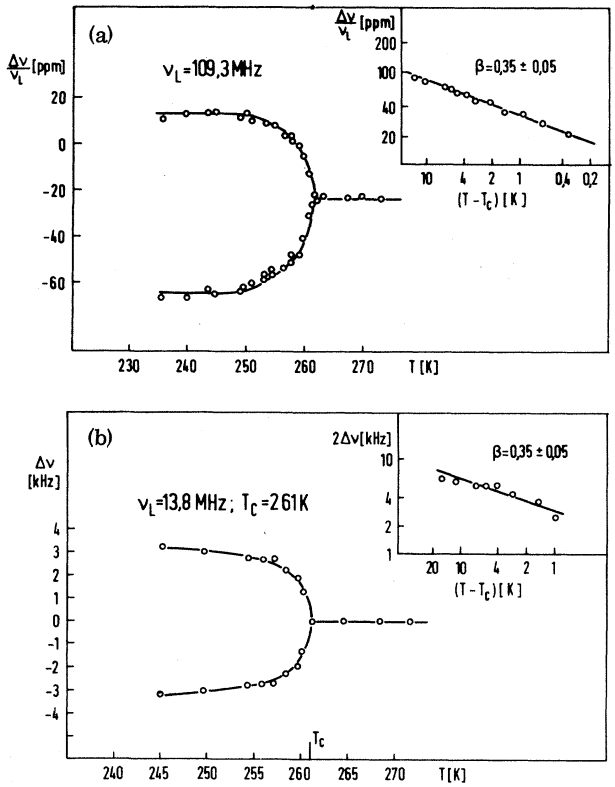

FIG. 3. (a) Temperature dependence of the splitting of the ^{31}P high-resolution NMR spectra in CsD_2PO_4 reflecting the effect of deuteron ordering on the ^{31}P chemical-shift tensor. (b) Temperature dependence of the quandrupole splitting of the deuteron NMR spectra of the long (Ref. 4) O−D···O bonds in CsD_2PO_4.

pendence of the splitting of the ^{31}P spectra was also measured in the case of RbH_2PO_4 where the ferroelectric transition is completely three dimensional and nearly continuous. In contrast to the case of CsH_2PO_4 and CsD_2PO_4, we obtained a classical value of the critical exponent, $\beta = 0.5$. At this moment we cannot make a definite statement about the origin of the nonclassical value of the exponent β in CsH_2PO_4 and CsD_2PO_4. One possibility is that the transition is close to being a tricritical one, i.e., it is of second order but close to being of first order.

Spin-lattice relaxation studies of the phase transition in CsH_2PO_4 and CsD_2PO_4 are in progress. Preliminary results show that the deuteron and ^{31}P spin-lattice relaxation rates are dominated by the critical slowing down of an overdamped soft mode, the frequency of which is much lower than in KH_2PO_4. Further studies of this system should throw some new light on the relation between lattice dimensionality and critical dynamics of ferroelectrics.

[1]F. Seidl, Tschermaks Mineral. Petrogr. Mitt. 1, 432 (1950).

[2]A. Levstik, R. Blinc, P. Kadaba, S. Čižikov, I. Levstik, and C. Filipič, Solid State Commun. 16, 1339 (1975).

[3]E. Kanda and T. Fujimura, J. Phys. Soc. Jpn. 43, 1813 (1977).

[4]Uesu and J. Kobayashi, Phys. Status Solidi (a) 34, 475 (1976).

[5]D. Semmingsen, W. D. Ellenson, B. C. Frazer, and G. Shirane, Phys. Rev. Lett. 38, 1299 (1977).

[6]J. W. Lynn, M. Iizumi, G. Shirane, S. A. Werner, and R. B. Sailant, Phys. Rev. B 12, 1154 (1975).

[7]N. Yasuda, M. Okamoto, H. Shimizu, S. Fujimoto, K. Yoshino, and Y. Inuishi, Phys. Rev. Lett. 41, 1311 (1978).

[8]A. V. de Carvalho and S. R. Salinas, J. Phys. Soc. Jpn. 44, 238 (1978).

[9]T. Chiba, J. Chem. Phys. 41, 1352 (1964); R. Blinc and D. Hadži, Nature (London) 212, 1307 (1966).

[10]R. N. P. Choudhary and R. J. Nelmes, Ferroelectrics 21, 445 (1978).

Magnetostriction in Single-Crystal and Polycrystalline Silver Doped with Rare Earths

I. A. Campbell, G. Creuzet, and J. Sanchez

Laboratoire de Physique des Solides, Université de Paris-Sud, 91405 Orsay, France

(Received 30 April 1979)

We have measured the low-temperature magnetostriction in silver–rare-earth single-crystal and polycrystaline alloys at rare-earth concentrations of about 0.5%. For each monocrystal, the ⟨100⟩ and ⟨111⟩ magnetostrictions are of the same sign and follow the sign of the Stevens factor α. Unannealed polycrystals show quite different behavior from the monocrystals.

