Magnetostriction in $PrBa_2Cu_3O_{7-\delta}$ single crystal

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(Submitted 10 January 1990)
Pis'ma Zh. Eksp. Teor. Fiz. **51**, No. 3, 172–175 (10 February 1990)

The anisotropic magnetostriction of a $PrBa_2Cu_3O_{7-\delta}$ single crystal has been studied for the first time. Anomalies have been found in this magnetostriction in the case **H**⊥**c**. The results are used to discuss the mechanism for the suppression of superconductivity in this compound.

The replacement of 60% of the Y in $YBa_2Cu_3O_7$ by Pr is known to suppress the superconductivity.[1,2] In order to determine the nature of this effect, it is important to determine the valence of praseodymium in the 1-2-3 compounds. The reports on this valence have been contradictory, ranging from 3, according to an x-ray spectral analysis,[2,4] to 3.5–4 according to magnetic measurements.[1,3] It is accordingly worthwhile to study characteristics which are sensitive to an instability of the Pr valence state. One such characteristic is the magnetostriction,[5] which has not been studied in $PrBa_2Cu_3O_7$. Another circumstance which attracts interest to the magnetostriction of $PrBa_2Cu_3O_7$ is that an antiferromagnetic order arises below $T_N = 17$ K in this compound.[6] A magnetic field may induce a change in the magnetic structure of the nature of a metamagnetic or orientational transition. The magnetostriction *measured on single crystals* is extremely sensitive to phase transitions of this type.

Single crystals of $PrBa_2Cu_3O_7$ were grown from a molten solution of nonstoichiometric composition as it was cooled from 1150 °C to 400 °C at a rate of 5 deg/h. The magnetostriction was measured in pulsed magnetic fields up to 75 kOe by means of a contact piezoelectric transducer (with a sensitivity $\sim 10^{-8}$). The magnetostriction was measured along the **a** and **b** axes of the orthorhombic crystal with an external magnetic field in various orientations (the axes were identified by an x-ray method) over the temperature range 4.2–200 K. It can be seen from Fig. 1 that the magnetostriction is extremely anisotropic at $T = 4.2$ K, differing in both magnitude and sign for different orientations of the field. The magnetostriction isotherm has its simplest shape when the field is oriented along the c axis. In this case, the values of λ_{ac} and λ_{bc} (the first index specifies the measurement direction, and the second the direction of the magnetic field) differ only slightly from each other, are negative in sign, and vary in proportion to the square of the magnetic field. The field dependence of the longitudinal magnetostriction, λ_{aa} and λ_{bb}, is qualitatively similar to that in the case **H**‖**c** but more complex. In comparatively weak fields the magnetostriction is negative in both cases. It increases with increasing field. The positive magnetostriction is a quadratic function of the field [Fig. 1(b)]. On the field dependence of the transverse magnetostriction, λ_{ab} and λ_{ba}, there is a slope change at a certain field ~ 20 kOe, as has been observed during orientational transitions ion antiferromagnets.[7] As the temperature is

