Anisotropic lattice expansion and magnetism in sputter-deposited $Ca(La)B_6$ films

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Nanocrystalline thin films of CaB₆ and Ca_{0.995}La_{0.005}B₆ were fabricated in this study using rf-magnetron sputtering. X-ray diffraction (XRD) measurements and scanning electron microscopy/energy dispersive spectrometer analyses revealed that lattice expansion of up to 6% with respect to the bulk value occurs along the direction perpendicular to the film plane. It is caused by the trapping of Ar gas into the film. On the other hand, in-plane XRD showed that spacing along the directions within the film plane is shrunk slightly. Large ferromagnetic moment of 0.01–0.02 $\mu_{\rm B}$ /f.u. was observed in some La-doped films only when the lattice expansion rate was larger than 2.5%. The Curie temperature was found to be markedly higher than 400 K.

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The reported weak ferromagnetism of Ca_{1-r}La_rB₆ has attracted great interest,¹ because: (i) that compound has no constituent 3d or 4f elements; (ii) it has an extremely high Curie temperature $T_{\rm C}(\sim 600 \text{ K})$ despite its tiny magnetic moment (~0.07 $\mu_{\rm B}$ /La); and (iii) the ferromagnetism appears only when the doping quantity of La is very low $(0.00 \le x \le 0.01)$. Ceperley *et al.* suggested that La-doped hexaboride might be an example of the long predicted, but never observed, ferromagnetic phase of a dilute electron gas.² Zhitomirsky et al. have presented another explanation based on a semimetallic band structure calculated by localdensity approximation (LDA).³ They proposed that the Ladoped hexaboride might be an electron-doped excitonic insulator, in which ferromagnetism appears to be caused by spontaneous time-reversal symmetry breaking. The latter interpretation was considered initially to be more persuasive. Therefore, some authors^{4,5} have attempted to improve that model. However, recent angle-resolved photoemission spectroscopy (ARPES) experiments for undoped CaB₆ have revealed that there is a sizable energy gap ($\sim 1 \text{ eV}$) at the X point between the valence and conduction bands.^{6,7} That finding is consistent with the calculated band structure revealed by the so-called GW approximation,⁸ which takes account of the dynamically screened Coulomb interaction. On the other hand, Monnier and Delley have investigated the possibility that the observed spontaneous magnetization is localized at imperfections in the CaB₆ lattice by selfconsistent electronic structure calculation.⁹ Consequently, they concluded that only the B₆ vacancy carries a large magnetic moment.

FMR measurements for bulk single crystals of $Ca_{0.995}La_{0.005}B_6$ have revealed that the magnetic moment is localized within a few μ m from the surface.¹⁰ Lofland *et al.* indicated that defects introduced by annealing enhance both magnetization and ordering temperature.¹¹ According to these experimental results, ferromagnetism seems difficult to interpret as a bulk or stoichiometric CaB₆ property. On the other hand, Matsubayashi *et al.* claimed that magnetism observed in this system is not intrinsic, but results instead from alien phases of iron.¹² Young *et al.* suggested that the physical characteristics of magnetic element doped hexaboride share many similarities with those of dilute magnetic semiconductor such as Mn-doped GaAs.¹³ Therefore, the origin

of the ferromagnetism remains controversial.

As mentioned previously, some experimental and theoretical results have implied that ferromagnetism is not native to bulk single crystals, especially to stoichiometric ones. Nevertheless, almost all experiments thus far have been conducted on single crystals. Therefore, a study addressing thinfilm samples would be advantageous to extract intrinsic properties of Ca(La)B₆ because sputter-deposited films generally consist of nanosized crystallites which have many grain boundaries and defects. This paper reports an experimental study of the structure and magnetism of sputterdeposited nanocrystalline films of La-doped and undoped CaB₆.

Thin films were fabricated using an rf-magnetron sputtering method. We used CaB₆ and Ca_{0.995}La_{0.005}B₆ targets of a sintered compact with 76-mm diameter and 5-mm thickness. Either Ar or Ne was used as a sputtering gas. Gas pressure $(P_{\text{Ar}}, P_{\text{Ne}})$ was controlled between 1 mTorr and 20 mTorr. During deposition, the Si (100) substrate was heated to T_{s} = 900 °C; the film thickness was changed from 0.2 μ m to 8.0 μ m.

The film structure was analyzed using x-ray diffraction (XRD) measurement with Cu K_{α} radiation. In addition to conventional XRD measurements in θ -2 θ mode, which give information regarding lattice spacing perpendicular to the film plane, we also examined an in-plane XRD pattern using an ATX-G system (Rigaku Corp.), which gives information along directions parallel to the film plane. In this method, the angle between the incident x-ray and the film plane can be as small as 0.4°. The angle between a plane of counter operation and the film is also very small so as to keep the scattering vectors almost parallel to the film plane. Magnetization measurements were carried out using a superconducting quantam interference device (SQUID) magnetometer between 2 K and 400 K. Samples' chemical compositions were analyzed quantitatively using scanning electron microscopyenergy dispersive spectrometer (SEM-EDS), Rutherford backscattering spectroscopy (RBS), and secondary-ion mass spectroscopy (SIMS).

