

Influence of the packing fraction and host matrix on the magnetoelastic anisotropy in Ni nanowire composite arrays

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The influence of the packing fraction on thermally induced magnetoelastic effects has been studied in Ni nanowires embedded in polycarbonate, poly(vinylidene difluoride), and alumina nanoporous membranes of different porosities for temperatures between 77 K and 345 K. For nanowires embedded in polymer membranes, the contrasting shift in the ferromagnetic resonance frequency when the temperature is either above or below ambient temperature is consistent with the occurrence of uniaxial magnetoelastic anisotropy effects due to the large thermal expansion coefficient mismatch between the metal nanowires and the membrane. A model which considers the influence of the nanowires packing fraction and the membrane material on the magnetoelastic effects, arising from the matrix-assisted deformation process, is proposed. The model is able to successfully explain the experimentally observed effects for the Ni nanowire arrays embedded in the different porous membranes and their variation with the packing fraction. The possibility to modulate the magnetic anisotropy of such nanocomposites by an appropriate choice of membrane material, packing fraction, and sample temperature is of considerable importance to achieve magnetically tunable devices. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4822307>]

I. INTRODUCTION

Arrays of parallel magnetic nanowires (NWs) embedded in non-magnetic dielectric templates are of considerable interest for fundamental physics studies and for their possible exploitations in relevant applications, such as patterned media for magnetic storage,^{1,2} unbiased nonreciprocal microwave devices,³⁻⁶ and spin-transfer torque devices.⁷⁻⁹ Compared to other magnetic particle/dielectric composites, arrays of nanowires embedded in nanoporous membranes allow controlling the magnetic material, NW height and diameter, and packing fraction. Particularly, the packing fraction modulates the magnitude of the dipolar interaction field that plays a key role in the magnetic properties of the assembly. Proper control and tuning of their magnetic properties requires further understanding of the interplay between intrinsic and shape effects as well as the interaction between the NWs and the host matrix. Magnetoelastic (ME) effects provide an additional parameter to control the magnetic properties of NW arrays because of the large surface to volume ratio, thus enhancing the mechanical coupling between the two phases. Although ME anisotropy is generally weak at room temperature, it is of the same order of magnitude as the shape anisotropy at low temperatures in specific systems, as already shown in Ni NWs embedded in polycarbonate (PC) membranes.¹⁰⁻¹² Besides, recent studies suggest the existence of magnetoelastic effects in Ni NW arrays embedded in porous alumina membranes.^{13,14} Furthermore, a magnetoelectric effect

arising from the mechanical coupling between Ni NWs and a piezoelectric poly(vinylidene difluoride) (PVDF) membrane was recently demonstrated from ferromagnetic resonance (FMR) experiments performed at room temperature by applying a static bias voltage.¹⁵ In these two examples, the magnitude of the effects depends primarily on the NWs packing fraction. However, up to now, no consistent overall description of the temperature-dependent magnetic anisotropy in NWs, that considers both the different membrane materials and packing fraction, is available.

In this work, Ni nanowire arrays embedded into nanoporous membranes with different thermal expansion and elastic properties have been investigated. It is shown that the thermally induced magnetoelastic effects strongly depend on the packing fraction as well as on the thermal expansion coefficient mismatch between the host matrix and metal nanowires. In order to account for the variation of the ME energy on the parameters mentioned above, a simple model that considers the influence of the NWs packing fraction and the matrix-assisted deformation process has been proposed. The comparison between the calculated data and the experimental results shows a fairly good agreement, thus providing support for this tendency prediction model, which can be used to tailor magnetic and magnetoelectric properties in such nanocomposite materials.

