarized tunneling*: Distance dependence of the spin-polarized tunneling was reported by Alvarado [4]. However, the expected magnitude of the effect is at least a few times less than observed.

(iv) *Tunnel barrier height variations*: One of the reasons for the observed behavior of the $R_T(z)$ curves behavior can be a variation of the potential barrier height with electrode separation. The calculations for Al [14] give nearly the correct magnitude of the effect (though at somewhat closer distances) but experimentally it was never observed with MCBJ technique for normal metals including Al.

(v) *Density of state effects*: The $R_T(z)$ dependence downward bending can be explained by a gradual decrease of the local density of states at the Fermi level as the electrodes are approaching each other [3,15]. Calculations for an Fe tip demonstrated that as z decreases the states above and below ε_F are gradually shifting to the top and bottom of the band inducing a strong hole in the middle of the apex LDOS. To check this suggestion qualitatively we performed tunneling spectroscopy at different separation between electrodes. Comparing the intensity of tunnel spectra around zero bias (after the usual normalizing procedure $(dI/dV)/(I/V)$) at different separations we found that the relative intensity drops as the distance between electrodes decreases. However, the magnitude of the effect does not exceed 15–30% for the smallest separations (about 2 Å) we were able to achieve. On the other hand it is not clear if the straightforward normalizing procedure of tunnel spectra is still valid at small separations for non-exponential $I(z)$ dependence. In addition for reasons which will be described later we were not able to measure tunnel spectra of the smallest particles at close distances or/and high voltage bias.

The conclusion from the above is that none of the mentioned reasons can be alone responsible for the observed effect. Only (i) and probably (ii) can be ruled out as possible explanations whereas (iii) and (iv) can never be excluded from consideration completely. The fact that the *negative* bending is characteristic only for MCBJ containing magnetic nanoparticles and takes place exactly at the range where short-range interaction is expected suggests a possible connection of these phenomena. Since the electronic properties of nanoparticles are supposed to be more sensitive to the different types of interactions than bulk electrodes it is not improper to suggest that the LDOS of small particles can be modified more drastically. The gradual developing of a *quasigap* in the LDOS around ε_F in small particles (and thus the reduction of the tunnel current at small electrode separation) can be regarded as the most probable explanation for the observed effect.

The second distinguishing feature we are reporting here is an abrupt increase of the tunnel resistance by a factor ranging from 2 to 20 at electrode separations between 1.5 and 2.0 Å (Fig. 4). It should be stressed that at sufficiently low bias voltages (5–10 mV) this effect was observed randomly and only for a minor part of all junctions. Usually from one to three-five such singularities were observed (Fig. 4a) but in some cases sequences of 20–30 jumps were recorded (Fig. 4b). In the latter case the $R_T(z)$ curve for Ni MCBJ shows some periodicity and the average increase in the distance between electrodes (~ 1.4 Å) is close to the distance between neighboring atomic planes in the Ni lattice. The overall picture bears a striking resemblance to the slip-stick motion data recorded with atomic force or friction force microscopy (see e.g. Ref. [16]). This behavior might be explained by a sudden

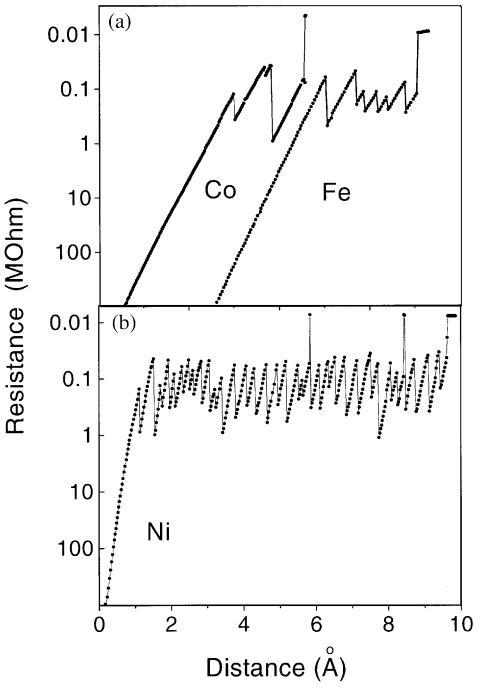

Fig. 4. Jump-like behavior of $R(z)$ at close electrode separation for MCBJ involving nanoparticle: (a)—Fe and Co tunnel junction; (b)—Ni MCBJ. All curves were recorded at bias voltage of 10 mV.