Figure 1 shows the thickness dependence of XRD patterns in θ -2 θ mode, in which all films were deposited using Ar gas. The peaks are extremely broad because of the nanocrystalline structure. The mean grain size is estimated using the



FIG. 1. (Color online) Film thickness dependence of XRD patterns in normal θ -2 θ scan. Vertical broken lines indicate peak positions of bulk CaB₆. The sharp peak at about 33° and the tail are ascribed to the Si substrate. The inset shows thickness dependence of the lattice constant calculated from the (110) peak position.

Scherrer's formula to be $d \sim 30$ nm. In addition, each Bragg peak position is shifted markedly toward the lower-angle side with respect to those for bulk CaB₆. This shift suggests that lattice spacing along the direction perpendicular to the film plane expands with respect to the bulk value of a_{bulk} =4.145 Å. We deduced a hypothetical cell parameter a_{\perp} according to the (110) peak position. It was found to decrease with increasing film thickness t for both doped and undoped films, as shown in the inset of Fig. 1. Nevertheless, it was about 1% larger than the bulk value for the sample with $t=8 \ \mu m$. XRD patterns for the same film measured by both θ -2 θ and in-plane modes are shown in Fig. 2(a). We found that peak positions measured by the in-plane mode are slightly higher than those for the bulk sample. This relative height indicates that spacing along the directions within the film plane are shrunk slightly $(a_{//} < a_{bulk})$, in striking contrast with $a_{\perp} > a_{\text{bulk}}$.

Composition analysis with SEM-EDS detected a peak that originated from the Ar which was trapped into the film during sputtering. As shown in Fig. 3, the Ar amount becomes larger in the sample with larger a_{\perp} . Figure 4 shows the $a_{//}$ and a_{\perp} values as a function of the Ar content for numerous films. With increasing Ar content of up to about 0.5 at %, a_{\perp} increases (to 6%), whereas $a_{//}$ decreases (to about 1%) with respect to a_{bulk} . That is, the lattice anisotropy becomes larger concomitant with increased quantities of Ar trapped in the film.

Average grain sizes estimated from width of the diffraction peaks are also anisotropic with $d_{//} \sim 10$ nm and $d_{\perp} \sim 30$ nm, respectively. The relative intensity of each diffraction peak reveals that the degree of preferred orientation varied from sample to sample. One sample appeared to be randomly aligned; another had a (100)-preference orientation. Notably, as shown in Fig. 2(b), no remarkable deviation of $a_{//}$ and a_{\perp} from the a_{bulk} was observed when Ne gas was used for sputtering.



FIG. 2. XRD patterns for $Ca_{0.995}La_{0.005}B_6$ films sputtered using Ar (a) and Ne (b) gases. Upper and lower patterns in each graph indicate data measured by in-plane mode and by normal θ -2 θ scan, respectively. Vertical broken lines indicate peak positions of bulk CaB_6 .

Such anisotropic transformation of crystal structures resulting from trapped Ar is an interesting phenomenon in itself. However, it is not easy to deduce a correct structural model using only diffraction patterns of such an assembly of nanosized crystallites. For example, a peak-splitting phenomenon resulting from tetragonal lattice distortion would be masked by the line-broadening effect caused by the small grain size. Detailed structural analysis, including location of trapped Ar atoms, is now in progress.

Magnetization isotherms of these films were measured at various temperatures. We found that some of La-doped samples exhibit ferromagneticlike hysteresis loops and others, including undoped samples, show paramagneticlike curves. Typical M-H curves at 300 K are shown in Fig. 5, where a component of diamagnetism originated from the Si



FIG. 3. (Color online) The detected Ar $K\alpha$ peak obtained by composition analysis with SEM-EDS. Results for three samples with different sputtering gases (Ar or Ne) and a_{\perp} values are shown.