II. EXPERIMENTAL

Arrays of Ni NWs have been grown by electrodeposition into the pores of selected nanoporous membranes

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by following the same procedure as the one described previously.¹¹ In the present work, the host polymer matrix consists in 25 μm thick track-etched membranes made of PC and PVDF with diameters ϕ in the range 50 nm–200 nm. Samples with different packing fractions P between 1% and 12% were fabricated in order to examine the influence of P on the magnetoelastic anisotropy energy. Additional 50 μm thick AAO membranes with $P=12\%$ and 15% were also used as templates. Prior to electrodeposition, a metallic layer was evaporated on one side of the membrane in order to cover the pores and use it as a cathode. Ni NWs were grown at a constant potential of -1.1 V from a 1 M $\text{NiSO}_4 \cdot 6\text{H}_2\text{O} + 0.5$ M H_3BO_3 electrolyte. For this study, temperature controlled FMR has been used as a characterization technique since it provides a precise and direct measurement of the effective anisotropy field of the material under test, then allowing an accurate determination of the ME field contribution. FMR measurements were performed by sweeping the magnetic field applied parallel to the NWs from 10 kOe down to zero and at a given constant frequency in the range from 100 MHz to 50 GHz. These measurements were repeated at different temperatures in the range from 77 K to 345 K by using a microstrip transmission line method inside a probe station measurement setup from Desert Cryogenics, as reported previously.¹¹

III. RESULTS AND DISCUSSION

Figure 1(a) shows FMR absorption spectra recorded at 30 GHz and at different temperatures for an array of Ni NWs embedded in a PVDF membrane with $\phi = 105$ nm and $P = 1.7\%$. It can be seen that the shift in the resonance field $\delta H_r = H_r - H_{r(295\text{K})}$, where H_r is the resonance field at the temperature T and $H_{r(295\text{K})}$ its value at 295 K is negative by cooling below room temperature ($\delta H_r \sim -6.5$ kOe at 77 K)

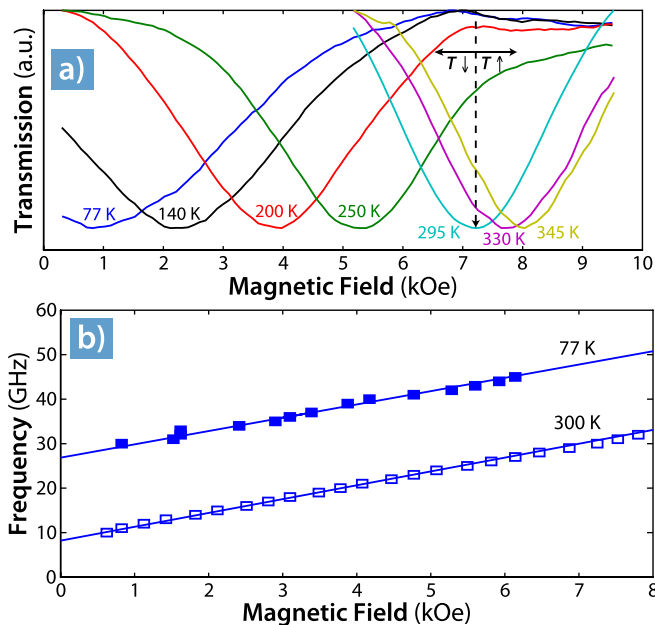


FIG. 1. (a) FMR absorption spectra measured at 30 GHz as a function of the temperature for Ni nanowires embedded in a PVDF membrane with $P = 1.7\%$ and (b) dispersion relations for the Ni-PVDF sample measured at 77 K (filled symbols) and 300 K (open symbols).

and positive with increasing the temperature ($\delta H_r \sim +0.85$ kOe at 345 K). Such behaviours are consistent with the presence of significant magnetoelastic effects as the temperature is modified, which is due to the Ni and the polymer thermal expansion coefficients mismatch.^{11,12} Since the thermal expansion coefficient for Ni is lower than the one for the polymer matrix, their mismatch induces a resultant stress that is exerted by the polymer matrix on the Ni NWs. As a result, the Ni NWs tend to contract and to expand less than the polymer matrix during cooling and during heating, respectively. Besides, for an array of metallic NWs with a low packing fraction embedded in a polymer matrix the axial stress is much larger than the radial stress,¹⁰ then such temperature variations lead to a significant compressive stress exerted by the polymer membrane along the nanowires axis upon cooling and to a tensile stress upon heating. In contrast, a much weaker temperature-dependent FMR was measured on the Ni-AAO sample, as concluded by the small positive shift of the resonance field ($\delta H_r \sim 0.1$ kOe) at 77 K (not shown), thus indicating a reduction of the total anisotropy along the NWs axis. Interestingly, we observed that in these measurements δH_r does not depend on the excitation frequency. As illustrated in Figure 1(b), the dispersion relations measured at 295 K and 77 K for the Ni-PVDF sample are parallel to each other, which leads to a full determination of the magnetoelastic energy K_{me} from absorption spectra measured at a given constant frequency.

