Enhanced Magnetoresistance in Insulating Granular Systems: Evidence for Higher-Order Tunneling

S. Mitani, S. Takahashi, K. Takanashi, K. Yakushiji, S. Maekawa, and H. Fujimori
Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
(Received 12 May 1998)

We study the temperature and bias-voltage dependence of the magnetoresistance (MR) in insulating Co-Al-O granular films. The MR exhibits strong temperature dependence and is enhanced more than 20% at low temperatures, while it has no appreciable change in the bias-voltage dependence. The results provide clear evidence for the successive onset of higher-order processes of spin-dependent tunneling between large granules through intervening small ones with strong Coulomb blockade. The remarkable contrast between the temperature and bias-voltage dependence of the MR is consistently explained. [S0031-9007(98)07235-4]

PACS numbers: 75.70.Pa, 73.40.Gk, 75.50.Cc, 81.05.Rm

There has been a growing interest in the magnetoresistance of magnetic nanostructures since the discovery of giant magnetoresistance (GMR) in magnetic multilayers [1] and granular alloys [2]. Among them, the observation of GMR in tunnel-type nanostructures, e.g., granular metals in an insulating matrix [3–8], polycrystalline metals with insulating grain boundaries [9,10], and in mesoscopic multitunnel junctions [11–13] has opened new perspectives. Of particular interest in such tunnel-type magnetic nanostructures is not only to find new phenomena due to nanostructuring but also potential applications for magnetoresistive devices.

In the tunnel-type magnetic nanostructures, the charge transport is caused by tunneling through insulating barriers. Electron tunneling depends on the relative orientation of magnetic moments between ferromagnetic granules or electrodes (spin-dependent tunneling). The tunnel resistance decreases when the magnetic moments of the granules are aligned in parallel in an applied magnetic field. In addition, tunneling of electric charge into a small granule or electrode increases the Coulomb energy by a charging effect, which opens the Coulomb gap and strongly enhances the tunnel resistance (Coulomb blockade). In granular materials consisting of ferromagnetic metal granules of nanometer size in an insulating matrix, the conduction of electrons involves a large number of granules with a broad distribution of size and randomly oriented magnetic moments. Therefore, we expect that the interplay between spin-dependent tunneling and Coulomb blockade causes novel magnetoresistive phenomena inherent in the granular structure.

In this Letter, we report on the temperature and bias-voltage dependence of MR in insulating Co-Al-O granular films. The MR exhibits an anomalous increase at low temperatures but no indication of change with bias voltage. We show that the anomalous increase of the MR indicates evidence for higher-order tunneling between large granules through intervening small granules. We emphasize that the existence of higher-order tunneling is a natural consequence of the granular structure, since a broad distribution of granule size is an intrinsic property of granular systems.

Co-Al-O granular films (1 to 2 μm in thickness) were prepared on glass substrates using a reactive-sputtering technique with a Co-Al alloy target and mixed gas of Ar + O_2. Details of the sample preparation and the structural characterization were described elsewhere [3,14]. Temperature dependence of electrical resistivity (ρ) and MR were measured using a dc four-terminal method in the range of 2 to 300 K. The maximum applied magnetic field is 150 kOe, where the observed MR is close to saturation for any temperature, even at 300 K. The bias-voltage (V_b) dependence of MR was measured at 4.2 K and 12 kOe in the current-perpendicular-to-plane (CPP) geometry where the Co-Al-O granular films were sandwiched with upper and lower electrodes of Au-Cr alloy.

Figure 1 shows the temperature dependence of the electrical resistivity ρ for the Co-Al-O films with different compositions: $Co_{54}Al_{21}O_{25}$, $Co_{52}Al_{20}O_{28}$, $Co_{46}Al_{19}O_{35}$, and $Co_{36}Al_{22}O_{42}$. It is seen that ρ increases with decreasing T and $\log \rho$ is approximately proportional to $1/\sqrt{T}$. This behavior of ρ is characteristic of insulating granular systems and is attributed to the charging effect and the broad size distribution of the nanometer-sized metallic granules [15]. TEM micrographs [14] and numerical simulations for the superparamagnetic magnetization curves [16] reveal that the diameter of Co granules d distributes from about 1.5 to 5 nm in Al-oxide matrix. The mean diameter of granules $\langle d \rangle$ and the mean distance between granules $\langle s \rangle$ are estimated to be $\langle d \rangle = 2-3$ nm and $\langle s \rangle = 1$ nm or less, respectively. The difference in slope of $\log \rho$ vs $1/\sqrt{T}$ is considered to be that in the charging energy, i.e., $1/\langle d \rangle$, of granules.