backward motion of the magnetic nanoparticle which is sliding back along the surface of the host electrode when repulsive forces are starting to outweigh the friction forces between the particle and host electrode. Very rough estimates of friction forces for magnetic particles with a typical dimension 20–50 nm based on the assumption that the load force is determined by the magnetic dipole interaction and the friction coefficient (depending on the surface roughness) is in the range 0.1–0.3, yields $\sim 10^{-6}$–10^{-8} N.

An attempt to observe the fine details of motion of the nanoparticles using TEM did not yet bring a desirable result chiefly because of non-sufficient resolution and probably due to the contamination of electrode's surface in a moderate (10^{-5} Torr) vacuum.

In our case the following forces must be taken into consideration: the long-range attractive Van der Waals and magnetic dipolar forces, short-range metallic adhesion and magnetic exchange forces. However, the contribution of the Van der Waals forces in the electrodes interaction at intermediate distances $\approx$2–5 Å is negligible [17] and the scale of its variation is much larger than the atomic scale. The same considerations fully apply to the magnetic dipole forces.

Metallic adhesion forces are attractive as well though our experimental data clearly show that adhesion forces between ferromagnetic nanoparticle and bulk electrode are suppressed (avalanche-like transition to the one-atom point contact occurs at distances 0.2–0.4 Å smaller than for usual Ni, Fe and Co MCBJ).

Magnetic exchange forces in the case of the antiparallel orientation of magnetic moments are repulsive and therefore, are the only possible candidate. Their estimated magnitude ($\sim 10^{-9}$ N) [3,18,19] is at least one order of magnitude too small to be accountable for the backward motion of nanoparticles. However, this explanation might still be plausible in the case of tiny clusters of a few tens of atoms.

Searching for alternative reasons for this effect we paid attention to the fact that the jumps in tunnel resistance were never observed when measured in He exchange gas or directly in liquid He. One of the possible explanations is that adsorbed He modifies the electronic structure of metals [20] and therefore the overall picture of the electrode interaction. On the other hand He changes the heat transfer conditions from the magnetic particle to the host electrode even more drastically.

In our experiment the bias voltage V_b was in the range of 1–10 mV and the tunnel current corresponding to the onset of resistance jumps changes from 10 to 100 nA. The estimated overheating of the electrode surface $\Delta T_S \sim IV_b/[2\pi\lambda K_S]$, where K_S is the surface thermal conductivity and λ is the elastic mean free path for electrons [21,22]. For the bulk electrodes ΔT_S is less than 10^{-3} K. In the extreme case of a thermally insulated magnetic particle (simulated for the purpose of estimations by a 50 nm long and 20 nm diameter cylinder) it will be overheated well over 1000 K in a matter of a nanoseconds [23]. In an actual situations the temperature increase is

determined by the thermal resistance between nanoparticle and host electrode.

We have found that at elevated bias voltages the periodic resistance jumps occur for nearly all junctions with heavily bent $R_T(z)$ characteristics. A typical example of $R_T(z)$ dependence is presented in Fig. 5 for iron MCBJ. At $V_b \geqslant 1.0$ V the transition to the point contact never occurs within the distance range we are able to cover with the piezodriver (10–20 nm).