From previous works, it is known that Ni NW arrays, fabricated following the procedure described in Sec. II, have a preferred orientation along the [110] direction, which is along the wires axis.^{10,16,17} Therefore, at low temperatures, the effect of the first magnetocrystalline anisotropy constant becomes large enough to contribute significantly to the total anisotropy energy. Moreover, it was shown that no significant changes in the magnetoelastic effects occur with variations in the NWs diameter while P is kept constant,¹¹ so that the packing fraction and the membrane material are the more relevant parameters. Using the same approach as in a previous study,¹¹ K_{me} is written as follows:

$$K_{\text{me}} = \frac{M_s}{12} \left[-A + \sqrt{A^2 - 8 \left(\frac{\lambda_{100}}{\lambda_{111}} + 1 \right) (B - B_{295\text{K}})} \right]. \quad (1)$$

In this equation, $A = (H_r + H_{\text{ms}} - 2H_{\text{A1}})(\lambda_{100}/\lambda_{111}) + 3H_r + 3H_{\text{ms}}$, $B = (H_r + H_{\text{ms}})^2 - H_{\text{A1}}(H_r + H_{\text{ms}} + 2H_{\text{A1}})$, where $H_{\text{ms}} = 2\pi M_s(1 - 3P)$ is the magnetostatic field including shape and dipolar interaction terms,¹⁸ M_s is the saturation magnetization, $H_{\text{A1}} = K_1/M_s$, K_1 is the first order anisotropy constant, λ_{100} and λ_{111} are the magnetostriction coefficients in the directions [100] and [111] for Ni, and $B_{295\text{K}}$ is the value of B at room temperature. Using Eq. (1), the variation of K_{me} with T was deduced from FMR fields using known values for bulk Ni of M_s ,¹⁹ K_1 ,²⁰ λ_{100} , and λ_{111} .²¹ Since the NW diameter considered here ranges from 50 to 200 nm, the values of the magnetic parameters correspond to those of the bulk. The temperature evolution of K_{me} obtained from the FMR measurements done on the Ni NW arrays grown in PVDF and PC membranes with selected packing fractions

(around 2% and 5%–6%) is reported in Fig. 2. It can be observed that K_{me} increases monotonically with decreasing the temperature in all cases. From Fig. 2, it also appears that K_{me} is enhanced for Ni-PVDF samples (squares) in comparison to Ni-PC samples (circles) considering similar P values. Besides this, for the two sets of Ni NW arrays embedded in polymer host membranes, the magnitude of K_{me} decreases as P is increased for temperature values below room temperature, in good agreement with previous results.¹¹

The enhanced ME effect in the PVDF based samples can be qualitatively understood by the larger thermal expansion coefficients mismatch between the Ni NWs ($\alpha_{Ni} = 1.3 \cdot 10^{-5} \text{ K}^{-1}$) and the PVDF membrane ($\alpha_{PVDF} = 12 \cdot 10^{-5} \text{ K}^{-1}$) than between the metal nanowires and the PC membrane ($\alpha_{PC} = 7 \cdot 10^{-5} \text{ K}^{-1}$). For the Ni-PVDF sample with $P = 1.7\%$, K_{me} is significantly large at 77 K ($\sim 11.2 \cdot 10^5 \text{ erg} \cdot \text{cm}^{-3}$), and therefore overcomes the evaluated magnetocrystalline energy in the [110] direction,²² $K_{mc} = K_1/4 \sim -2 \cdot 10^5 \text{ erg} \cdot \text{cm}^{-3}$ and the magnetostatic energy $K_{ms} = \pi M_s^2(1 - 3P) \sim 7.8 \cdot 10^5 \text{ erg} \cdot \text{cm}^{-3}$ at 77 K. At $T = 295 \text{ K}$ $K_{ms} \sim 7 \cdot 10^5 \text{ erg} \cdot \text{cm}^{-3}$ while both K_{mc} and K_{me} are negligible, then the large increase in the uniaxial anisotropy at low temperature is primarily mediated by the ME anisotropy. It is interesting to note that when heated above room temperature, both the PVDF and the PC based Ni NW samples display a negative ME energy. In this case, the NWs are forced to expand together with the polymer matrix, thus resulting in a tensile stress along the NWs axis. A moderate increase of 50 °C in the sample temperature can significantly shift the FMR field by about 1 kOe (see Fig. 1(b)), which in turn leads to a decrease of K_{me} , as shown in Fig. 2. As suggested by the results shown in Fig. 2, the ME energy strongly depends not only on the temperature but also on both the packing fraction and the membrane material. Therefore, all these quantities can be considered together as input parameters in a simplified model for the ME energy. An estimation of the ME anisotropy energy K_{me} can be made through^{23,24}

