# Magnetoresistance at Room Temperature of Oleic Acid Coated Fe$_{3-x}$Co$_x$O$_4$ ($x$ = 0, 0.1 and 0.3) Nanocrystal Drop-Cast Films

Koichiro Nara,[1] Daiki Namimatsu,[1] Masanori Mitome,[2] and Shigemi Kohiki[1,*]

1 Department of Materials Science, Kyushu Institute of Technology,
1-1 Sensui, Tobata, Kitakyushu, Fukuoka 804-8550, Japan
2 International Center for Materials Nanoarchitectonics, National Institute for Materials Science,
1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
* Corresponding author: Fax: 81-93-884-3310, and/or e-mail: kohiki@che.kyutech.ac.jp

Oleic acid coated Fe$_{3-x}$Co$_x$O$_4$ ($x$ = 0, 0.1 and 0.3) nanocrystal self-assembled films were fabricated via drop-casting of colloidal particles on a SiO$_2$/Si substrate. Nanocrystals of the Fe$_{3-x}$Co$_x$O$_4$ exhibited bifurcation of the zero-field-cooled and field-cooled magnetizations at 300 K. The Fe$_{3-x}$Co$_x$O$_4$ nanocrystal drop-cast films demonstrated nonlinear current-voltage characteristics between the source and drain electrodes in magnetic fields of zero and 0.2 T, and magnetoresistance reached into −46% for the $x$ = 0 film and −50% for both the $x$ = 0.1 and 0.3 films at 300 K. Oleic acid coated Fe$_{3-x}$Co$_x$O$_4$ ($x$ = 0.1 and 0.3) nanocrystal would boost developments of a high performance current switching device using negative magnetoresistance.

Key words: negative magnetoresistance, Fe$_{3-x}$Co$_x$O$_4$ nanocrystal, coercivity, oleic acid

## 1. INTRODUCTION

Oleic acid coated (OA-) cobalt-substituted magnetite (Fe$_{3-x}$Co$_x$O$_4$) nanocrystal (NC) drop-cast films are expected to display a large negative magnetoresistance (MR) at room temperature (RT). MR in NC arrays of the half-metal Fe$_3$O$_4$ and its analogs with high Curie temperatures and fully spin-polarized ($P$ = 1) charge carriers [1,2] is of great interest for development of spin-devices operating above RT [3,4]. Arrays of Fe$_{3-x}$Co$_x$O$_4$ NCs isolated by insulating OA thin layers display electron tunneling and Coulomb blockade at low temperatures, and electron hopping between the NCs at high temperatures [5,6]. In three-dimensional systems of OA-Fe$_{3-x}$Co$_x$O$_4$ NCs, MR is connected to $P$ and the relative magnetization of the system ($m$) by MR $\equiv$ $P^2m^2/(1 + P^2m^2)$ [5]. Here, $m$ relates to the angle ($\theta$) between the magnetic moment of adjacent NCs as $m^2 = \langle\cos\theta\rangle$. MR is also defined experimentally as MR = ($R_H − R_0$)/$R_0$, where $R_H$ and $R_0$ are the differential resistance ($R$ = d$V$/d$I$) for nonlinear current and voltage $I(V)$ characteristics in non-zero and zero magnetic fields ($H$), respectively. When the tunneling resistivity is varied from high to low by $H \neq 0$ which is strong enough to change the configuration of the magnetic moments in the system to be in parallel ($\theta = 0$), the sign of MR becomes negative. Both $m$ = 1 and $P$ = 1 conditions give rise to MR = −50%. However, thermal energy at RT enlarges $\theta$, and lessens $m$ for the system. The large MR brings about very high performance for the spin-devices [3,4].

Cobalt is known as an anisotropic moment carrier. Fe$_{3-x}$Co$_x$O$_4$, where Co$^{II}$ replaces Fe$^{II}$ in the Fe$_3$O$_4$ crystal lattice as shown in Fig. 1, exhibited a large magnetocrystalline anisotropy energy constant ($K$) [7]. A large magnetic coercivity ($H_c$) was reported for self-assembled Fe$_{3-x}$Co$_x$O$_4$ NC arrays [8], which

enhances the magnetic coupling between adjacent NCs, and prevents enlargement of $\theta$ with increasing temperature. To date, there are some reports on magnetism of Fe$_{3-x}$Co$_x$O$_4$ NCs [8,9]. There have been no studies of MR for Fe$_{3-x}$Co$_x$O$_4$ NCs, as we know.