Figure 2 shows the temperature dependence of MR for the Co-Al-O films. It is clearly seen that the MR is remarkably enhanced at low temperatures while it is nearly independent of temperature above ~100 K. For $Co_{36}Al_{22}O_{42}$, the MR below 3 K is anomalously large

 © 1998 The American Physical Society

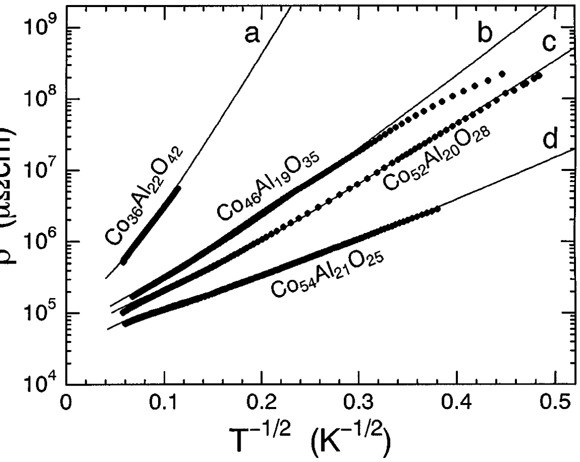

FIG. 1. ρ vs $1/T^{1/2}$ for Co-Al-O films (black dots). Solid lines represent the theoretical results given by Eq. (2) with charging energy E_c; a: $E_c/k_B = 110$ K; b: $E_c/k_B = 25$ K; c: $E_c/k_B = 18$ K; d: $E_c/k_B = 9$ K.

and reaches more than twice the value given by $P_{\mathrm{Co}}^2/(1 + P_{\mathrm{Co}}^2)$ [18], where the formula is half of that for magnetic tunnel junctions (MTJ) because of the difference between random and antiparallel alignment of magnetic moments. In the case of MTJ, the temperature dependence of MR is discussed on the basis of magnetic impurity or magnon scattering [19,20]. However, it is considered that magnetic impurity or magnon scattering does not give rise to the plateau in the temperature dependence of MR, as in the present result observed above $\sim$100 K. Helman and Abeles [21] proposed a theory of spin-dependent tunneling in insulating granular systems and predicted a temperature dependence $1/T$ for MR. However, the dependence $1/T$ does not fit the present results.

Figures 3(a) and 3(b) show ρ and MR at 4.2 K, respectively, as functions of bias voltage V_b for a $\mathrm{Co_{36}Al_{22}O_{42}}$ film. ρ decreases rapidly by 3 orders of magnitude with increasing bias voltage from $V_b = 0$ up to 600 mV. Nevertheless, the magnitude of the enhanced MR is almost constant. This is in clear contrast with the case of MTJ with macroscopic size, where both MR and ρ decrease gradually with increasing bias voltage [20]. Furthermore, the bias-voltage dependence of MR is much smaller than the temperature dependence of MR in Fig. 2. The film thickness of $\mathrm{Co_{36}Al_{22}O_{42}}$ is 1 μm. $\langle d \rangle = 2$–3 nm and $\langle s \rangle \sim$ 1 nm, as mentioned above. We can consider that about 200–300 of Co granules exist in the direction normal to the film plane between the upper and lower electrodes. Therefore, the applied bias voltage per one microjunction consisting of two neighboring Co granules may be estimated to be 2–3 mV at $V_b = 600$ mV, which corresponds to 20–30 K in temperature. As seen in Fig. 2, the enhanced MR decreases rapidly with increasing temperature and becomes flat around 20–30 K, while it is independent of V_b at least up to 600 mV.