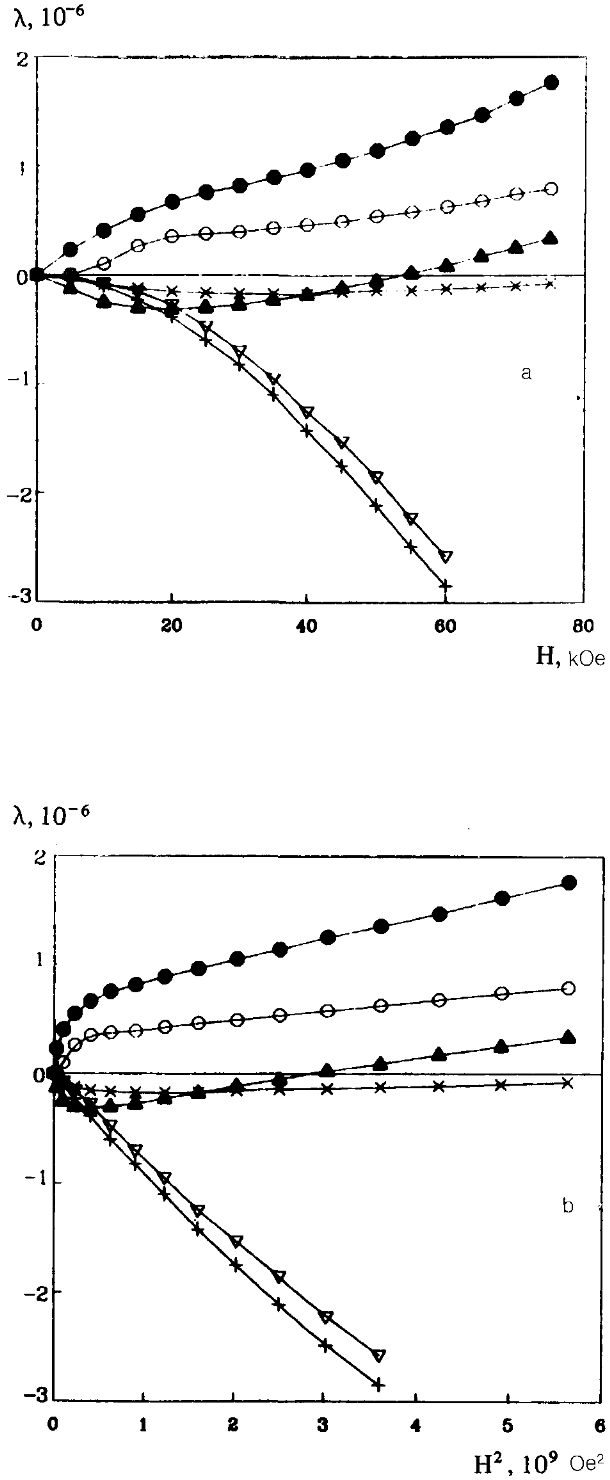

FIG. 1. Magnetostriction isotherms at $T = 4.2$ K. a: Field dependence ●—λ_{ab}; ○—λ_{ba}; ▲—λ_{aa}; ×—λ_{bb}; ▽—λ_{bc}; +—λ_{ac}. b: The same quantities versus the square of the magnetic field.

raised in the interval 4.2–80 K, the magnetostriction decreases $\sim(T-\theta)^{-2}$ ($\theta=-17$ K) for all field orientations. At a certain temperature there is a slope change on the plot of $\lambda_{ac,bc}^{-1/2}(T)$ (Fig. 2). The temperature-field dependence of the magnetostriction is thus described by the following simple expression over a wide temperature range:

$$\lambda_{nh}(H,T)=\lambda_{nh}^{(0)}[\mu_B H/(T-\theta)]^2. \tag{1}$$

Let us examine some possible mechanisms for magnetostriction in $PrBa_2Cu_3O_{7-\delta}$, primarily the mechanism involving a valence instability of the praseodymium. In a $PrBa_2Cu_3O_{7-\delta}$ sample, the Pr^{3+} and Pr^{4+} ions are at equilibrium. By virtue of the difference in the magnetic properties of these ions, this equilibrium is sensitive to changes in the magnetic field. A shift of the equilibrium causes a lattice deformation because of the difference between the ionic radii of Pr^{3+} and Pr^{4+}. We denote by ν_H and $1-\nu_H$ the concentrations of Pr^{3+} and Pr^{4+} ions in the field **H**. The magnetostriction, e.g., λ_{ah}, is then given by $\lambda_{ah}(H,T)=[a(\nu_H)-a(\nu_0)]/a(\nu_0)$, where a is the lattice constant. A similar magnetoelastic-coupling mechanism was discussed in Ref. 5, but only for the bulk magnetostriction, since the anisotropy of the *g*-tensor of the ground state of the rare-earth ions in the crystal field