$$K_{me} = \frac{3\lambda_{110}\sigma}{2}, \quad (2)$$

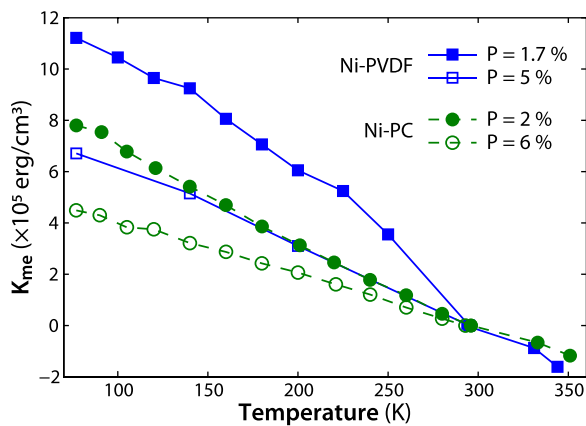


FIG. 2. Variation of K_{me} with T for Ni nanowire arrays with different packing fractions embedded in PC and PVDF templates. Ni-PVDF with $P = 1.7\%$ (filled squares) and $P = 5\%$ (open squares); Ni-PC with $P = 2\%$ (filled circles) and $P = 6\%$ (open circles).

where $\sigma = E_{Ni}\epsilon$ is the axial stress induced on the Ni NWs and ϵ is the strain, $E_{Ni} \sim 214 \text{ GPa}$ is the Young modulus for Ni, and $\lambda_{110} \sim -34 \cdot 10^{-6} \text{ K}^{-1}$ is the room temperature saturation magnetostriction constant ($\lambda_{110} \sim -54 \cdot 10^{-6} \text{ K}^{-1}$ at 77 K). To calculate the dependence of the matrix-assisted strain on the packing fraction for arrays of parallel Ni NWs embedded in a host matrix, we used the following expression:²⁴

$$\epsilon = \frac{(1 - P)E_{MATRIX}}{(1 - P)E_{MATRIX} + PE_{Ni}}(\alpha_{MATRIX} - \alpha_{Ni})\Delta T, \quad (3)$$

where ΔT is the change in temperature, α_{Ni} and α_{MATRIX} are the thermal expansion coefficients for Ni and the host matrix, respectively (with $\alpha_{AAO} \sim 10^{-5} \text{ K}^{-1}$ the estimated thermal expansion coefficient for amorphous alumina²⁵) and E_{MATRIX} is the Young modulus for the host matrix ($E_{PC} \sim E_{PVDF} \sim 2.3 \text{ GPa}$; $E_{AAO} \sim 350 \text{ GPa}$). As a rough estimate, we will use α -values at room temperature to calculate ϵ . For the Ni-PVDF sample with $P = 1.7\%$, the calculated strain $\epsilon \sim 0.9\%$ in the direction of the NWs axis when the temperature varies from 295 K to 77 K is equivalent to an axial compressive stress $\sigma \sim 1.9 \text{ GPa}$. Figure 3 shows the variation of the calculated K_{me} at 77 K as a function of the packing fraction P considering the different host nanoporous membranes. In this figure, the estimated variation is compared to the experimental values extracted from FMR measurements using Eq. (1), where a very good agreement is found. Error bars for the packing fraction arise from the uncertainty generated by the pores size distribution, as determined by SEM observations over large areas. Not only large positive values of K_{me} are obtained for Ni NW arrays with low packing fractions grown in polymer membranes but also an increase in the packing fraction causes a rapid drop in K_{me} . Such features can be understood in terms of the matrix-assisted compressive stress on the Ni NWs upon cooling and to the P dependence of the strain reflected by the much lower elastic modulus in polymers than in metals. Therefore, the magnitude of the ME anisotropy energy depends strongly on the effective volume ratio