Oleic acid CH$_3$(CH$_2$)$_7$CH=CH(CH$_2$)$_7$COOH is an unsaturated carboxylic acid with a *cis*-double-bond kink in the middle of its C$_{18}$ tail. The polar head group chemisorbs to the hydrophilic surface of the NC, and steric repulsion of the long chain prevents the NCs from agglomerating.

As a foundation of such a device, MR of OA-Fe$_{3-x}$Co$_x$O$_4$ ($x$ = 0, 0.1 and 0.3) NC self-assembled films fabricated via drop-casting of colloidal particles were examined. The NCs, synthesized by refluxing Iron(III) acetylacetonate Fe(acac)$_3$ and Cobalt(II) acetylacetonate Co(acac)$_2$ in a solution of dibenzylether mixed with OA, demonstrated $H_c$ of 380 Oe for $x$ = 0.1 and 740 Oe for $x$ = 0.3 at 300 K. The spontaneous self-assembly phenomenon is commonly used to control the arrangement of the NCs into hexagonally ordered arrays [10,11]. Slow drying of a hexane colloidal suspension dropped onto a substrate results in a film with hexagonal networks of self-assembled NCs [3]. Geometrically frustrated networks of collinear magnetic moments cause a spin-glass (SG) transition for two-dimensional (2D) ordered NC arrays. The OA-Fe$_{3-x}$Co$_x$O$_4$ NC drop-cast films exhibited bifurcation of the zero-field-cooled (ZFC) and field-cooled (FC) magnetizations at 300 K. The nonlinear current-voltage $I(V)$ characteristics between the source and drain electrodes observed in both $H$ = 0 and 0.2 T resulted in MR = −50%. The $m$ = 1 and $P$ = 1 conditions were accomplished in the OA-Fe$_{3-x}$Co$_x$O$_4$ ($x$ = 0.1 and 0.3) NC drop-cast films even at 300 K. So, Fe$_{3-x}$Co$_x$O$_4$ is

promising for high performance spin-polarized current switching device applications.
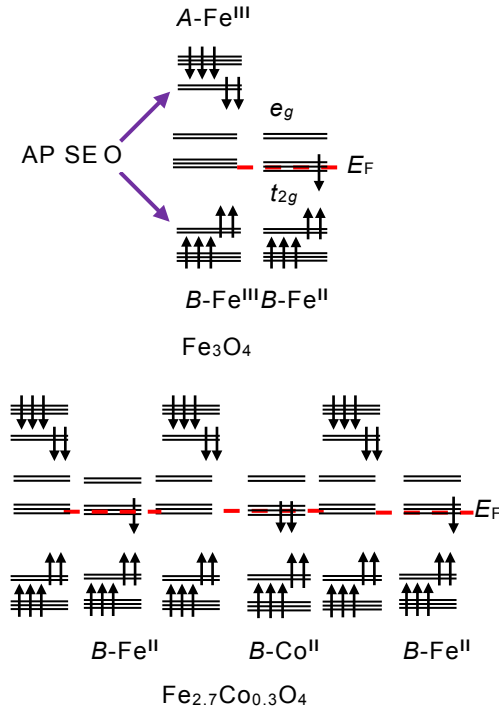


Fig. 1 Upper illustration: The magnetic moments of $Fe^{III}$ at the *A*- and *B*-sites are antiparallel (AP), and compensate for each other due to an antiferromagnetic superexchange (SE) interaction mediated by the apical oxygen (O) ion. The $Fe^{III}$ and $Fe^{II}$ $3d$ states with $t_{2g}$ and $e_g$ symmetry are separated by crystal-field splitting due to the octahedral coordination field of the *B*-site. The $t_{2g}$ spin-down electron hops between the $Fe^{III}$ and $Fe^{II}$ at the *B*-site. Lower illustration: In the $Fe_{2.7}Co_{0.3}O_4$ crystal, $Co^{II}$ is substituted for a third of the *B*-site $Fe^{II}$ ions. Two spin-down $t_{2g}$ electrons are supplied from the *B*-site $Co^{II}$. The sketch is for the ideal case of $Fe_{2.7}Co_{0.3}O_4$. Generally, Co can occupy also the A-site to some extent.