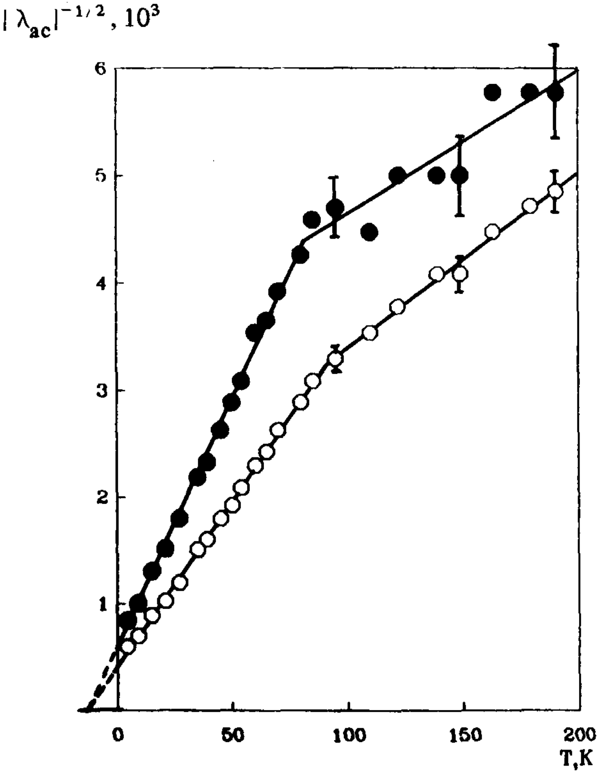

FIG. 2. Temperature dependence of $|\lambda_{ac}|^{-1/2}$ at H = 60 kOe (open circles) and at H = 40 kOe (filled circles).

was disregarded. According to estimates,[8] three closely spaced, low-lying levels of the Pr^{3+} ion are separated by a gap ~ 900 K from the excited states. In other words, they form a random triplet. The ground state of Pr^{4+} is a Kramers doublet, isolated by a gap ~ 200 K. A calculation leads to expression (1) with

$$\lambda_{ah}^{(o)} = \frac{a(0)-a(1)}{a(0)} \nu_0(1-\nu_0) \sum_{\alpha=xyz} (g_{3\alpha}^2/12 - g_{4\alpha}^2/8)h_\alpha^2, \tag{2}$$

where $g_{3\alpha}$ and $g_{4\alpha}$ are the diagonal components of the g-tensors of the ground triplet and ground doublet of Pr^{3+} and Pr^{4+}. This mechanism explains the observed temperature-field dependence of the magnetostriction in $PrBa_2Cu_3O_{7-\delta}$ if, following Ref. 5, we assume that ν_0 does not depend on the temperature. Working from the assumption that this mechanism is predominant in the magnetostriction of $PrBa_2Cu_3O_{7-\delta}$, we find an estimate of ν_0. The sum on the right side of (2) is equal to unity in absolute value. Assuming $\nu_0 \ll 1$, we find

$$\nu_0 = \frac{|\lambda_{ah}^{(o)}|}{[a(0)-a(1)]/a(0)}. \tag{3}$$

We use the experimental values $\lambda_{ac}^{(0)} = -8.8 \times 10^{-5}$, and as $a(0)$ and $a(1)$ we use the lattice constants of the compounds $PrBa_2Cu_3O_7$ and $LuBa_2Cu_3O_7$ (Ref. 9), since the ionic radii of Pr^{4+} and Lu^{3+} are approximately the same.[10] As a result, we find $[a(0)-a(1)]/a(0) = 1.0 \times 10^{-2}$, from which we in turn find $\nu_0 \sim 1\%$.

We now consider the single-ion component of the magnetostriction. According to Ref. 11, the single-ion magnetostriction of rare-earth compounds is given by

$$\lambda_{nh}(H,T) = -\sum_{\alpha\beta\gamma\delta} \sum_{nm} a_n B_{nm}^{\alpha\beta} S_{\alpha\beta\gamma\delta} n_\gamma n_\delta \langle \delta Y_n^m(\hat{J}) \rangle_H, \tag{4}$$

