Giant magnetostriction in the Van Vleck paramagnet $LiTmF_4$

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Stimulated longitudinal magnetostriction was measured at helium temperatures for the first time in a tetragonal $LiTmF_4$ crystal with Tm^{3+} ions in the singlet ground state. A strong magnetostriction anistropy, which varied from $<10^{-6}$ for **H**||[001] to the enormous value of -1.1×10^{-3} for **H**||[100] in a $\leqslant$30-kOe magnetic field, was observed.

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The stimulated magnetostriction of paramagnetic crystals is proportional to the ir magnetization and external magnetic field. In normal paramagnets with a magnetic ground state (effective spin of $\frac{1}{2}$), the magnetic moment is proportional to $\tanh(g\beta H/2kT)$; therefore, an increase in magnetostriction, which is quadratic with respect to the magnetic field in weak fields, is linear under saturation conditions ($g\beta H\sim kT, g\beta H$ is the Zeeman splitting of the ground state). In Van Vleck paramagnets the magnetic moment induced by the external field is proportional to $\beta H/\Delta$, where Δ is the energy of excited states in the crystal field, and does not saturate up to fields $H\sim\Delta/\beta$. In concentrated, rare-earth (RE) normal paramagnets at helium temperatures in fields with an intensity of several tens of kOe, the magnetostriction reaches an enormous value of the order of 10^{-4} (Ref. 1); so far as we know, the magnetostriction in Van Vleck paramagnets has not been measured; however, as the basic arguments presented above show, when the excited Stark sublevel is sufficiently close to the singlet ground state ($\beta H\sim\Delta$), the magnetostriction in a Van Vleck paramagnet can be, in comparable fields, of the same order of magnitude as that in a normal paramagnet and the magnetostriction in normal paramagnets, which is related to the induced magnetic moment, can dominate in a strong magnetic field ($kT<\beta H\sim\Delta$). Our measurements of the magnetostriction in an $LiTmF_4$ crystal confirmed these theoretical conclusions.

The $LiTmF_4$ crystal has the structure of scheelite[2]; the unit cell contains two magnetically equivalent Tm^{3+} ions, and the lower part of the energy spectrum of Tm^{3+} ions includes three Stark sublevels of the $^3H_6$ ground term which is split a in crystal field of S_4 symmetry: the ground singlet Γ_1, the non-Kramers doublet $\Gamma_{3,4}$ with an energy of ~30 cm^{-1} and the singlet Γ_2 with an energy of ~60 cm^{-1}. The remaining Stark sublevels have an energy greater than 300 cm^{-1} (Ref. 3).

The relative change in the length $\Delta l/l$ of cylindrical samples with a diameter of 5–6 mm and a length of 6–7 mm along the [001], [110], and [100] crystallographic directions was measured as the magnetic field parallel to the sample was increased from 0 to 30 kOe in the temperature interval 1.5–4.2 K. We were unable to detect magnetostriction in a field $\mathbf{H}||[001]$ using instrumentation with a sensitivity of at least 10^{-6}. The sample deformation in a magnetic field perpendicular to the crystal symmetry axis increased rapidly with increasing field intensity and reached enormous values -11×10^{-4} and -5.5×10^{-4} along the [100] and [110] axes, respectively, at $H=30$ kOe; the temperature variations do not influence the deformation within the limits of the aforementioned interval. The measurement results are shown in Fig. 1. At weak fields the dependence of the deformation on the field is described by a quadratic function $\Delta l/l \sim -kH^2$; at fields $H>10$ kOe this dependence is stronger.

The data obtained agree both qualitatively and quantitatively with the results of a theoretical analysis performed within the framework of the single-frequency magnetostriction mechanism. The values of the longitudinal static magnetostriction are linearly related to the components e_{ij} of the strain tensor: $(\Delta l/l) = \sum_{ij} n_i n_j e_{ij}$, where n_i are the direction cosines of the magnetic field. The tensor components of the strain induced by the external magnetic field are determined from the minimum free energy of the paramagnet. The population of the excited states of the paramagnet's ions can be ignored at low temperatures ($kT<\Delta$), and the magnetostriction is determined by the correction to the ground-state energy for the lattice deformation in the magnetic field. This correction, which is an even function of the field, can be calculated in a weak field $\beta H \ll \Delta$ in the third approximation of perturbation theory, where the Zeeman energy $\mathscr{H}_z g_J \beta \mathbf{HJ}$ ($\mathbf{J}$ is the angular momentum operator of the rare-earth ion) appears twice as a perturbation and the variation of the ion energy in the crystal field as a result of lattice deformation $\mathscr{H} = \sum_{nmkl} B^m_{n,kl} O^m_n e_{kl}$ (O^m_n are the irreducible tensor operators and $B^m_{n,kl}$ are the parameters of the linear electron-phonon interaction[1]) appears once as a perturbation. Within the framework of the stated approximations the longitudinal