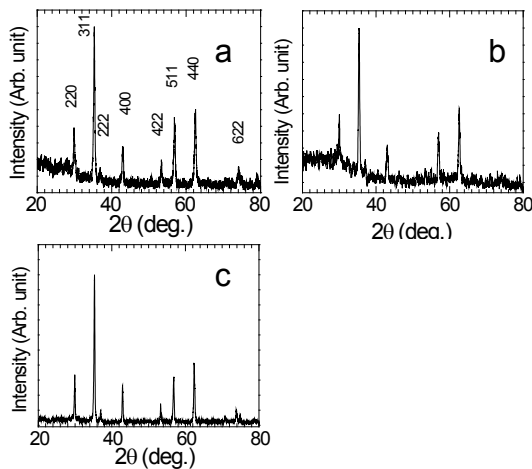Fig. 2 XRD patterns of $Fe_{3-x}Co_xO_4$ NCs with $x = 0$ (a), 0.1 (b) and 0.3 (c).

## 2. EXPERIMENTAL

### 2.1 Synthesis of $Fe_{3-x}Co_xO_4$ NCs and Fabrication of the NC Drop-cast Films.

$Fe_{3-x}Co_xO_4$ NCs were synthesized by refluxing mixed solutions of $Fe(acac)_3$, $Co(acac)_2$, dibenzylether, and OA at 573 K for half an hour. The solution of $Fe(acac)_3$ : dibenzylether : OA = 6 : 157 : 12 was used for the $x = 0$ NC synthesis. For syntheses of the $x = 0.1$ and 0.3 NCs, solutions of $Fe(acac)_3$ : $Co(acac)_2$ : dibenzylether : OA = 29 : 1 : 900 : 60 and 5 : 1 : 157 : 12 were used, respectively [12]. After cooling to RT, NCs were precipitated from the crude solution by adding a mixture of toluene : hexane = 1 : 1 followed by centrifugation. The precipitated NCs were washed with anhydrous chloroform, then the NCs were dispersed in a weak alkaline (pH = 10.4) aqueous solution. After stirring for 10 minutes, additional OA (molar ratio of [Fe + Co] : [OA] = 1 : 42) was added to the solution with vigorous stirring. After stirring for 20 minutes, 1N HCl aqueous solution was added to neutralize the solution. After removal of the transparent solvent, the precipitated NCs were dispersed in hexane. As-synthesized NCs were used without post-preparative size selection for fabrication of drop-cast films. The colloidal suspensions in hexane were dropped onto a $SiO_2/Si$ substrate, and then dried at 573 K for half an hour at 100 Pa to yield OA-$Fe_{3-x}Co_xO_4$ NC self-assembled film.

### 2.2 Structural, Magnetic and Magnetoelectric Characterization.

In energy dispersive X-ray analysis, the NCs from the solutions of $Fe(acac)_3$ : $Co(acac)_2$ = 29 : 1 and 5 : 1 demonstrated atomic ratios of Fe : Co = 28 : 1 and 9 : 1, respectively. So, the composition of the $Fe_{3-x}Co_xO_4$ NCs can be denoted as $x = 0.1$ and 0.3. A Rigaku CN2013 diffractometer with Cu $K\alpha$ radiation was used for X-ray diffraction (XRD) of $Fe_{3-x}Co_xO_4$ ($x = 0$, 0.1 and 0.3) NCs. Magnetic characterization was carried out using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS-5S). For the temperature dependent DC magnetization $M(T)$ measurements, the sample was cooled from RT to 5 K in $H = 0$, and then $H = 0.01$ T was applied. The zero-field-cooled (ZFC) magnetization was recorded with rising temperature to 300 K. After the ZFC measurement, the sample was again cooled to 5 K in $H = 0.01$ or 0.03 T, and then the field-cooled (FC) magnetization was recorded with rising temperature to 300 K. For magnetoelectric measurements, Cu microprobes with a space of 0.3 mm apart were point contacted to the NC film surface, and wired to a Keithley Instruments Inc. Model 6487 Picoammeter/Voltage source. In $I(V)$ measurements, the $H = 0$ character was measured first, followed by that in $H = 0.2$ T applied perpendicularly to the NC film surface.