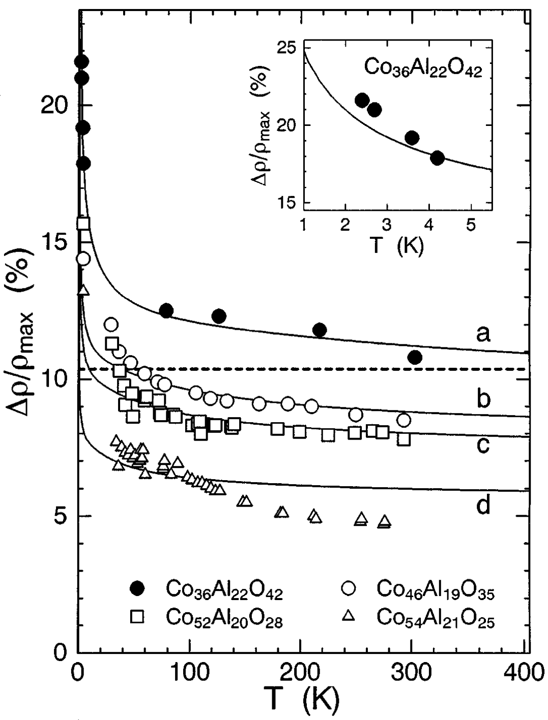

FIG. 2. Temperature dependence of MR for Co-Al-O films. Dashed lines represent the MR value of $P_{\mathrm{Co}}^2/(1 + P_{\mathrm{Co}}^2)$ expected from spin polarization of Co, $P_{\mathrm{Co}} = 0.34$ [17], in Co-based granular systems. Solid curves (a, b, c, and d) represent the theoretical MR given by Eq. (3) with spin polarization P; a: $P = 0.306$; b: $P = 0.290$; c: $P = 0.275$; d: $P = 0.250$. Other parameters are the same as those in Fig. 1.

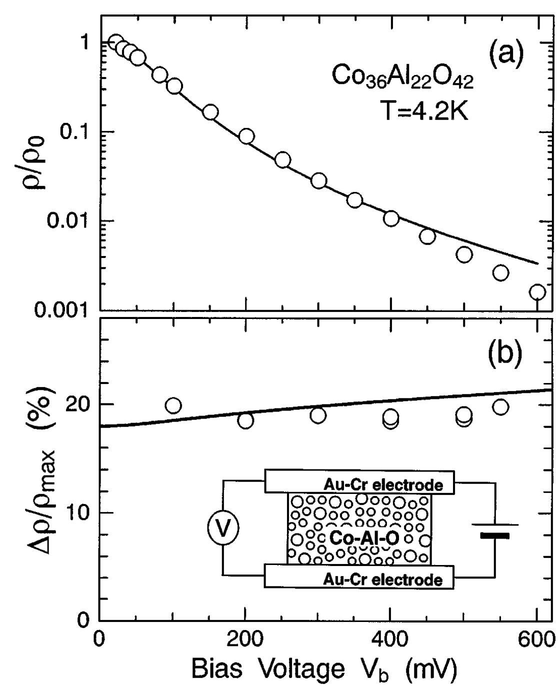

FIG. 3. Bias-voltage (V_b) dependence of ρ at $H = 0$ Oe (a) and MR (b) for a $\mathrm{Co_{36}Al_{22}O_{42}}$ film at 4.2 K. Open circles represent the experimental results and solid curves represent the theoretical ones using the same parameter values as in Fig. 2. The inset shows a schematic illustration of a Co-Al-O film for the measurement in CPP geometry.

Let us now turn to an interpretation of our experimental results, particularly, the enhancement of MR and the striking difference in the T and V dependence of MR. We first propose a model for the magnetic granular systems and present a mechanism for the enhancement as well as a consistent explanation for the T and V dependence. In the magnetic granular systems, the fundamental quantities that determine the transport properties are (i) the charging energy E_c required to generate (fully dissociated) positively and negatively charged granules, (ii) a broad distribution of E_c due to the variation of granule size d ($E_c \sim e^2/d$), and (iii) the tunneling probability depending on the relative orientation of magnetic moments between ferromagnetic granules.

The characteristic temperature dependence of the resistivity, $\ln \rho(T) \propto 1/\sqrt{T}$, observed in nonmagnetic granular systems, has been explained on the basis of the model [15] that the granules on each conduction path are equal in size d and separated by barrier thickness s, keeping the ratio s/d (or equivalently $E_c s$) constant for a given composition. An extension to the magnetic granular systems has been made by incorporating the effect of spin-dependent tunneling into the model [18], yielding the T-independent MR: $\Delta\rho/\rho_0 = P^2/(1 + P^2)$. It should be noted that the model makes a gross simplification by not taking into account tunneling between granules of different size. We extend the above model to include tunneling between those granules, which plays a crucial role for the MR in the magnetic granular systems.