where a_n are the Stevens coefficients, $B_{nm}^{\alpha\beta}$ are magnetoelastic constants, $S_{\alpha\beta\gamma\delta}$ are components of the elastic compliance tensor, and $\langle \delta Y_n^m(\hat{J}) \rangle_H = \langle Y_n^m(\hat{J}) \rangle_H - \langle Y_n^m(\hat{J}) \rangle_0$ is the change in the multipole moments of the rare-earth ions in the magnetic field. To calculate the quantities $\langle \delta Y_n^m(\hat{J}) \rangle_H$ for the Pr^{3+} ions, which determine the temperature-field dependence of the magnetostriction in $PrBa_2Cu_3O_{7-\delta}$ according to (4), we use the high-temperature approximation $T \gg \mu_B H$. We find $\langle \delta Y_n^m(\hat{J}) \rangle_H = A_{nm}^h (\mu_B H/T)^2$. The coefficient A_{nm}^h depends on only the direction of the magnetic field:

$$A_{nm}^h = \frac{8}{75} \{ Sp[Y_n^m(\hat{J})(\hat{J}h)^2] - Sp[Y_n^m(\hat{J})] \sum_{\alpha=xyz} g_\alpha^2 h_\alpha^2/6 \}, \tag{5}$$

The trace (Sp) is over the states of the ground triplet. Incorporating the R-R interaction in the standard approximation, i.e., using the replacement $H \to H + H_{ex} = HT/(T-\theta)$, $T > T_N$, we again find expression (1), with

$$\lambda_{nh}^{(o)} = -\sum_{\alpha\beta\gamma\delta} \sum_{nm} a_n B_{nm}^{\alpha\beta} S_{\alpha\beta\gamma\delta} n_\gamma n_\delta A_{nm}^h, \tag{6}$$

and $\theta \approx -T_N = -17$ K. Under the assumptions above, both of these mechanisms thus lead to the observed temperature dependence of the magnetostriction. This result is evidence that the Pr ions are for the most part in the Pr^{3+} state (the Pr^{4+} admixture is $\nu_0 \sim 10^{-2}$). Under these conditions the reason for the disruption of superconductivity in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ may be a *pf* hybridization or transitions $Pr^{3+} + p \rightarrow Pr^{4+}$, where p is a hole in a CuO_2 plane. In other words, from the mathematical standpoint this mechanism is similar to the known mechanism for the disruption of superconductivity by magnetic impurities[12] and is not a compensation for holes, as has been suggested previously.[1] The same reaction is apparently responsible for the magnetic order in $PrBa_2Cu_3O_7$. The anomalies which we have observed in the field dependence of the magnetostriction in the case $\mathbf{H}_\perp \mathbf{c}$, and which apparently stem from magnetic phase transitions, may prove important for reaching an understanding of the magnetic properties and their interplay with superconducting order in these compounds.

[1] C.-S. Jee *et al.*, Solid State Commun. **69**, 379 (1989); A. Matsuda *et al.*, Phys. Rev. B **338**, 2910 (1988).

[2] U. Neukirch *et al.*, Europhys. Lett. **5**, 567 (1988).

[3] E. Moran *et al.*, Solid State Commun. **67**, 369 (1988); D. B. Mitzi *et al.*, Phys. Rev. B **38**, 6667 (1988).

[4] L. Soderholm and G. L. Goodman, J. Solid State Chem. **81**, 121 (1989).

[5] J. Zieglowski *et al.*, Phys. Rev. Lett. **56**, 193 (1986).

[6] W.-H. Li *et al.*, "Magnetic Order of Pr in $PrBa_2Cu_3O_7$," Preprint, 1988.

[7] K. P. Belov *et al.*, *Orientational Transitions in Rare-Earth Magnetic Materials,* Nauka, Moscow, 1979.

[8] V. Nekvasil *et al.*, J. Phys. (Paris) **49**, Suppl. No. 12, C8-2177 (1988).

[9] N. E. Alekseevskiĭ *et al.*, Zh. Eksp. Teor. Fiz. **94(5)**, 281 (1988) [Sov. Phys. JETP **67**, 1025 (1988)].

[10] R. D. Shannon, Acta Crystallog. A **32**, 751 (1976).

[11] N. F. Vedernikov *et al.*, Zh. Eksp. Teor. Fiz. **94(8)**, 358 (1988) [Sov. Phys. JETP **67**, 1719 (1988)].

[12] A. A. Abrikosov and L. P. Gor'kov, Zh. Eksp. Teor. Fiz. **39**, 178 (1960) [Sov. Phys. JETP **XXX**, XXX (year)].

Translated by Dave Parsons