## 3. RESULTS AND DISCUSSION

As shown in Fig. 2, the $x = 0$, 0.1 and 0.3 NCs demonstrated XRD patterns attributable to the inverse spinel type cubic lattice with space group $F$d$-3m$, such as $Fe_3O_4$ (JCPDS 19-0629) and $Fe_{2.5}Co_{0.5}O_4$ (ICDD 04-006-3507). The lattice parameter $a$ was estimated to 0.84 nm for all the NCs, and the crystallite size was

estimated to 50, 38 and 36 nm for the $x = 0$, 0.1 and 0.3 NCs, respectively.

As shown in Fig. 3a, the $x = 0.1$ and 0.3 NCs demonstrated ferromagnetic hysteresis loops at 300 K with $H_c$ = 380 and 740 Oe, respectively. However, the $x = 0$ NCs, synthesized under the same conditions except for a lack of $Co(acac)_2$ exhibited a sigmoidal curve with $H_c$ = 70 Oe. An increase in $H_c$ with increasing $x$ is what expected for the chemical substitution. $M$ at 0.2 T reached 90% of that at 1 T, and $M$ almost saturated above 0.4 T. $M$ at 1 T of the NCs decreased gradually with increasing $x$ from 81 emu/g ($x = 0$) to 79 emu/g ($x = 0.1$) and to 70 emu/g ($x = 0.3$). $K$ derived from the equation $K = H_c M_{1T}/2$ are shown in Fig. 3b. $K$ for the $x = 0$, 0.1 and 0.3 NCs were 0.06 × $10^4$ J/m³, 0.7 × $10^4$ J/m³ and 1.4 × $10^4$ J/m³, respectively. The anisotropy energy barrier ($KV$), limiting free rotation of the magnetic moments away from the easy axis, of the $x = 0$, 0.1 and 0.3 NCs amounted to 0.078, 1.26 and 2.14 eV, respectively, where the volume $V$ was derived from the crystallite size. For the $x = 0.1$ and 0.3 NCs, the $KV$ values are much larger than the thermal energy at 300 K (0.026 eV), then the magnetic moment of individual NC cannot reverse direction rapidly as a result of the thermal energy. An enlarged magnetization reversal energy would bring about an enhanced magnetic coupling between adjacent NCs. Consequently the $x = 0.1$ and 0.3 NCs are expected to exhibit a large MR at RT.

$M(T)$ curves shown in Fig. 4 demonstrated bifurcation of FC and ZFC magnetizations for the $x = 0$, 0.1 and 0.3 NCs below 300 K. FC magnetization is larger than ZFC one at every temperature. Splitting between FC and ZFC $M(T)$ is the most apparent for the $x = 0.3$ NCs. FC magnetization remained at almost constant below 300 K, whereas ZFC magnetization decreased almost linearly with decreasing temperature. Such a cooling history-dependence of the DC magnetization is indicative of the slow dynamics common in self-assembled ferromagnetic NCs [13,14]. A high bifurcation temperature (≥300 K) indicates strongly competing magnetic dipolar interactions among the NCs. Spin-polarized current flowing in self-assembled OA-$Fe_{3-x}Co_xO_4$ NC arrays is affected by dipolar interactions in percolating current paths. The ferromagnetic moments of the NCs in the film are still probably, randomly, and yet cooperatively switching in $H = 0$, and then the $R_0$ value becomes larger. Since the $R_H$ value diminishes largely in the $H \neq 0$ which can rotate the magnetic moments to mutual alignment ($m = 1$), a large MR even at RT is expected for the OA-$Fe_{3-x}Co_xO_4$ NC drop-cast films.

