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Boltzmann distribution of bond orientations and perpendicular anisotropy in amorphous rare-earth–transition-metal films

Hong Fu and M. Mansuripur
Optical Sciences Center, University of Arizona, Tucson, Arizona 85721

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We show that the Boltzmann distribution of bond orientations induced by a perpendicularly magnetized layer in the growth process of an amorphous rare-earth–transition-metal film always leads to the bulk perpendicular magnetic anisotropy, irrespective of the specific functional form of the bond energy. The initial perpendicularly magnetized layer can arise from the surface anisotropy produced by antiparallel dipoles or even from spontaneous magnetization.

I. INTRODUCTION

The uniaxial anisotropy with the easy magnetization direction perpendicular to the film plane ($K_u > 0$) is a common characteristic for most amorphous rare-earth–transition-metal (RE-TM) thin films. However, since Chaudhuri, Cuomo and Gambino discovered $K_u > 0$ in sputtered amorphous Gd-Co and Gd-Fe films in 1973,[1] the origin of K_u in amorphous RE-TM thin films has remained unexplained. It is generally recognized that $K_u > 0$ originates mainly from atomic-scale structures. Among the various proposed structural models are the pair ordering model,[2] the single-ion model,[3,4] and the bond orientational anisotropy.[5,6] The problem associated with these models is twofold. First, especially for the pair ordering model and the single-ion model, the mechanism that causes an amorphous material to have the preferential directional structures or charge distributions similar to its crystal counterparts is unknown. Second, especially for pair ordering model and the bond orientational anisotropy, the assumed structure does not necessarily give the desired anisotropy. These problems are serious as one notices that so many different RE-TM amorphous films exhibit perpendicular anisotropy,[7] and that even in atomically well-ordered materials such as the hexagonal compounds YCo_5 and Y_2Co_{17} it is not well understood why the former has $K_u > 0$ (easy magnetization along the *c* axis) while the latter has $K_y < 0$ (easy magnetization in the basal plane).[8] It is hopeless to try to answer these questions at present from a quantum mechanical point of view because of the extremely complicated 3*d*-electron behavior of the transition metals involved.

In a previous publication we showed that the magnetic dipolar interaction of antiparallel dipoles in the surface layers give a generic contribution to $K_u > 0$ for amorphous RE-TM films.[9] One consequence of this surface effect is that the first few layers of the film in the growth process may experience a net perpendicular anisotropy, i.e., $K_u - 2\pi M_s^2 > 0$, where M_s is the saturation magnetization and $-2\pi M_s^2$ is the shape anisotropy energy density, and may therefore be perpendicularly magnetized. For example, for the first three layers of an amorphous Gd-Co film, which is about 10 Å thick, the surface effect can cause $K_u - 2\pi M_s^2 \simeq 10^5 - 10^6 \text{ erg cm}^{-3}$ and make these layers perpendicularly magnetized. This magnitude of K_u is also valid for Tb-Fe, since Tb-Fe and Gd-Co have comparable magnetic dipole moments. However, this anisotropy will decrease with increasing film thickness and hence it alone is insufficient to explain the observed K_u in most situations, which typically range from 10^5 erg cm^{-3} for Gd-Co films to over 10^6 erg cm^{-3} for Tb-Fe films.

In this paper we show that the Boltzmann distribution of bond orientations, which is induced by an initial perpendicularly magnetized layer and will be built in the growth process of an amorphous RE-TM film, always leads to bulk perpendicular magnetic anisotropy, irrespective of the concrete form of the bond energy. Therefore, without going into the very complicated behavior of 3*d* electrons, we are able to explain why amorphous RE-TM thin films tend to have perpendicular anisotropy. The first perpendicularly magnetized layer serves as a seed for the anisotropic bond orientations. It can be generated by the surface anisotropy produced by antiparallel dipole pairs[9] or by the spontaneous magnetization as will be discussed in Sec. V.

Our work is based on the so-called pair model, i.e., we consider the energy of the total system to be the sum of a series of terms each related to a pair of nearest-neighbor atoms. The pair model was developed by Van Vleck in 1937 (Ref. 10) to explain the anisotropy of cubic ferromagnetic crystals.[10] It was further developed by Néel in 1954 to investigate the surface anisotropy of ferromagnetic crystals and anisotropic bond orientations in ferromagnetic solid solutions.[11] In that classic paper Néel studied the Boltzmann distribution of bond orientations (he called it orientational superlattice) caused by spontaneous magnetization in solid solutions and pointed out that the magnetic easy axis due to such a bond orientational structure is along the direction of the spontaneous magnetization. The purpose of the present paper is to discuss the formation of the Boltzmann distribution of bond orientiations in amorphous RE-TM films and the character of the resultant anisotropy.

The paper is organized as follows. In Sec. II we discuss the mechanisms responsible for bond energy and the corresponding bond energy strength. A concrete and very simplified model for the bond energy is described in Sec. III. The main part of the paper is Sec. IV, where we describe how the Boltzmann distribution of bond orientations emerges in the deposition process and prove the properties of the resultant perpendicular anisotropy. Conclusions and some discussions are presented in Sec. V. There we point out that a perpendicularly magnetized layer can also come about from spontaneous magnetization.

II. THE BOND ENERGY

In this paper bond means the vector joining the centers of two adjacent atoms and bond energy means the pair energy of the two atoms. The spin-dependent bond energy is called magnetic bond energy. It depends generally on the relative orientations of the bond and the spins of the two atoms.