In the granular systems with a broad distribution in granule size, it is highly probable that large granules are well separated from each other due to their low number density (i.e., the larger the granule size is, the more separated the granules are), and there may be a number of smaller granules between large granules as shown in Fig. 4(a). For modeling the structural feature of granular systems we assume that large granules with size $n\langle d\rangle$ and charging energy $\langle E_c\rangle/n$ are separated by an array of n granules with average size $\langle d\rangle$ and charging energy $\langle E_c\rangle$ on a conduction path, as shown in Fig. 4(b).

The temperature dependence of the zero-bias conductivity $\sigma(T)$ is calculated as follows: In the case of the conduction path in Fig. 4(b), thermally activated charge carriers occupy the large granule of charging energy $\langle E_c\rangle/n$ in the probability proportional to the Boltzmann factor $\exp[-\langle E_c\rangle/2nT]$ in units of $k_B = 1$. Since the large granules are separated by the smaller ones, the ordinary tunneling of an electron from the large granule to the small one increases the charging energy by $\delta E_c \sim \frac{1}{2}\langle E_c\rangle/(1 + 1/n)$, and thus is suppressed by the Coulomb blockade at low temperatures $T < \delta E_c$. In this regime, the dominant contribution to $\sigma(T)$ comes from higher-order processes of spin-dependent tunneling where the carrier is transferred from the charged large granule to the neighboring neutral large granule through the array of small granules, using the successive tunneling of single electrons, i.e., the cotunneling of $(n + 1)$ electrons. Figure 4(a) shows an example of the third order process ($n = 2$). Summing up all of these higher-order processes, we have

$$\sigma(T) \propto \sum_n e^{-\langle E_c\rangle/2nT}[(1 + P^2m^2)e^{-2\kappa s'}]^{n+1} \times \left(\frac{(\pi T)^2}{(\delta E_c)^2 + \gamma^2(T)}\right)^n f(n). \quad (1)$$

Here, $[\cdots]$ is the spin-dependent tunneling probability between the neighboring granules, $m = M/M_s$ the magnetization normalized to the saturation magnetization M_s, and $s' = 2n\langle s\rangle/(n + 1)$ with $\langle s\rangle$ being a mean separation of granules with size $\langle d\rangle$. The factor $(\cdots)^n$ represents the finite temperature effect that electrons (or holes) in the energy interval of πT around the Fermi level participate in the intermediate states of the higher-order process [22], and $\gamma(T)$ is the decay rate given by $\gamma(T) \approx gT$ with g being a constant [23]. The function $f(n)$ represents a distribution of the conduction paths. In Eq. (1), $\exp[4\tilde{\kappa}n\langle s\rangle - \langle E_c\rangle/2nT]$ is a peaked function of n and has its maximum at $n^* = (\langle E_c\rangle/8\tilde{\kappa}\langle s\rangle T)^{1/2}$, where $\tilde{\kappa}/\kappa \approx 1 + (1/4\kappa\langle s\rangle)\ln[(g/\pi)^2 + (\langle E_c\rangle/2\pi T)^2]$. At low temperatures ($T \ll \langle E_c\rangle$), n^* becomes large so that n is treated as a continuous variable. Replacing the summation by the integration in Eq. (1) and using the method of steepest descent [15], we obtain

$$\sigma(T) \propto (1 + P^2m^2)^{n^*+1}(n^*/\tilde{\kappa}\langle s\rangle)^{1/2}f(n^*) \times \exp[-2\sqrt{2\tilde{\kappa}\langle s\rangle\langle E_c\rangle/T}\,]. \quad (2)$$

In Fig. 1, the calculated resistivity for $m = 0$ is shown by the solid lines. Here and hereafter, we assume $f(n^*) \propto 1/n^*$ [24], and take $2\kappa\langle s\rangle = 3$, $g = 0.3$, and the values of $\langle E_c\rangle$ indicated in Fig. 1. Our model reproduces the T dependence of resistivity in Co-based granular films.