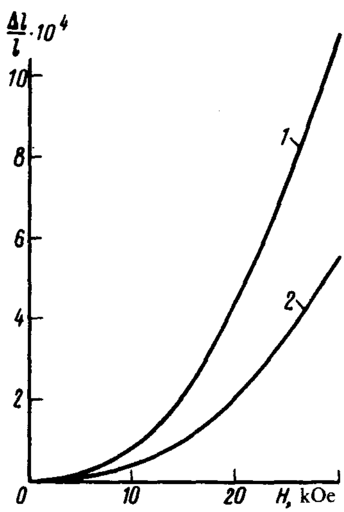

FIG. 1. Dependence of static magnetostriction $\Delta l/l$ on the magnetic field. 1, $\mathbf{H}||[100]$; 2, $\mathbf{H}||[110]$.

magnetostriction is described by the expression:

$$\frac{\Delta l}{l} = -\frac{nH^2}{v_0}(g_J\beta)^2 \sum_{ijklpqnm} n_i n_j S_{ijkl} B^m_{n,kl} n_p n_q$$

$$\times \{ \sum_{\alpha\beta} \Delta_\alpha^{-1} \Delta_\beta^{-1} [<0|J_p|\alpha><\alpha|J_q|\beta><\beta|O_n^m|0>]_s$$

$$-<0|O_n^m|0> \sum_\alpha \Delta_\alpha^{-2} <0|J_p|\alpha><\alpha|J_q|0> \}, \qquad (1)$$

where n is the number of paramagnetic ions in a cell with volume v_0, S_{ijkl} are the elasticity moduli, $|0\rangle$, $|\alpha\rangle$ are, respectively, the cut-vectors of the ground and excited states, and the symbol $[.....]_S$ denotes the symmetrized sum of the three products of the matrix elements.

In the case of interest to us -- Tm^{3+} ions in the $LiTmF_4$ crystal -- we can restrict ourselves in the summations over the excited states to a consideration of the aforementioned doublet $\Gamma_{3,4}$ and singlet Γ_2. Since these states do not mix with the ground singlet Γ_1 in a magnetic field $\mathbf{H}||[001]$, the theory predicts an insignificant striction along the optical axis (the minimum is two orders of magnitude smaller than in the magnetic field perpendicular to the optical axis, in agreement with the measurement data). Quantitative estimates of the longitudinal magnetostriction in the {001} plane was estimated using Eq. (1), the elastic constants of the $LiYF_4$ isomorphous crystal (Ref. 2), and the electron-phonon coupling parameters that were calculated within the framework of the charge-exchange model.[4] For the coefficients of proportionality between $\Delta l/l$ and H^2 we obtained the values (in units of 10^{-6} kOe^{-2}) $k = 0.69$ (0.80; $\mathbf{H}||[100]$) and $k = 0.18$ (0.33; $\mathbf{H}||[110]$), which agree in magnitude and sign with the measurements (in the parentheses). We note that the interaction of the rare-earth ions with the rhombic deformation $e_{xx} - e_{yy}$ is the major contribution to magnetostriction. In the case of a strong field the calculations using Eq. (1) give a strain that is too small; more precise estimates are possible if the total energy matrix of a rare-earth ion in crystal and magnetic fields is numerically diagonalized.

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Generally, the change in energy of the rare-earth ion should be taken into account not only because of uniform macroscopic deformation but also because of internal deformation (displacement and polarization of sublattices); therefore, the quantities $B^m_{n,kl}$ should be considered as effective renormalized parameters of electron-phonon coupling.

[1]K. P. Belov, V. I. Sokolov, and Tkhan Dyk Khien, Fiz. Tverd **10**, 3706 (1968) [Sov. Phys. Solid State **10**, 2946 (1968)].
[2]P. Blanchfield and G. A. Sauders, J. Phys. C **12**, 4673 (1979).
[3]H. P. Christensen, Phys. Rev. B **19**, 6573 (1979).
[4]B. Z. Malkin, A. I. Ivanenko, and I. B. Aizenberg, Fiz. Tverd. Tela **12**, 1873 (1970) [Sov. Phys. Solid State **12**, 1491 (1970)].