In amorphous RE-TM films the strongest magnetic interaction between neighbor atoms is the exchange interaction. In most cases the exchange integrals are positive for RE-RE and TM-TM pairs and negative for RE-TM pairs. The typical values are $J_{\text{RE-RE}} \simeq 10^{-16}$, $J_{\text{TM-TM}} \simeq 10^{-14}$ and $J_{\text{RE-TM}} \simeq -10^{-15}$egr.[12] This leads to a parallel alignment of the like spins and an antiparallel alignment of the unlike spins. Consequently, the spin vectors are either parallel or antiparallel to the net magnetization, forming ferromagnetic subnetworks.

The energy of a bond in the ferromagnetic subnetworks depends on the magnetization direction $\mathbf{e}_m$ and the bond orientation $\mathbf{e}_b$. In the spherical coordinate system defined in Fig. 1, where $\mathbf{e}_x$ and $\mathbf{e}_y$ are in-plane unit vectors and $\mathbf{e}_z$ is the unit vector along the film's normal direction, they can be specified by

$$\mathbf{e}_m = \sin\theta_m \mathbf{e}_x + \cos\theta_m \mathbf{e}_z \ , \tag{1}$$

and

$$\mathbf{e}_b = \sin\theta_b \cos\phi_b \mathbf{e}_x + \sin\theta_b \sin\phi_b \mathbf{e}_y + \cos\theta_b \mathbf{e}_z \ . \tag{2}$$

In Eq. (1) we have assumed $\phi_m = 0$, which is adequate in the case that the distribution of bond orientations is symmetric in the azimuthal directions. The angle between $\mathbf{e}_m$ and the bond orientation $\mathbf{e}_b$, which is defined as θ_{m-b}, satisfies the relation

$$\cos\theta_{m-b} = \mathbf{e}_m \cdot \mathbf{e}_b = \sin\theta_m \sin\theta_b \cos\phi_0 + \cos\theta_m \cos\theta_b \ . \tag{3}$$

The bond energy E has the following transformation properties. First, it should be invariant under a rigid rotation of the two spins about the bond orientation. This implies that E only depends on $\mathbf{e}_m \cdot \mathbf{e}_b = \cos\theta_{m-b}$. Second, it should be invariant by permutation of the two spins, which corresponds to the transformation $\mathbf{e}_b \rightarrow -\mathbf{e}_b$. This requires the bond energy to be a function of $(\mathbf{e}_m \cdot \mathbf{e}_b)^2 = \cos^2\theta_{m-b}$. Therefore, for each type of bond (between RE and RE, between RE and TM, or between TM and TM) the bond energy can be expanded in the Legendre polynomials of even orders:

$$E(\cos\theta_{m-b}) = g_1(\cos^2\theta_{m-b} - \tfrac{1}{3}) + g_2(\cos^4\theta_{m-b} - \tfrac{6}{7}\cos^2\theta_{m-b} + \tfrac{3}{35}) + \cdots \ . \tag{4}$$

In Eq. (4) we have neglected a θ_{m-b} independent term g_0. This term includes the chemical binding energy between the two atoms, which can be as large as 10^{-11} erg (several eV) (Ref. 13) and is by far the largest one among all g_i. However, in the pair-model approximation, the binding energy is a constant for given length of bond and does not depend on the spin orientation. Therefore, it has no effect on the magnetic structure and anisotropy. The exchange energy is also part of g_0. The exchange interaction causes the alignment or antialignment of two dipoles, but the exchange energy does not depend on θ_{m-b}, indicating that it does not cause directly the anisotropy. Equation (4) contains only spin-dependent (magnetic) bond energy as contributed by g_i with $i \geq 1$. Since a constant term in Eq. (4) has no effect on anisotropy, the strength of the bond energy $E(\cos\theta_{m-b})$ is measured by the oscillation amplitude $(\Delta E)_{\max}$ defined by

$$(\Delta E)_{\max} = \max_{\theta_{m-b} \in (0,\pi)} E(\cos\theta_{b-m}) - \min_{\theta_{m-b} \in (0,\pi)} E(\cos\theta_{b-m}) \ .$$

The various terms in Eq. (4) are described in Refs. 10, 11, and 14. The first and the second terms are called dipolar and quadrupolar terms. A possible but usually minor source of g_1 is the magnetic dipolar interaction. For Gd-Co, using the zero-temperature dipole moments $m_{\text{Gd}} = 7\mu_B$, $m_{\text{Co}} = 1.7\mu_B$,[12] where $\mu_B = 9.27 \times 10^{-21}$ emu is the Bohr magneton, and using the bond lengths $d_{\text{Gd-Gd}} = 3.64$ Å, $d_{\text{Gd-Co}} = 3.07$ Å, and $d_{\text{Co-Co}} = 2.5$ Å,[15] the pure magnetic dipolar interaction leads to $g_1 = 2.6 \times 10^{-16}$, 1.1×10^{-16}, and 0.48×10^{-16} erg for Gd—Gd, Gd—Co and Co—Co bonds, respectively. Similar values can be found for Tb—Tb, Tb—Fe, and Fe—Fe bonds. It is well known that the magnetic dipolar interactions are too weak to cause the observed anisotropies in most situations.[10,11,14]

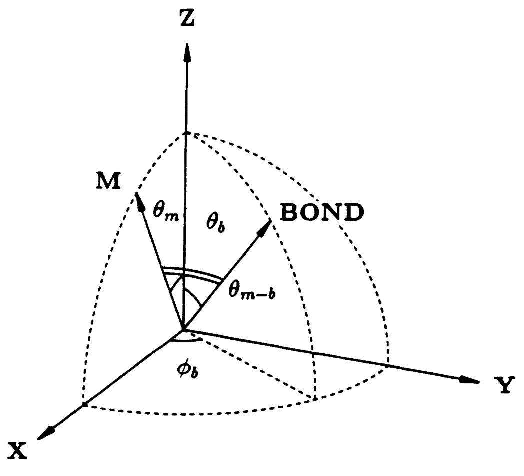

FIG. 1. Definitions of the angles θ_m, (θ_b, ϕ_b), and θ_{m-b} denoting the magnetization direction, bond orientation and their relation. The x-y plane is the film plane.