Electron transport via OA-$Fe_{3-x}Co_xO_4$ NCs requires the charging energy $E_C = \{e^2/8\pi\varepsilon_0\varepsilon_r\}\{[1/r] - [1/(r + s)]\}$,
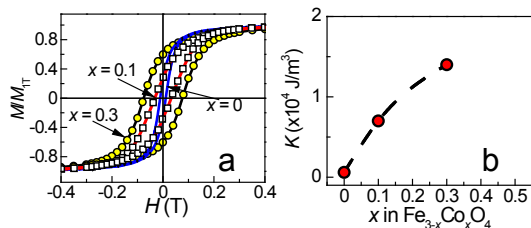


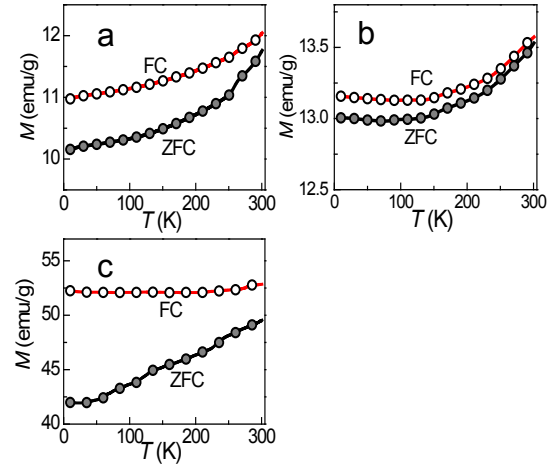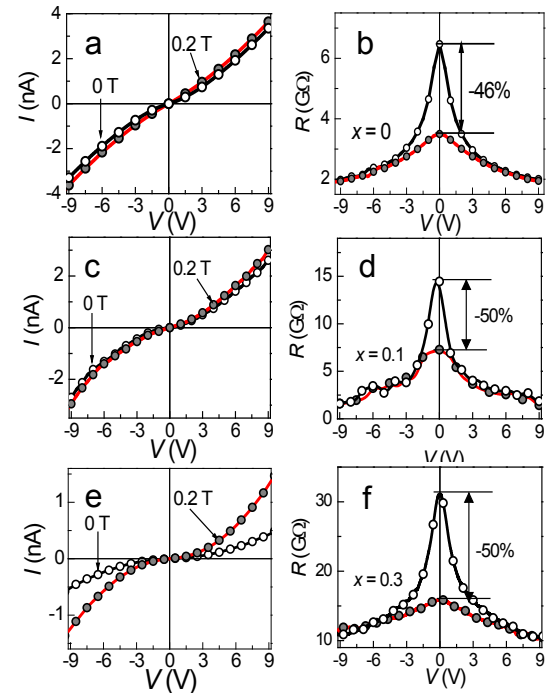Fig. 4 FC and ZFC $M(T)$ of $Fe_{3-x}Co_xO_4$ NCs with $x = 0$ (a) in 0.03 T, 0.1 (b) and 0.3 (c) in 0.01 T.



Fig. 5 $I(V)$ and $R(V)$ in 0 T (open symbols) and 0.2 T (closed symbols) of OA-$Fe_{3-x}Co_xO_4$ NC drop-cast films with $x = 0$ (a and b), 0.1 (c and d) and 0.3 (e and f).

where $e$, $\varepsilon_0$ and $r$ are the elementary charge, the vacuum permittivity and radius of the crystallite, respectively [15]. Assuming an inter-NC space $s$ of 4 nm and the relative permittivity $\varepsilon_r = 2$ for OA, $E_C$ amounts to 1.5, 3.3 and 3.6 meV for the $x = 0$, 0.1 and 0.3 NCs, respectively. Because the thermal energy of electrons at 300 K is larger than $E_C$, conduction paths of spin-polarized electrons by hopping via the NCs are still opened even at $V \sim 0$ V. While the Coulomb blockade threshold becomes zero ($V_T = 0$ V), the OA-$Fe_{3-x}Co_xO_4$ ($x = 0$, 0.1 and 0.3) NC drop-cast films were highly resistive at 300K. The NC films demonstrated the



Fig. 3 $M(H)$ normalized at 1 T (a) and $K$ *vs*. $x$ (b) of $Fe_{3-x}Co_xO_4$ ($x = 0$, 0.1 and 0.3) NCs.

nonlinear $I(V)$ characteristics shown in Figs. 5a, c and e. However, $R$ (= d$V$/d$I$) in 0 T and 0.2 T were high and low, respectively, as shown in Figs. 5b, d and f. The $R(V)$ curves peaked around $V = 0$ V and fell off rapidly with increasing $V$. $R$ around 0 V in $H = 0$ T and 0.2 T resulted in negative MR of $-46\%$ for the $x = 0$ NC film, and $-50\%$ for both the $x = 0.1$ and 0.3 NC films. An increase in the temperature should lessen the degree of spin-polarization near $E_F$, although a large MR is still retained at 300 K. Assuming $m = 1$ in $H = 0.2$ T, the MR $= -46\%$ and $-50\%$ corresponds to $P = 0.92$ and 1 even at 300 K, respectively.