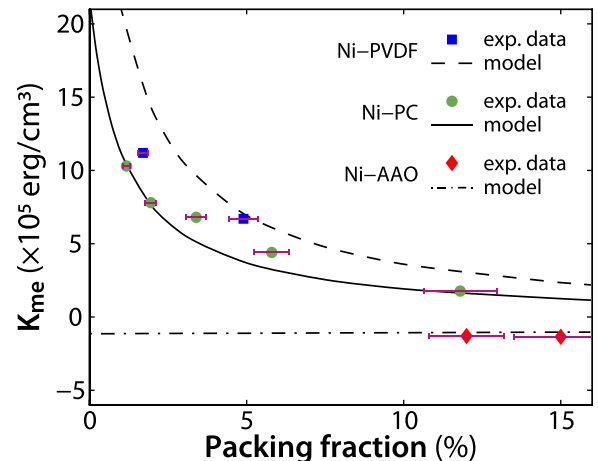


FIG. 3. Experimental and calculated magnetoelastic anisotropy energy K_{me} as a function of the packing fraction for Ni-PVDF, Ni-PC, and Ni-AAO samples.

of the polymer to the metal nanowire. The enhancement of K_{me} for the Ni-PVDF samples in comparison to the Ni-PC samples with similar P values by about a factor of 2 is due to the fact that the former has a larger thermal expansion coefficients mismatch than the later. In contrast, for the Ni-AAO sample with $P = 15\%$, the small shift in the absorption peak to higher field values at 77 K indicates a higher negative value of K_{me} since the thermal expansion coefficient for amorphous alumina is slightly smaller than that for Nickel. Therefore, a relatively low tensile stress on the NWs takes place upon cooling from room temperature down to 77 K. In addition, the relatively small difference in Young modulus between Ni and alumina leads to a weaker P dependence of K_{me} . Using the above-mentioned values, one can estimate $K_{\text{me}} \sim -1.4 \cdot 10^5 \text{ erg} \cdot \text{cm}^{-3}$ at 77 K, which has to be compared to $K_{\text{ms}} \sim -2 \cdot 10^5 \text{ erg} \cdot \text{cm}^{-3}$ and to the magnetostatic energy increment $\delta H_{\text{ms}} = K_{\text{ms}}(77\text{K}) - K_{\text{ms}}(295\text{K}) \sim 0.5 \cdot 10^5 \text{ erg} \cdot \text{cm}^{-3}$. Thus overall, a reduction of the effective anisotropy along the NW axis takes place gradually upon cooling.

IV. CONCLUSIONS

In arrays of Ni NWs electrodeposited into porous PVDF and PC membranes, large ME effects have been observed as the temperature is modified from room temperature, which are attributed to the thermal expansion coefficients mismatch between the Ni NWs and the membrane. Particularly, the ME energy is larger for the Ni-PVDF than for the Ni-PC nanocomposites as a result of the larger thermal expansion coefficients mismatch of the former. On the contrary, lower ME effects have been observed in Ni NWs grown into nanoporous alumina membranes, which is ascribed to the relatively lower thermal expansion coefficients mismatch between the NWs and the alumina membrane. In order to account for these effects, a simple model for the ME anisotropy energy that depends on parameters like the packing fraction, the coefficients of thermal expansion and elastic modulus of constituents, and the temperature has been proposed and a very good agreement with the experimental data has been obtained. This demonstrates that the magnetic anisotropy of arrays of ferromagnetic NWs embedded in nanoporous membranes is tunable by an appropriate choice of the parameters mentioned above, which is of considerable importance for the design of magnetically adjustable devices based on nanocomposites.

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