The main source of the g_i factors ($i \geq 1$) is the combined effect of the exchange interaction, the spin-orbit interaction, and the Coulomb interaction between two atoms, provided both atoms have unquenched orbital angular momenta.[10,11,14] That is, a part of the orbit of each atom will follow the orientation of the magnetic spin due to the spin-orbit coupling. This alters their overlapping status and leads to a change in the Coulomb interaction energy.

In Gd-Co amorphous films, wince Gd has zero orbital angular momentum (the distribution of the $4f$ electrons has spherical symmetry), only Co—Co bonds have unquenched orbital moments. Experimentally, it is found that in Gd-Co and Gd-Fe amorphous films the anisotropy is mainly contributed by Co—Co or Fe—Fe pairs.[16] The magnitude of anisotropy in Gd-Co and Gd-Fe films is on the order of 10^5 erg cm^{-3}. From the anisotropies of Co and Fe single crystals, it is found that g_1 for both Co—Co and Fe—Fe bonds is on the order of 10^{-15} erg,[10,11,14] which is larger than the magnetic dipolar energy of a Gd—Co pair; see the discussions below Eq. (5). In Sec. IV we shall show that, if there is Boltzmann distribution of bond orientations, this amount of g_i of Co—Co pairs is sufficient to produce $K_u \simeq 10^5$ erg cm^{-3}.

For Tb-Fe amorphous films, the main contribution to anisotropy comes from Tb—Fe bonds. There are two reasons that Tb—Tb bonds do not make the main contribution. First, the exchange energy between Tb atoms, which tends to make a parallel arrangement of two Tb spins, is only 2×10^{-16} egr,[12] while the Coulomb energy between the $4f$ orbital electrons, which tends to break the parallel arrangement, is on the order of 7×10^{-14} erg, which is several hundred times the exchange energy (see the end of Sec. III). Therefore, the exchange interaction is too weak to bring the two Tb spins parallel. The orientations of the Tb spins are thus mainly determined by the Coulomb interaction, but hardly affected by the magnetization direction. Consequently, the contribution of Tb—Tb bonds to the anisotropy is small. Second, due to the negative heat of mixing, dissimilar atoms tend to join together.[8] In amorphous Tb-Fe films, where the Tb atomic concentrations is usually low ($<40\%$), this effect could reduce the probability of forming Tb—Tb bonds. A recent EXAFS (extended x-ray-absorption fine structure) study of amorphous $Tb_{20}Fe_{80}$ showed that there is no evidence of Tb—Tb bond.[17] The Fe—Fe bond energy is smaller than the Tb—Fe bond energy, because a Tb atom has a more localized and a more asymmetric charge distribution than an Fe atom. In the next section we propose a simple model to illustrate how the bond energy is contributed by the combined effect of the exchange interaction, the spin-orbit coupling and the Coulomb interaction. Based on this model and the data for Tb and Fe, we find that the Tb—Fe bond energy is mainly (99%) contributed by the quadrupolar term with $g_2 \simeq 6.13\times10^{-15}$ erg. Since this is a simplified model, we will not restrict ourselves to this particular form of bond energy. Rather, we consider it as an estimate of the Tb—Fe bond energy strength, which in this case can be shown to be $(\Delta E)_{\max} = 16g_2/49 \simeq 2\times10^{10^{-15}}$ erg, almost equal to the exchange energy. In Sec. IV we shall show that, this amount of $(\Delta E)_{\max}$, whether it is contributed by g_1 or g_2, or by both of them, will produce a K_u over 10^6 erg cm^{-3}.

III. A SIMPLIFIED MODEL FOR BOND ENERGY

Now we consider a simplified model to see how the combined effect of the exchange interaction, the spin-orbit coupling and the Coulomb interaction contributes to the energy. In this model the orbital electrons of an atom are assumed to move in a ring. Due to the spin-orbit interaction, the spin of the electron is perpendicular to the ring plane. For a pair of neighboring atoms, the exchange interaction brings the two spins parallel or antiparallel, which, in either case, causes the planes of the two rings to be parallel. Figure 2(a) shows the geometry