Because of the higher-order processes, the spin-dependent part of $\sigma(T)$ in Eq. (2) is amplified to the $(n^* + 1)$th power of $(1 + P^2m^2)$, so that $\sigma(T)$ is sensitive to the applied magnetic field since m varies from $m = 0$ to $m = 1$ (the fully magnetized state) by application of the magnetic field. Using Eq. (2) the MR, $\Delta\rho/\rho_0 = 1 - [\sigma(T)]_{m=0}/\sigma(T)$, is expressed as

$$\Delta\rho/\rho_0 = 1 - (1 + m^2P^2)^{-(n^*+1)}. \quad (3)$$

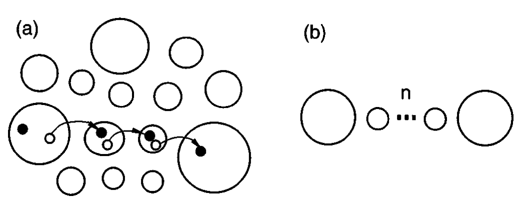

FIG. 4. (a) Schematic illustration of granular structure and a higher-order tunneling process where a charge carrier is transferred from the charged large granule (left), via the two small ones, to the neutral large one (right). (b) Model structure used for the calculation of conductivity.

The calculated MR is shown by the solid curves in Fig. 2, where the value of P is chosen to fit the experimental data. For small P^2, Eq. (3) is approximated to be

$$\Delta\rho/\rho_0 \approx P^2 m^2 (1 + \sqrt{C/T}), \tag{4}$$

where $C = \langle E_c \rangle / 8\tilde{\kappa}\langle s \rangle$, indicating an anomalous increase of $\Delta\rho/\rho_0$ at low temperatures due to the onset of higher-order processes between larger granules, i.e., $n^* \propto 1/\sqrt{T}$. At $T = 2$ K, n^* takes the value of 1.6, so that one or two small granules intervene between larger ones in the higher-order processes. As seen in curve a, the MR grows rapidly around 10 K well below $E_c = 110$ K. Similar behavior is seen in a double junction system [25].

We next calculate the bias-voltage dependence of conductivity $\sigma(V_b)$ at low temperatures. $\sigma(V_b)$ at $T = 0$ is obtained if the factor $(\pi T)^{2n}$ in Eq. (1) is replaced by $(e\Delta V_b)^{2n}/(2n)! \simeq (2eV_b/N_g)^{2n}$ [22], where $\Delta V_b = (2n/N_g)V_b$ is the voltage drop between the large granules and N_g the number of granules of size $\langle d \rangle$ along a conduction path between the electrodes. At finite temperatures, we use the interpolation formula $[(\pi T)^2 + (2eV_b/N_g)^2]^n$ for the factor. In addition, application of finite voltage reduces effectively the charging energy: $\langle E_c \rangle_{\text{eff}} = \langle E_c \rangle - e\Delta V_b/(n+1) \approx \langle E_c \rangle - eV_b/N_g$. Making use of these replacements, we obtain $\sigma(V_b)$. Since the number of granules along the conduction path is very large in the granular films ($N_g \sim$ several hundreds), the effective reduction of charging energy is small for a wide range of V_b, so we neglect it in the following.

In Fig. 3(a), we show the calculated resistivity by the solid curves for $T = 4.2$ K and $N_g = 140$. The steep decrease of the calculated resistivity is in good agreement with that of the experimental data. For $2\kappa s \gg 1$, $\rho(V_b)/\rho_0$ reduces to $[1 + (2eV_b/\pi N_g T)^2]^{-n_0^*}$, where $n_0^* = (\langle E_c \rangle / 8\kappa\langle s \rangle T)^{1/2}$. The V_b dependence of the MR is also given by Eq. (3), where $\tilde{\kappa}$ in n^* should read $\tilde{\kappa}/\kappa \approx 1 - (1/4\kappa\langle s \rangle)\ln[(4eV_b/N_g\langle E_c \rangle)^2 + (2\pi T/\langle E_c \rangle)^2]$ for $T \ll \langle E_c \rangle$. In Fig. 3(b), the calculated MR is shown by the solid curve. The enhanced MR is maintained upon application of higher voltages, which is consistent with the experimental result.