FIG. 4. Trapped Ar content plotted against hypothetical cell parameters $a_{//}$ and a_{\perp} calculated from the (110) peak position.

substrate was subtracted. Sample B shows a ferromagnetic *M*-*H* curve with a coercive field of about 70 Oe, whereas the curve of sample A exhibits nonmagnetic behavior. Although samples A and B in Fig. 5 were fabricated with the same conditions ($P_{Ar}=5$ mTorr, and $T_s=700$ °C), their magnetism and structure are quite different, as shown in Fig. 5 including the inset. This difference is caused by the amount of the trapped Ar, that is, 0.01 at % in sample A and 0.35 at % in sample B. These results led us to infer that there is a correlation between their structure and magnetization. Then we plotted the spontaneous magnetization value M_s in Fig. 6. It was deduced by linear extrapolation of M-H curve in the high-field region to zero field, as a function of a_{\perp} . The data points are scattered, but there is a tendency for M_s to increase with increasing a_{\perp} from a_{bulk} . The Ca_{0.995}La_{0.005}B₆ samples produced with the Ne gas have comparatively small a_{\perp} , being almost equal to a_{bulk} , and show small M_{s} values. In contrast, Ar-sputtered films exhibit larger a_{\perp} and magnetization values. Especially, samples with $a_{\perp} \approx 4.3$ Å show the largest M_s values, which amount to 0.02 $\mu_{\rm B}$ per formula unit. Assuming nominal concentration of the doped La (0.5 at %), this value is equivalent to 4 $\mu_{\rm B}$ per La, which is 50 times larger than that reported by Young *et al.*¹ Nevertheless, it should be noted that samples with a large a_{\perp} do not always exhibit ferromagnetism. This fact suggests that lattice expan-



FIG. 5. (Color online) Magnetization curves measured at 300 K for two samples A and B for which XRD patterns are shown in the inset. Magnetization is expressed in units of magnetic moment per formula unit.



PHYSICAL REVIEW B 69, 140406(R) (2004)

FIG. 6. (Color online) Spontaneous magnetic moment deduced at 300 K plotted as a function of a_{\perp} for both Ar- and Ne-sputtered films. Two symbols for the Ar-sputtered films denote a different series of experiments.

sion is not just a sufficient, but a necessary, condition for a $Ca_{0.995}La_{0.005}B_6$ to show ferromagnetism with large magnetization. Regarding the undoped CaB_6 samples, we have not observed ferromagnetism in this experiment, as shown in Fig. 6; however, the number of examined samples is not large compared with that for the La-doped sample.

We also plotted the M_s value as a function of temperature in Fig. 7. We were unable to observe magnetization above 400 K because of limitations of our device, but we found that $M_s(T=400 \text{ K})$ is about 80% of $M_s(T=5 \text{ K})$, suggesting that T_C is much higher than 400 K, being 550–650 K.

It is important to investigate the correlation between observed ferromagnetism presented here and the Fe impurity, which might inevitably be incorporated into the film during a sputtering process. We measured the Fe content carefully for various samples using SEM/EDS analysis, especially for films exhibiting ferromagnetic behavior. The intensity caused by the Fe $K\alpha$ was below the detection limit of our EDS apparatus in every film, demonstrating that the Fe content is less than 0.1 at %. Presuming that all Fe impurities of 0.1



FIG. 7. Temperature dependence of spontaneous magnetic moments in some ferromagnetic samples.

at % have a ferromagnetic moment equal to that of bcc Fe (2.2 μ_B), the resultant magnetic moment is $2.2 \times 10^{-3} \mu_B$ per formula unit, which is too small to explain the current observation. Therefore, we conclude that the ferromagnetism presented here is not the result of the impurity Fe, but is an intrinsic characteristic of our Ca(La)B₆ films.

Present results are consistent with some theoretical models. It is interesting to note that the magnitude of the ferromagnetic moment observed here is of the same order as that caused by the B_6 vacancy⁹ if we assume the number of B_6 vacancy is equal to that of the trapped Ar. Hotta *et al.*,¹⁴ on the other hand, proposed that ferromagnetism can be stabilized when the original cubic symmetry of CaB₆ is removed to create a tetragonal structure. Therefore, this result seems to concur with our experiments.

We must mention the stability of the observed ferromagnetic moment. During the course of measurements, we found that the observed ferromagnetic moment is not stable, but instead decreases with time. Although decay time varies from 1 to 90 days depending on the sample, the final M-Hcurve becomes a straight line, just like that of sample A shown in Fig. 5. After finding that such phenomena of timedependent magnetization decrease, we attempted to trace whether there are any structural or compositional changes over time. Although films that have been examined by XRD and SEM/EDS are not numerous, we did not detect any timedependent change of a_{\perp} values and the Ar content in films which had already become "nonmagnetic." We have not measured the structures of identical films that exhibit a large ferromagnetic moment as a function of time because separate portions of a film with different sizes were used for magnetic and structural measurements. For that reason, results in this study do not preclude the possibility that the structure and/or Ar content of a film whose ferromagnetic moment decreases with time are also time dependent. Therefore, we infer that a sort of metastable state that is correlated with the trapped Ar and lowering of the lattice-symmetry engender the observed ferromagnetism. The decay time of such a metastable state would be dependent on the local environmental situation. Large scattering of observed ferromagnetic moment values given in Fig. 6 would then be attributable to distribution of such a "time constant." It is clear that further experimental and theoretical studies are required to determine the origin of ferromagnetism reported here.

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