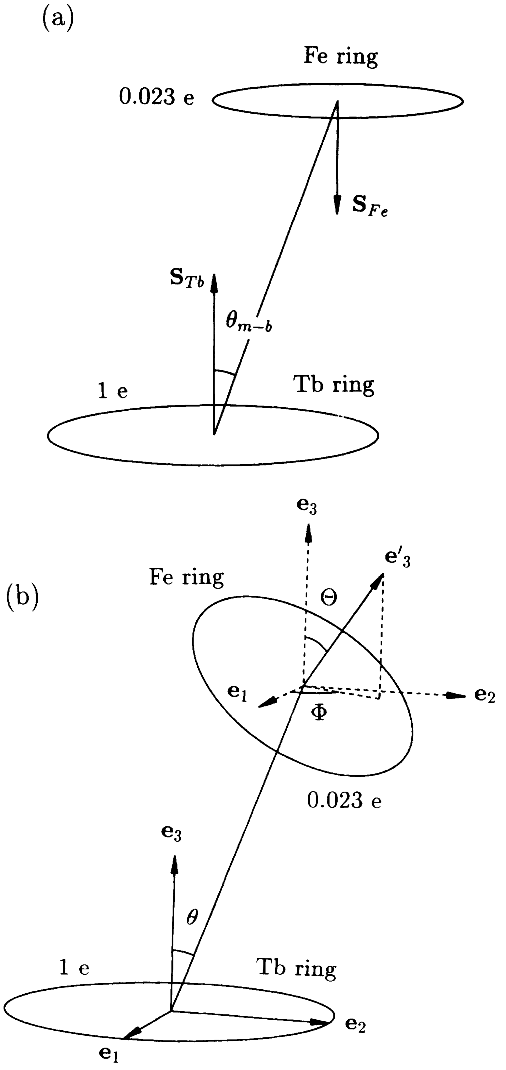

FIG. 2. Geometry of the two-ring system. (a) The two rings are parallel due to the exchange and the spin-orbit couplings. The bond energy is equal to the Coulomb interaction between the two rings and depends on θ_{m-b}. (b) If the two rings were decoupled, they could have different orientations and the Coulomb energy depends on θ and (Θ,Φ).

of this model for a Tb—Fe bond (the numbers there will be discussed later in this section). When the two parallel coupled rings change direction relative to the bond orientation, the Coulomb interaction energy between the two charged rings changes, leading to a bond energy of the form of Eq. (4). Based on this model we show that only a small fraction (2.3%) of an unquenched 3*d* orbital electron of an Fe atom is used to produce the Tb—Fe bond energy. The corresponding bond energy strength is $(\Delta E)_{\max} \simeq 2\times 10^{-15}$ erg.

Let us consider a Tb—Fe bond. A free Tb atom has eight 4*f* electrons. According to Hund's rules,[15] seven of the 4*f* electrons form a filled shell. Since a filled shell has a spherically symmetric charge distribution, it does not contribute to the bond energy. The bond energy is contributed by the remaining 4*f* electron. The picture should hold in amorphous Tb—Fe films, since the 4*f* electron is well shielded by the 4*s* shell and will not be affected by neighbor atoms. The behavior of the 3*d* electrons of Fe atoms is somewhat more complicated. Most orbital angular momentum of Fe is quenched and only a small fraction of the 3*d* electrons may contribute to angular momentum and hence to the bond energy.

For simplicity, we assume that the 4*f* electron of Tb is distributed in a ring of radius 1 Å, which is equal to the radius of the 4*f* orbit of Tb. The small fraction of the 3*d* electrons of Fe is distributed in another ring of radius 0.75 Å, which is equal to the radius of the 3*d* orbit of Fe.[15] At this stage we let the amount of 3*d* electrons be an adjustable quantity. Later we shall fix it by considering the balance between the effect of exchange plus spin-orbit interaction, which tends to keep the two rings parallel to each other, and the effect of Coulomb interaction of the two rings, which tends to make them nonparallel. The centers of the two charged rings are separated by 3 Å, which is the typical length of a Tb—Fe bond.

To look at the effect of the Coulomb interaction separately, we first neglect the effect of the exchange and the spin-orbit interactions. In this case the two rings are not necessarily parallel. Their relative orientations corresponds to the minimum of Coulomb interaction energy. Let $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$ be three orthogonal unit vectors and the Tb ring lie in the plane of $\mathbf{e}_1$ and $\mathbf{e}_2$, and let $\mathbf{e}'_3$ be the unit vector along the normal direction of the Fe ring. Then we can use three angles to specify the relative orientations, one (θ) denoting the bond orientation and two (Θ and Φ) specifying $\mathbf{e}'_3$, see Fig. 2(b). We have calculated the Coulomb energy for the two rings with arbitrary orientations. As an example, Fig. 3 shows the Coulomb interaction energy as a function of (Θ,Φ) for give $\theta=20°$. The charge of the Tb ring is equal to 1*e*, and that of the Fe ring is assumed to be equal to 0.023*e*. The minimum energy appears at $(\Theta,\Phi)=(60°,177°)$. Here we see that the Coulomb interaction tends to bring the two rings to a nonparallel arrangement. The Coulomb energy difference or barrier between the minimum state at $(\Theta,\Phi)=(60°,177°)$ and the parallel arrangement $\Theta=0°$ is equal to 1.4×10^{-15} erg. For a given charge the barrier changes with θ and it reaches the maximum at $\theta=0°$, which, in the case of 0.023*e* in the Fe ring, is equal to $2\times 10^{10^{-15}}$ erg. This Coulomb energy barrier will increase linearly with increasing charge of the Fe ring.

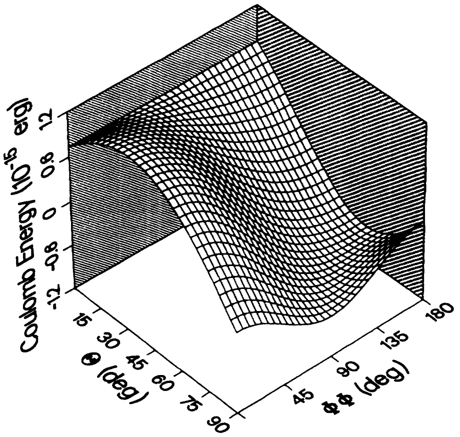

FIG. 3. Dependence of the Coulomb energy of the two-ring system on (Θ,Φ) for given $\theta=20°$. The minimum energy corresponds to a nonparallel arrangement $(\Theta,\Phi)=(60°,177°)$.