Silver–rare-earth alloys have been studied in detail using magnetization, EPR, and transport techniques[1-4] and a phenomenological interpretation of the different data has been obtained in terms of an ionic model in which cubic crystal fields act on the rare earth. However, to fully

understand the origin of these crystal fields (which is certainly more complex than a simple point-charge mechanism) it would be useful to have other data on the ion-lattice interactions. The strength of the anisotropic interaction has been estimated from EPR measurements on strained thin films of *Ag*Dy and *Ag*Er alloys[5-7] but in these experiments the state of the sample is difficult to control. Alternatively, magnetostriction experiments can give very much more complete information on unstrained bulk samples.

We have measured the low-temperature magnetostriction of a number of Ag–rare-earth single crystals and polycrystals; although the magnetostriction of pure rare-earth metals and of certain rare-earth intermetallic compounds has been studied[8,9] there is very little known about dilute magnetic alloys in which crystal fields are important and where interaction effects between rare earths are negligible. Experiments on dilute magnetic rare earths in $LaPd_3$ polycrystals[10] showed that the magnetostriction per ion was of the same order of magnitude as in the pure rare-earth metals, but the signs of the effects observed were not understood. The present data, including single-crystal results on systems where the crystal field and elastic parameters are well known *a priori*, help provide a clearer picture of what turns out to be an interesting but complex situation.

Silver–rare-earth alloys containing about 0.5% rare earth were prepared, the single crystals being made using the Bridgman technique.[11] Samples in the form of cubes about 4 mm on a side were cut out by electroerosion. The magnetostriction measurements were done using a capacitance bridge; with the geometry of the experiment relative changes in length $\delta l/l$ of the order of 10^{-8} could be observed. The sample was held at fixed temperatures between 1.4 and 20 K in a cryostat where magnetic fields could be applied up to 70 kG parallel to the capacitance-cell axis and up to 35 kG perpendicular to the axis. The observed length changes were up to a few parts per million in the fields available as against a few parts per thousand in pure rare-earth metals).

The general expression for the orbit-lattice interaction for rare earths in a strained cubic environment is

$$V_{\mathrm{OL}}=\sum_{ilp} V(\Gamma_i,l)O(\Gamma_i,l,p)S_l e(\Gamma_i,p)\ldots, \qquad (1)$$

where the Γ_i are the irreducible group of symmetry operations around the rare-earth site, the $e(\Gamma_i,p)$ are strains transforming as the pth component of Γ_i, the S_l are Stevens factors, the $O(\Gamma_i,l,p)$ are linear combinations of angular momentum operators, and the $V(\Gamma_i,l)$ are coefficients of which there are eleven for a rare earth in a cubic site.[12]

We will focus attention on the linear magnetostriction along the ⟨001⟩ axis. For a strain

$$\epsilon_{xx}=\epsilon_{yy}=-\tfrac{1}{2}\epsilon_{zz},$$

the expression simplifies to

$$V_{\mathrm{OL}}=\left[\tfrac{1}{2}\alpha V(\Gamma_3,2)O_2^0-\frac{\sqrt{5}}{16\sqrt{3}}\beta V(\Gamma_3,4)(O_4^0-7O_4^4)+\frac{\sqrt{14}}{64}\gamma V(\Gamma_3,6)(O_6^0+3O_6^4)\right]e_3^1\cdots, \qquad (2)$$

where α, β, and γ are again the Stevens factors and the O_l^m are angular momentum operators.[13]

This interaction will lead to a macroscopic magnetostriction along the ⟨001⟩ axis,

$$\left(\frac{\delta l}{l}\right)_{\langle 001\rangle}=\frac{-c}{(C_{11}-C_{12})}\left[\tfrac{1}{2}\alpha V(\Gamma_3,2)\langle O_2^0\rangle+\ldots\right], \qquad (3)$$

where c is the rare-earth concentration, C_{11}, C_{12} are the host elastic coefficients, and $\langle O_2^0\rangle$, etc., are thermal averages of the operators when a magnetic field is applied along the ⟨001⟩ axis at a given temperature. Similar but more complicated expressions can be obtained for fields applied along other axes, and for the volume magnetostriction (which will also vary with field direction). In order to calculate the thermal averages we need to know the crystal-field parameters in the Hamiltonian:

$$\mathcal{H}=\beta C_4(O_4^0+5O_4^4)+\gamma C_6(O_6^0-21O_6^4).$$

In the calculations quoted below we will take $C_4=-65$ K, $C_6=14.3$ K derived from experiments on *Ag*Dy and *Ag*Er (Ref. 3) and we will assume that they are constant for all the heavy rare earths in Ag. This is consistent with results of other experiments.[2,4]

We will now summarize our results.