For usual Ni, Fe and Co MCBJ resistance jumps of gradually decreasing amplitude were observed at $V_b \geqslant 1.0$ V (Fig. 6), but for a smaller electrode separation. In this case the main reasons for the abrupt changes in the tunnel current are field desorption and field-induced surface diffusion of atoms although the heating of the electrode surface is an important factor as well. This effect was used for the surface modification of ferromagnets and results in significant reduction of structural defects on the electrode surfaces and a marked improvement of tunnel and point-contact spectra quality [24].

At low bias voltages the field-induced effects are negligible and therefore we can suggest that for the case of nanoparticles a temperature-assisted diffusion of adatoms out of the tunnel gap is a key reason for the jumps in the tunnel current.

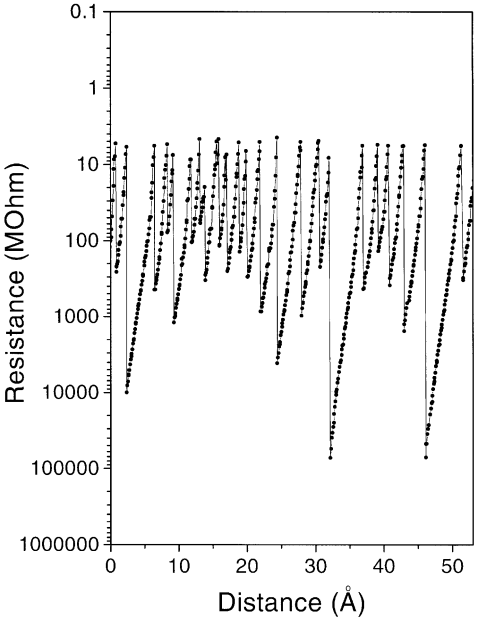

Fig. 5. $R(z)$ dependence for Fe MCBJ containing small magnetic particle at elevated bias voltage $V_b = 1100$ mV.

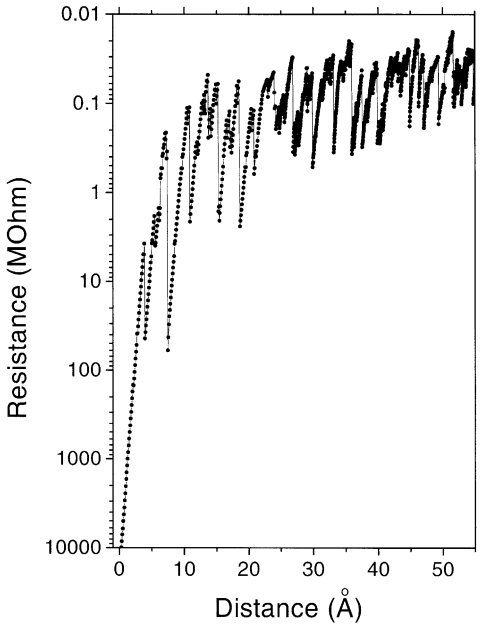

Fig. 6. $R(z)$ dependence for usual Co MCBJ (without magnetic particles between electrodes). The abrupt jumps of decreasing amplitude in junction resistance related at initial step to the field desorption of weakly bound adatom and then to the field induced diffusion of the surface atoms [24].

4. Conclusion

We found that magnetic nanoparticles can be produced in the course of breaking of brittle ferromagnetic wires and trapped in a gap between the electrodes of MCBJ. We suggested that the main reason for heavy deviation of $I(z)$ curves from exponential behavior in these junctions is a reduction of the LDOS around the Fermi level as a result of interaction between the electrodes at intermediate (2–5 Å) distances. The jump-like behavior of the tunnel current can be ascribed to backward motion of the smallest particles due to repulsive magnetic exchange interaction. However, a more probable mechanism behind this effect is the diffusion of adatoms out of the point of the

closest proximity of electrodes because of overheating of nanoparticles.

Acknowledgements

The authors are grateful to J. Hermsen and J. Gerritsen for invaluable technical assistance, Antony Keen for carefully reading the manuscript. Part of this work was supported by the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO). O.I.S. wishes to acknowledge the NWO for a visitor's grant.

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