On the other hand, we know that Tb spin and Fe spin form a good antiparallel pair in amorphous Tb-Fe films. That is, the Tb ring and Fe ring are parallel. Therefore, to realize the parallel arrangement, the maximum Coulomb energy barrier (the one for $\theta=0$) must be overcome by the effect caused by the exchange and the spin-orbit interactions. The exchange energy between Tb and Fe spins is 2×10^{-15} erg,[12] the spin-orbit coupling energies in free Tb and Fe atoms are $\Delta_{\mathrm{Tb}} \simeq 6\times 10^{-14}$ erg (Ref. 18) and $\Delta_{\mathrm{Fe}} \simeq 3\times 10^{-15}$ erg,[19] respectively. Approximately speaking, the strength of the combined effect of the exchange and spin-orbit interactions should not exceed the smallest one among the three energies. This suggests that, if the data of free atoms apply to amorphous films, the Coulomb energy barrier could not be greater than 2×10^{-15} erg. Assume the barrier is equal to 2×10^{-15} erg, then we find the charge of the Fe ring to be 0.023*e*.

Now we assume the charge of the Fe ring to be 0.023*e* and the two charged rings are always parallel. Then the Coulomb energy of the system only depends on the angle between the bond orientation and the common normal direction of the two rings. This angle has been defined as θ_{m-b} in Fig. 1. Figure 4 shows the bond energy of the two-ring system as a function of θ_{m-b}. Using the dipolar and quadrupolar terms to fit the curve, we find that about 99% of the bond energy of the two-ring system is contributed by the quadrupolar term with $g_2=6.13\times 10^{-15}$ erg. The corresponding bond energy strength $(\Delta E)_{\max}$ defined in Eq. (5) is $(\Delta E)_{\max}=2\times 10^{-15}$ erg. In Sec. IV we will show that this value of $(\Delta E)_{\max}$ can lead to a K_u over 10^6 erg cm^{-3}.

We have performed similar calculations for two Tb rings and found that the Coulomb energy barrier is about 7.6×10^{-14} erg. This value is two orders of magnitude larger than the exchange energy 0.4×10^{-16} erg (Ref. 12) between two Tb spins. Therefore, Tb pairs are not parallel pairs. As mentioned in Sec. II, this is one of the reasons that Tb—Tb bonds do not make a significant contribution to anisotropy.

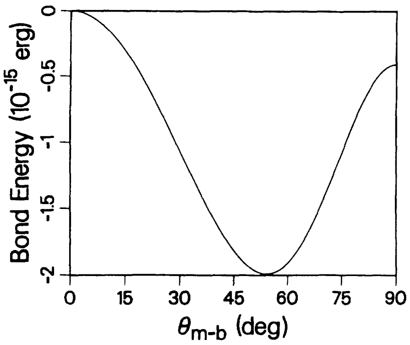

FIG. 4. The bond energy as a function of θ_{m-b} for the parallel arrangement Fig. 2(a). This curve can be fit by a quarudpolar term with $g_2 = 6.13 \times 10^{-15}$ erg.

IV. THE BOLTZMANN DISTRIBUTION OF BOND ORIENTATIONS

Now we discuss how the bond orientational structures can be induced in the deposition process by an initial perpendicularly magnetized layer of dipole moments. The perpendicular magnetization of the initial layer may come from the surface effect discussed in our previous paper.[9] It worth pointing out that many kinds of interfaces can induce perpendicular surface anisotropies, some of them are discussed in Ref. 11. In Sec. V we will point out that a perpendicularly magnetized layer can also arise from spontaneous magnetization. Since we are interested in the magnetization induced structures, our discussion is valid for cases where the substrate temperature in the deposition process is below the Curie temperature of the growing films.

There are two limit cases with respect to the substrate temperature.[2] If the substrate temperature is sufficiently high, the adatom will move by surface diffusion to an equilibrium sticking site, resulting in a crystal structure. This is obviously not the case for amorphous films. If the temperature is sufficiently low, the adatom will stick where it lands and the resultant structures of the amorphous film are determined solely by the impingment angle of the adatoms and shading effects. Such structures can have strong effects on magnetic anisotropies, but they are not the intrinsic and generic source of perpendicular anisotropy in amorphous RE-TM films, because the rearrangements of the adatoms in many cases tend to increase the anisotropy. This is evidenced by that K_u in amorphous Gd-Co and Gd-Fe films increases with increasing resputtering but decreases at high deposition rates and low substrate temperatures.[2]

The most general case is that the substrate temperature is somewhat intermediate. In this case, the adatoms, which may jump several times on the film to lose their kinetic energy, are expected to be loosely anchored on the film at first and then adjust themselves locally to equilibrium positions, resulting in certain atomic scale structures. Basically, two classes of energies are involved in the adjustments: the spin-independent (nonmagnetic) binding energy and the spin-dependent (magnetic) energy. The former is on the order of 10^{-11} erg (several eV), while the latter is on the order of 10^{-15} erg. The question is, do the magnetic forces influence the atomic structures?

The positive answer to the above question has already been given by many magnetic annealing experiments. Here we mention the experiments done by Suran and Sztern,[20] where they found that an in-plane uniaxial anisotropy on the order of 10^5 erg cm^{-3} in amorphous $Co_{1-\alpha-\beta}Dy_\alpha Zr_\beta$ films can be induced by applying an inplane dc magnetic field of 1000 Oe during the rf sputter deposition. This means that the dc magnetic field induces anisotropic atomic structures in the film during sputter deposition. In our case the perpendicularly magnetized interface layer produces the effective magnetic field by exchange coupling. Taking the exchange coupling constant to be 10^{-15} erg per atom and the magnetic moment of an adatom to be $5\mu_B$, the effective magnetic field produced by each atom to which the adatom is attached is about 20 kOe. This is a strong perpendicular magnetic field and it must influence the formation of atomic structures during film growth process. The fact that the magnetic interactions do affect the structure in the presence of the much stronger binding energy indicates that the total binding energy is highly degenerate with respect to different atomic structures. This is an important property of amorphous materials.