We discuss the origin of the striking difference in the T and V_b dependence of the MR. From Eq. (3) for small P^2, $\Delta\rho/\rho_0 \approx (1 + n^*)P^2$, implying that the MR is directly related to the order of tunneling process $(1 + n^*)$. As seen in the derivation of Eq. (2), the singular behavior $n^* \sim 1/\sqrt{T}$ is brought about by the Boltzmann factor that determines the carrier distribution on the granules. As temperature is lowered, the number of thermally activated carriers decreases exponentially and they occupy only large granules whose charging energy is smaller, so that the order of tunneling processes increases rapidly with decreasing temperature. On the other hand, V_b does not affect directly the distribution of carriers. In addition, the energy gain due to the voltage drop $\sim V_b/N_g$ between neighboring granules is still smaller than the charging energy. Therefore the granular films show almost no V_b dependence in the MR.

In conclusion, we have studied the magnetotransport phenomena in the Co-based insulating granular systems. The size distribution plays a crucial role for MR in the granular structures. The anomalous increase of the MR at low temperatures is due to the successive onset of higher-order processes of spin-dependent tunneling between large granules through intervening small ones with strong Coulomb blockade. The enhanced MR shows no appreciable change in the bias-voltage dependence despite the rapid decrease of resistivity with increasing voltage. The marked contrast between the temperature and bias-voltage dependence of the magnetotransport phenomena is consistently explained in terms of higher-order tunneling in the granular structures.

We are grateful to J. G. Ha for his cooperation and P. Grünberg for critically reading the manuscript. This work was supported by a grant from JSPS, Research for the Future and Priority Areas Grants from the Ministry of Education, Science and Culture of Japan.

[1] M. N. Baibich *et al.*, Phys. Rev. Lett. **61**, 2472 (1988).
[2] A. E. Berkowitz *et al.*, Phys. Rev. Lett. **68**, 3745 (1992); J. Q. Xiao *et al.*, Phys. Rev. Lett. **68**, 3749 (1992).
[3] H. Fujimori *et al.*, Mater. Sci. Eng. B **31**, 219 (1995); S. Mitani *et al.*, J. Appl. Phys. **83**, 6524 (1998).
[4] J. I. Gittleman *et al.*, Phys. Rev. B **5**, 3609 (1972).
[5] A. Milner *et al.*, Phys. Rev. Lett. **76**, 475 (1996).
[6] S. Barzilai *et al.*, Phys. Rev. B **23**, 1809 (1981).
[7] T. Furubayashi and I. Nakatani, J. Appl. Phys. **79**, 6258 (1996).
[8] S. Honda *et al.*, J. Magn. Magn. Mater. **165**, 153 (1997).
[9] H. Y. Hwang *et al.*, Phys. Rev. Lett. **77**, 2041 (1996).
[10] J. M. D. Coey *et al.*, Phys. Rev. Lett. **80**, 3815 (1998).
[11] K. Ono *et al.*, J. Phys. Soc. Jpn. **66**, 1261 (1997).
[12] L. F. Schelp *et al.*, Phys. Rev. B **56**, R5747 (1997).
[13] K. Inomata *et al.*, Jpn. J. Appl. Phys. **36**, 1380 (1997).
[14] M. Ohnuma *et al.*, J. Appl. Phys. **82**, 5646 (1997).
[15] B. Abeles *et al.*, Adv. Phys. **24**, 407 (1975).
[16] K. Yakushiji *et al.* (unpublished).
[17] P. M. Tedrow and R. Meservey, Phys. Rev. B **7**, 318 (1973); Phys. Rep. **238**, 173 (1994).
[18] J. Inoue and S. Maekawa, Phys. Rev. B **53**, R11 927 (1996).
[19] S. Zhang *et al.*, Phys. Rev. Lett. **79**, 3744 (1997).
[20] J. S. Moodera *et al.*, Phys. Rev. Lett. **80**, 2941 (1998).
[21] J. S. Helman and B. Abeles, Phys. Rev. Lett. **37**, 1429 (1976).
[22] D. V. Averin *et al.*, J. Appl. Phys. **73**, 1297 (1993).
[23] D. V. Averin *et al.*, Phys. Rev. Lett. **78**, 4821 (1997).
[24] The conductance between the large grains in Fig. 4(b) is proportional to $\Delta V_b (\propto n)$ and the density of the conduction path normal to the current direction ($\propto 1/n^2$), so that $f(n) \propto 1/n$.
[25] S. Takahashi and S. Maekawa, Phys. Rev. Lett. **80**, 1758 (1998).