(i) The magnetostriction of *Ag*Gd is considerably smaller than that for alloys with rare earths having orbital moments, as would be expected. We will discuss this case elsewhere.[14]

(ii) The volume magnetostriction is small and positive. Thus for the 0.5% Dy alloy in an ap-

plied field of 35 kG along a ⟨001⟩ axis, $\Delta V/V = +2.7\times 10^{-7}$ which is, perhaps fortuitously, in excellent agreement with the prediction of a simple model in which C_4 and C_6 vary as R^{-5} and R^{-7}, respectively, where R is the interatomic distance.[13]

(iii) For ⟨100⟩-axis single crystals, the magnetostriction in applied fields parallel to the capacitance-cell axis, Fig. 1(a), was positive for Tb, Dy, and Ho alloys and negative for Er and Tm alloys. The magnetostriction thus follows the sign of the Stevens factor α as would be expected if only the first (electronic quadrupole) term in Eq. (3) was important. If we calculate theoretical curves, Fig. 1(b), using the first term of Eq. (3) only and a constant value of $V(\Gamma_3, 2) = +280$ K taken from EPR estimates,[5] we find that magnetostriction and EPR are in good agreement where they can be compared directly—i.e., under low applied fields on the Γ_7 ground-state systems *Ag*Er and *Ag*Dy. Results at higher fields and on other alloys are in tolerable agreement with the calculations; the general shapes of the curves and the temperature dependences (which we have not shown here) follow qualitatively the calculated behavior.

(iv) For ⟨111⟩-axis single crystals the parallel-field magnetostriction was again positive for Tb, Dy, and Ho alloys and negative for Er and Tm alloys, Fig. 2(a). If this magnetostriction is again ascribed purely to the electronic quadrupole term, the signs correspond to a negative value of the parameter $V(\Gamma_5, 2)$ in contradiction to the predictions of the point-charge model. Again, the low-field results on *Ag*Er are in good agreement with the values calculated using the EPR estimate $V(\Gamma_5, 2) = -700$ K (Ref. 7), but results for other alloys are in very poor agreement with calculations.

(v) Finally and unexpectedly, polycrystals showed qualitatively different behavior from the corresponding single crystals; for instance, a magnetostriction of the opposite sign or a magnetostriction that changed sign as a function of applied field. We show, Fig. 3, single-crystal and polycrystal data for *Ag*Dy. We have found similar contrasts between single-crystal and polycrystal behavior for *Ag*Er and *Ag*Ho but not for *Ag*Tb or *Ag*Tm. However, these polycrystal samples although carefully handled had not been annealed before measuring; after a thorough anneal the same samples gave results in line with the data on the monocrystals (which had been annealed). It appears that the magnetostriction is very sensitive to the strain state in these alloys.

We suggest that for a fuller understanding of what turns out to be a more complicated phenomenon than expected, it is necessary to take into consideration three factors which have been neglected up to now: ion-lattice interactions of higher order than quadrupole, effects of the local magnetostriction energy, and strain effects. The second is the energy associated with the local magnetostrictive changes of atomic distances around a rare-earth site and in general will vary strongly depending on the magnetization direction.

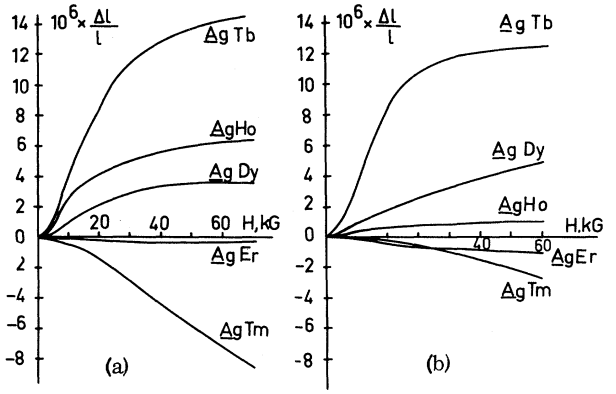

FIG. 1. (a) Experimental parallel-magnetostriction data for applied field along the ⟨001⟩ axes of silver–0.5%-rare-earth single crystals at 1.4 K. (b) Calculated parallel magnetostriction for the same conditions as in (a). Parameters used in the calculation are $C_4 = -65$ K, $C_6 = 14.3$ K, and $V(\Gamma_3, 2) = +280$ K (see text).