To describe the magnetic energy, we consider the extreme case where the total energy can be expanded into bonds consisting of two atoms (the pair-model approximation). In this case the chemical binding energy becomes independent of bond orientations; in other words, the atomic structures are solely determined by magnetic energies. Strictly speaking, using a collection of bonds to describe the total system is an approximation, since the energy is not additive.[11] This approximation is inherent in all kinds of pair models. However, if the atomic structures do not deviate too far from isotropic distributions, the correlations between bonds, i.e., the many-body effects, can be small and the pair model can be very useful. In any event, much of our knowledge of crystal anisotropies is derived from pair models.[10,11,14]

Under the pair-model approximation, the formation of atomic structures would be expected to consist of the following steps. First, the adatoms form a lot of bonds amongst themselves or with the previous layer film atoms due to binding energy. Second, as soon as the atoms are bound together, their spins will be perpendicularly oriented by the initial layer through the exchange interactions. At this stage, it holds by definitions (see Fig. 1) $\theta_b = \theta_{m-b}$, and each type of bond possesses a magnetic bond energy of the form of Eq. (4). In the third step, the bonds adjust their orientations to minimize the total magnetic energy. For an assembly of bonds under given substrate temperature, the equilibrium bond orientations must obey the Boltzmann distribution. Since the electron spins are coupled to the already perpendicularly magnetized film layer, they remain perpendicular to the film plane during the adjustments. Thus, $\theta_b = \theta_{m-b}$ remains valid for all the bonds and so does $E(\cos\theta_{m-b}) = E(\cos\theta_b)$. Let $\rho(\theta_b, \phi_b)$ be the probability of a bond oriented in the (θ_b, ϕ_b) direction; the

Boltzmann distribution is

$$\rho(\theta_b,\phi_b)=c_n\exp\left[-\frac{E(\cos\theta_b)}{k_B T_{\text{sub}}}\right] , \tag{6}$$

where k_B is the Boltzmann constant and T_{sub} the substrate temperature. c_n is the normalization factor to be determined by

$$\int_0^{\pi}\int_0^{2\pi}\rho(\theta_b,\phi_b)\sin\theta_b d\theta_b d\phi_b=1 . \tag{7}$$

The Boltzmann distribution of bond orientations is thus introduced to the newly deposited layer by an initially perpendicularly magnetized layer. Since such a distribution always contributes to $K_u>0$ as we shall show in the next paragraph, the perpendicular magnetization is retained in the new layer. Thus, the Boltzmann bond orientational structures are built up in the bulk of the film. It is worth pointing out that we have neglected correlations between the orientational bonds. This approximation should be good since the Boltzmann distribution Eq. (6) is usually only slightly different from an isotropic distribution. The largest difference between the two is given by $\Delta\rho\simeq 1-\exp[-(\Delta E)_{\max}/(2k_B T_{\text{sub}})]$. Using $(\Delta E)_{\max}=2\times 10^{-15}$ erg and $T_{\text{sub}}=300$ K, we have $\Delta\rho<2.5\%$.

Now we show that the Boltzmann distribution Eq. (6) always leads to perpendicular anisotropy. The physics is very simple: most bonds in this distribution are in a direction that has minimum energy for perpendicular magnetization. The bulk anisotropy energy density contributed by a particular type of bond (i.e., RE-RE, RE-TM, or TM-TM) with the Boltzmann distribution is given by

$$U(\theta_m)=N\int_0^{\pi}\int_0^{2\pi}E(\cos\theta_{m-b})\rho(\theta_b,\phi_b)\sin\theta_b\, d\theta_b\, d\phi_b , \tag{8}$$

where N is the density of the particular type of bonds involved. Substituting Eq. (3) into Eq. (8) and noticing that the terms with odd powers of $\cos\phi_b$ vanishes after the integration over ϕ_b, we can expand $U(\theta_m)$ into the series

$$U(\theta_m)=K_0+K_1\sin^2\theta_m+K_2\sin^4\theta_m+\cdots . \tag{9}$$

The anisotropy energy $U(\theta_m)$ has the following two properties: (i) K_1 is always positive,

$$K_1=\frac{\pi c_n N}{k_B T_{\text{sub}}}\int_0^1(1-\alpha^2)\left[\frac{dE(\alpha)}{d\alpha}\right]^2 \times\exp\left[-\frac{E(\alpha)}{k_B T_{\text{sub}}}\right]d\alpha>0 , \tag{10}$$

where $\alpha=\cos\theta_b$, and (ii) the perpendicular direction $\theta_m=0$ or π is the minimum of $U(\theta_m)$

$$U(0)<U(\theta_m) \text{ for } 0<\theta_m<\pi . \tag{11}$$

These two inequalities demonstrate the perpendicular nature of the anisotropy. The key point is that they do not depend on the concrete form of the bond energy. Therefore, without going into the much complicated mechanisms of bond energy, we are able to answer the question why amorphous RE-TM thin films tend to have perpendicular anisotropy.

Now we describe briefly how Eqs. (10) and (11) can be proved. To prove Eq. (10), one can calculate $K_1=\frac{1}{2}\lim_{\theta_m\to 0}d^2U(\theta_m)/d\theta_m^2$ and use Eqs. (3) and (8). Eq. (11) is essentially the same as the following statement: if the two series $\{a_i\}$ and $\{b_i\}$ with $i=1,2,\ldots,N$ satisfy $a_i\le a_{i+1}$ and $b_i\ge b_{i+1}$, then $\sum_{i=1}^N a_i b_i\le\sum_{i=1}^N a_i b_{j(i)}$, where $\{j(i)\}$ can be any arrangement of $i=1,2,\ldots,N$. This statement can be proved by mathematical induction. In our case E, ρ, and (θ_b,ϕ_b) play the rules of $\{a_i\}$, $\{b_i\}$, and $\{i\}$, respectively.