The dimensionality of the spin-polarized current flow can be examined via power-law scaling with the equation $I \sim (V - V_T)^{\xi}$ [15,16]. As shown in Fig. 6a, $I(V)$ for the $x = 0$ NC film in 0 T and 0.2 T were fitted well with the critical exponent $\xi = 1.4$ and 1.2, respectively. The $\xi$ values for the $x = 0.1$ NC film in 0 T and 0.2 T were 1.48 and 1.555, respectively, as shown in Fig. 6b. As shown in Fig. 6c, the $\xi$ values for the $x = 0.3$ NC film in 0 T and 0.2 T were 1.85 and 2.00, respectively. The power law is related to the progressive opening of conduction channels. The critical exponents $\xi$ for 1D and 2D NC arrays have been analytically determined to be 1 and 5/3, respectively [16]. In the $x = 0.3$ NC film, spin-polarized current flows through nearly 2D percolated paths among the NCs. The dimensionality of the spin-polarized current flow increased with increasing $x$. For the NC films with MR $= -50\%$, application of $H = 0.2$ T enlarged dimensions of current flowing through percolated paths by hopping of the spin-polarized electrons. The present MR $= -50\%$ at 300 K in $H = 0.2$ T around $V \approx 0$ V is due to spin-dependent electron hopping among magnetically coupled Fe$_{3-x}$Co$_x$O$_4$ NCs isolated and self-assembled by OA.

## 4. CONCLUSION

Drop-casting method was employed to build ordered arrays of OA-Fe$_{3-x}$Co$_x$O$_4$ NCs using the spontaneous self-assembly phenomenon of colloidal particles. The Fe$_{3-x}$Co$_x$O$_4$ NCs, Co$^{II}$ substituted partially for the Fe$^{II}$ site in Fe$_3$O$_4$, exhibited an increase in $H_c$ from 70 to 740 Oe with increasing $x$ from 0 to 0.3. From the enlarged magnetization reversal energy for the $x = 0.3$ NCs, a large MR even at RT was expected for OA-Fe$_{3-x}$Co$_x$O$_4$ ($x = 0.3$) NC drop-cast film since an enhanced magnetic coupling between adjacent NCs leads larger spin-polarized current flow via NCs. MR $= -50\%$ at 300 K in $H = 0.2$ T observed for the $x = 0.3$ NC film is based on the progressive opening of 2D percolated spin-polarized electron hopping paths. MR $= -50\%$ was also observed for the $x = 0.1$ NC film at 300 K in $H = 0.2$ T. However, higher dimension of current flowing paths is advantageous for practical switching devices operable above RT. Therefore, Fe$_{3-x}$Co$_x$O$_4$ ($x = 0.3$) NCs are promising for a high performance current switching device using magnetoresistance.
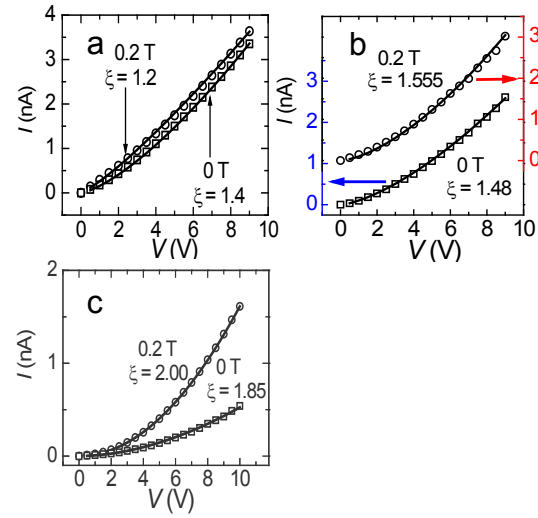
Fig. 6 Fitting of the $I(V)$ curves in 0 T and 0.2 T to estimate the $\xi$ values under $V_T = 0$ V for OA-Fe$_{3-x}$Co$_x$O$_4$ NC drop-cast films with $x = 0$ (a), 0.1 (b) and 0.3 (c).

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