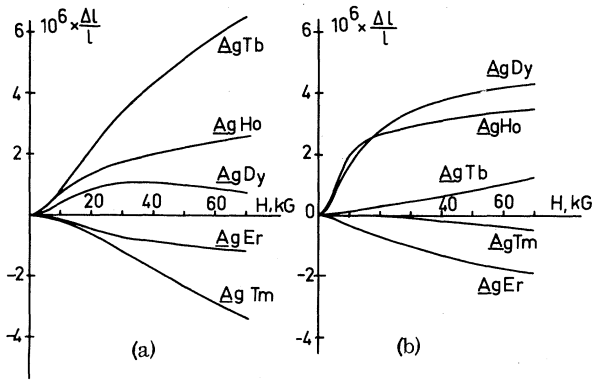

FIG. 2. Experimental parallel-magnetostriction data for applied field along the ⟨111⟩ axes of silver–0.5%-rare-earth single crystals at 1.4 K. (b) Calculated parallel magnetostriction for the same conditions as (a). Parameters used in the calculation are $C_4 = -65$ K, $C_6 = 14.3$ K, and $V(\Gamma_5, 2) = -700$ K.

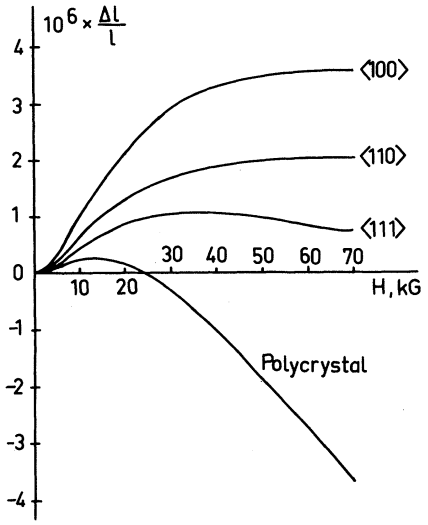

FIG. 3. Experimental parallel-magnetostriction data for Ag–0.5%-Dy single crystals along the ⟨100⟩, ⟨111⟩, and ⟨110⟩ axes and for a Ag–0.5%-Dy polycrystal, at 1.4 K.

To minimize the total magnetic-plus-magnetostrictive energy the local magnetization direction will in general not be collinear with the applied magnetic field. The combination of this noncollinearity and higher-order ion-lattice terms could help explain the differences between the calculated and experimental single-crystal curves in Figs. 1 and 2. The anomalous behavior of the polycrystal data such as that shown in Fig. 3 seems to be associated with strain in the samples. We have no simple explanation of this sensitivity to strain.

We would like to thank D. Spanjaard, P. Levy, A. Fert, and D. Wohlleben for helpful discussions. Laboratoire de Physique des Solides is a Laboratoire associé au Centre National de la Recherche Scientifique.

[1]D. Griffiths and B. R. Coles, Phys. Rev. Lett. 16, 1093 (1966).

[2]G. Williams and L. L. Hirst, Phys. Rev. 185, 407 (1969).

[3]S. Oseroff, M. Passeggi, D. Wohlleben, and S. Schultz, Phys. Rev. B 15, 1283 (1977).

[4]A. Fert, R. Asomoza, D. H. Sanchez, D. Spanjaard, and A. Friedrich, Phys. Rev. B 16, 5040 (1977).

[5]D. Arbilly, G. Deutscher, E. Grunbaum, R. Orbach, and J. T. Suss, Phys. Rev. B 12, 5068 (1975).

[6]S. A. Dodds and J. Sanny, Phys. Rev. B 18, 39 (1978).

[7]G. E. Barberis, J. F. Sussuna, C. Rettori, and C. A. Pelá, Solid State Commun. 23, 603 (1977).

[8]J. J. Rhyne, in *Magnetic Properties of Rare Earth Metals*, edited by R. J. Elliot (Plenum, New York, 1972).

[9]P. Morin, J. Ronchy, and E. duTremolet de Lacheisserie, Phys. Rev. B 16, 3182 (1977).

[10]K. Nicholson, U. Häfner, E. Müller-Hartmann, and D. Wohlleben, Phys. Rev. Lett. 41, 1325 (1978).

[11]We are grateful to Professor Chapelle for putting the resources of his laboratory at our disposal and to Mr. Godard for preparing the single crystals.

[12]See, e.g., M. Blume and R. Orbach, Phys. Rev. 127, 1587 (1967); M. Borg, R. Buisson, and C. Jacolin, Phys. Rev. B 1, 1917 (1970); J. M. Baker and D. van Ormondt, J. Phys. C 7, 2060 (1974).

[13]M. T. Hutchings, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. 16, p. 227.

[14]I. A. Campbell and G. Creuzet, to be published.