To obtain an explicit relation between the anisotropy and the bond energy, we consider the fact that the bond energy strength $(\Delta E)_{\max}$ ($\simeq 10^{-15}$ erg) is usually much smaller than $k_B T_{\text{sub}}$ ($=4\times 10^{-14}$ erg for $T_{\text{sub}}=300=$K). Thus, it follows from Eqs. (6) and (7) that

$$\rho(\theta_b,\phi_b)\simeq\frac{1}{4\pi}\left[1-\frac{E(\cos\theta_b)}{k_B T_{\text{sub}}}\right] . \tag{12}$$

We assume further than the bond energy $E(\cos\theta_{m-b})$ contains only dipolar and quadrupolar terms (i.e., $g_i=0$ for $i\ge 3$). In this case we can calculate Eq. (8) analytically and obtain

$$U(\theta_m)=\frac{2N}{15k_B T_{\text{sub}}}\left[g_1^2+\frac{32}{147}g_2^2\right]\sin^2\theta_m -\frac{8Ng_2^2}{315k_B T_{\text{sub}}}\sin^4\theta_m . \tag{13}$$

This equation shows how K_1 and K_2 are related to g_1 and g_2. Here we see that it is not the signs but the absolute values of the g_i constants that play a role in the perpendicular anisotropy. It is worth mentioning that $K_2<0$ is not a general property, but a consequence of assuming $g_i=0$ for $i\ge 3$.

The Boltzmann distribution of bond orientations does give the correct order of magnitude of the perpendicular anisotropy in amorphous RE-TM films. Let us first consider amorphous Tb-Fe films. In this case the anisotropy is mainly contributed by Tb—Fe bonds. The Tb—Fe bond density N depends on the concentrations X_{Tb} and X_{Fe} of Tb and Fe atoms. Assume $X_{\text{Tb}}=20\%$, $X_{\text{Fe}}=80\%$, the total atomic density $n=8\times 10^{22}$ cm^{-3}, and the average coordination number (number of nearest-neighbor atoms) $Z=12$, then the number of Tb—Fe bonds per unit volume for a random distribution of atoms is equal to $N=nX_{\text{Tb}}X_{\text{FE}}Z=1.54\times 10^{23}$ cm^{-3}. In the following cases we assume $T_{\text{sub}}=300$ K and $(\Delta E)_{\max}=2\times 10^{-15}$ erg.

Suppose the bond energy is purely dipolar, i.e., $g_1\ne 0$ and $g_i=0$ for $i\ge 2$, then $g_1=(\Delta E)_{\max}=2\times 10^{-15}$ erg. As shown in Fig. 5(a), the distribution of bond orientations $\rho(\theta,\phi_b)$ depends on the sign of g_1, and it is only slightly ($\le 3.4\%$) deviated from an isotropic distribution $4\pi\rho=1$. For both positive and negative g_1 the uniaxial anisotropy constant given by Eq. (8) is $K_1=1.98\times 10^{16}$ erg cm^{-3}

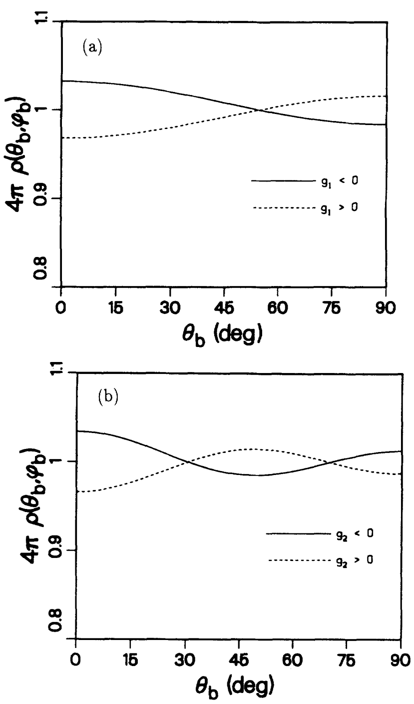

FIG. 5. The Boltzmann distribution as a function of bond orientation θ_b. (a) The bond energy is purely dipolar. (b) The bond energy is purely quadrupolar. The distribution depends on whether the bond energy is dipolar or quadrupolar, and on the sign of g_i.

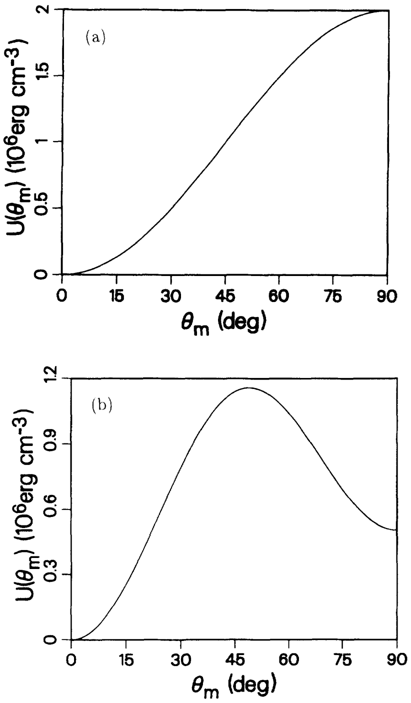

FIG. 6. The anisotropy energy density $U(\theta_m)$ vs the magnetization direction θ_m. (a) The bond energy is purely dipolar. (b) The bond energy is purely quadrupolar. The shape of the curves depend on whether the bond energy is dipolar or quadrupolar, but not on the sign of g_i. The minimum of $U(\theta_m)$ always appears at $\theta_m=0$.

and $K_i=0$ for $i\geq 2$. The anisotropy energy density $U(\theta_m)$ contains only the term $K_1\sin^2\theta_m$ and is plotted in Fig. 6(a).

Now we assume the bond energy to be purely quadrupolar, i.e., $g_2\neq 0$ and $g_i=0$ for $i\neq 2$, such as the two-ring model discussed in Sec. III. The distribution functions $\rho(\theta_b,\phi_b)$ for $g_2>0$ and $g_2<0$ are plotted in Fig. 5(b). Taking $g_1=0$ and $|g_2|=6.13\times 10^{-15}$ erg in Eq. (8), which were given by the two-ring model in Sec. III, we find the anisotropy constants to be $K_1=4.05\times 10^6$ erg cm^{-3}, $K_2=-3.54\times 10^6$ erg cm^{-3}, and $K_i=0$ for $i\geq 3$. The anisotropy energy density $U(\theta_m)$ is plotted in Fig. 6(b).

For amorphous Gd-Co films, the main source of K_u comes from Co—Co bonds. In this case, we have $N=nX_{\mathrm{Co}}^2Z/2$. Assuming $X_{\mathrm{Co}}=80\%$, n, Z, T_{sub} to be the same as we used for Tb-Fe, and assuming the bond energy is purely dipolar, then Eq. (13) yields $K_1=6.6\times this^{35}g_1^2$ erg^{-2} cm^{-3}. From this relation an anisotropy with $K_1=5\times 10^5$ erg cm^{-3} corresponds to a dipolar interaction strength $|g_1|=8.7\times 10^{-16}$ erg. This value is fully consistent with the order of 10^{-15} erg, as estimated from anisotropies of ferromagnetic crystals.[10,11,14]

V. CONCLUSION AND DISCUSSION

We have showed that a perpendicularly magnetized layer can induce the Boltzmann distribution of bond orientations in the amorphous RE-TM films. The bond orientational structures depend both on the sign and amplitude of the bond energy, but the resultant bulk perpendicular anisotropy depends only on the amplitude and is always positive. By the proposed mechanism, a bond energy on the order of 10^{-15} erg, which is consistent with that estimated from crystalline anisotropies, can lead to a perpendicular anisotropy on the order of 10^6 erg cm^{-3}. This kind of bond orientational structure and the perpendicular anisotropy may be present only in films deposited below the Curie temperature.

According to the Boltzmann distribution, Eq. (6), bonds of largest energy will form the most anisotropic structure. Therefore, in amorphous Gd-Co (or Tb-Fe) films, the orientations of the Co—Co (or Tb—Fe) bonds should have the most anisotropic distribution compared to the Gd—Gd and Gd—Co (or Tb—Tb and Fe—Fe) bonds. This result is consistent with the assumption of the pair ordering model for amorphous Gd-Co films and the experimental EXAFS results for $\mathrm{Tb}_{20}\mathrm{Fe}_{80}$ films,[17] based on which the bond orientational anisotropy model was proposed. In the pair ordering model the anisotropic distribution of Co—Co bonds was attributed to the topology of the adatoms.[2] In the bond orientational anisotropy model the anisotropic distribution of Tb—Fe bonds was explained based on the anelastic deformation.[21] Using the Boltzmann distribution of bond orientations, one can understand the bond orientational structures in different films based on the same physics.

We must point out that a perpendicularly magnetized layer can also come about from spontaneous magnetization. To see this, we consider the early deposition stage of an amorphous film. Before a homogeneous magnetized layer is formed, the film consists of a lot of small disconnected regions of atoms, each having its own magnetization direction. These spontaneous magnetizations will induce an easy anisotropy axis within the region due to the Boltzmann distribution. Statistically, due to the azimuthal symmetry of the deposition process (which is realized by perpendicular deposition or rotating the substrate during sputtering), the distribution of the in-plane components of the anisotropies is symmetric with respect to the azimuthal angle. This symmetry helps to cancel the overall in-plane anisotropy. Therefore, when these disconnected regions merge together after enough atoms have been deposited, a dipole, being exchange coupled to atoms in all the regions, mainly feels the averaged perpendicular component of the anisotropies of the regions, plus an in-plane shape anisotropy. In amorphous RE-TM films the shape anisotropy is reduced by the antiparallel subnetworks of RE and TM dipoles and the perpendicular component may be stronger. In this case, the net anisotropy will be perpendicular and a perpendicularly magnetized layer will be formed. It will then induce the Boltzmann bond orientational structure in a systematic way.

It is worth pointing out that, in the framework of the Boltzmann distribution of bond orientations, the antiparallel magnetic subnetworks in amorphous RE-TM films are always in favor of building a perpendicular anisotropy. In the surface effect,[9] the antiparallel dipole pairs produce directly the perpendicular anisotropy and provide the initial perpendicularly magnetized layer. In the case that a perpendicularly magnetized layer results from the spontaneous magnetization, and in the formation of the Boltzmann distribution of bond orientations, the antiparallel subnetworks cause the reduction of the net magnetization. It thus reduces the in-plane shape anisotropy and increases the perpendicular component of the effective magnetic field. The latter is helpful in building a perpendicular anisotropy. This may explain why it is mostly amorphous RE-TM films but not amorphous TM films[22] that have perpendicular anisotropies.

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