

Low-temperature anomaly of the elastic modulus in $\text{Tb}_2\text{Ti}_2\text{O}_7$

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The elastic modulus in $\text{Tb}_2\text{Ti}_2\text{O}_7$ decreases appreciably at low temperatures. The electron-strain interaction and the particular features of the structure of the lower-lying energy levels of a Tb^{3+} ion in the crystal field of the $\text{Tb}_2\text{Ti}_2\text{O}_7$ lattice are responsible for this effect. The critical temperature of the cooperative Jahn-Teller transition in $\text{Tb}_2\text{Ti}_2\text{O}_7$ is estimated to be $T_c \approx 0.1$ K.

Studies of the magnetic properties of the compound $\text{Tb}_2\text{Ti}_2\text{O}_7$ with a pyrochlore-type cubic structure (space group $Fd\bar{3}m$) have shown that near the ground state of a Tb^{3+} ion (non-Kramers doublet) there is a doubly degenerate excited level situated at a distance $\Delta = 16$ K (Ref. 1). A level structure of this sort, when combined with a moderately strong electron-deformation coupling (evidence of such coupling is the enormously large values of the magnetostriction of the paramagnetic dititanate¹ $\text{Tb}_2\text{Ti}_2\text{O}_7$), can account at low temperatures for the cooperative Jahn-Teller effect in this compound.

One of the effective ways of obtaining information on the magnitude of the Jahn-Teller interaction is from the analysis of the temperature dependence of the elastic moduli.²

In our experiment we studied the behavior of Young's modulus $\mathcal{E}(T)$ in $\text{Tb}_2\text{Ti}_2\text{O}_7$ in the temperature range 1.7–300 K. We calculated Young's modulus from the measurements of the longitudinal velocity of sound, using the method of composite vibrator (sample-quartz) with a natural oscillation frequency of 130 kHz. The measurements were carried out with four polycrystalline samples $\text{Tb}_2\text{Ti}_2\text{O}_7$ taken from different batches and with an isomorphic diamagnetic compound $\text{Y}_2\text{Ti}_2\text{O}_7$. The results of the measurements are shown in Fig. 1.

We see that at temperatures between 100 K and 300 K the $\mathcal{E}(T)$ curve has a standard shape, while Young's modulus of $\text{Tb}_2\text{Ti}_2\text{O}_7$ falls off anomalously by $\sim 25\%$ in the temperature interval $1.7 < T < 95$ K (curve 1). A comparison with the results for $\text{Y}_2\text{Ti}_2\text{O}_7$ (curve 2) shows that the elastic modulus decreases because of the presence of the Tb^{3+} magnetic ions in $\text{Tb}_2\text{Ti}_2\text{O}_7$.

A microscopic calculation on the basis of a Hamiltonian, which takes into account the interaction of $4f$ electrons with the static crystal field and with the deformation field $\epsilon_{\alpha\beta}$, showed that this effect can be explained in terms of the deformation-induced change of the crystal field, without allowance for other interactions of any sort (exchange interaction, quadrupole-quadrupole interaction).

In the calculation we have expanded the free energy in a series in the parameters

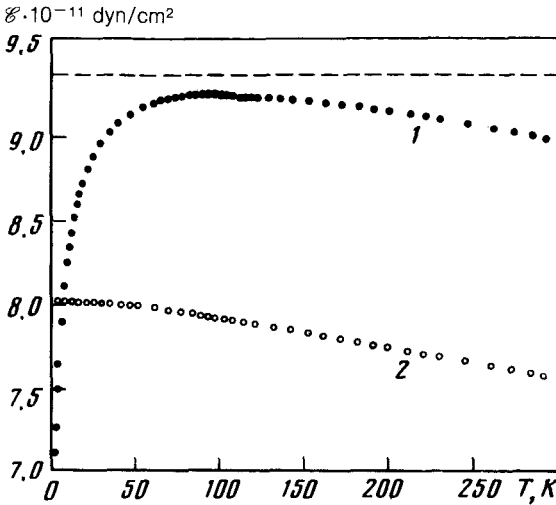


FIG. 1. The temperature dependence of Young's modulus. 1— $Tb_2Ti_2O_7$; 2— $Y_2Ti_2O_7$; the dashed curve—the value of \mathcal{E}_∞ for $Tb_2Ti_2O_7$.

$\epsilon_{\alpha\beta}$ to within second-order terms inclusively.³ In terms of a system of two doublets, which have nonzero matrix elements of the electron-strain interaction and which appear in the Tb^{3+} ions in $Tb_2Ti_2O_7$ (Ref. 1), we can write the expression for $\mathcal{E}(T)$ in the form

$$\mathcal{E}(T) = \mathcal{E}_\infty + \delta \mathcal{E}(T) = \mathcal{E}_\infty + \Phi(T). \quad (1)$$

Here \mathcal{E}_∞ is Young's modulus which results from the elastic lattice energy without consideration of the electron-strain interaction, and the temperature dependence of the elastic modulus is given by the function

$$\Phi(T) = \sum_{p=1}^4 e_p \varphi_p(\Delta/2T), \quad (2)$$

where $\varphi_1(x) = -x(1 + \tanh x)$, $\varphi_2(x) = -2 \tanh x$, $\varphi_3(x) = -x(1 - \tanh x)$, and $\varphi_4 = -x/2(1 - \tanh^2 x)$. The first three terms of sum (2) correspond to the contribution from the nondiagonal matrix elements between the components of the main doublet (e_1), the excited doublet (e_3), and the doublets (e_2). The fourth term contains the diagonal matrix elements which account in first-order perturbation theory for the lattice-strain-induced relative shift of the two doublets. The shape of the corresponding temperature functions $\varphi_p(\Delta/2T)$ with $\Delta = 16$ K is shown in Fig. 2.

A comparison of the experimental data for various polycrystalline samples (whose porosity was in the range of 18 to 32%) showed that the $\mathcal{E}(T)$ dependence remains the same for each sample but the values of the parameters \mathcal{E}_∞ and e_p differ appreciably. The latter circumstance can be explained by the fact that the strain tensor of an individual crystal ($\epsilon_{\alpha\beta}^{cryst}$) differs from the strain tensor of the entire sample ($\epsilon_{\alpha\beta}^{sample}$) because of the presence of inhomogeneities in the space between the grains.

Using a very simple model in which $\epsilon_{\alpha\beta}^{cryst} = \alpha_s \epsilon_{\alpha\beta}^{sample}$, we find instead of (1) the

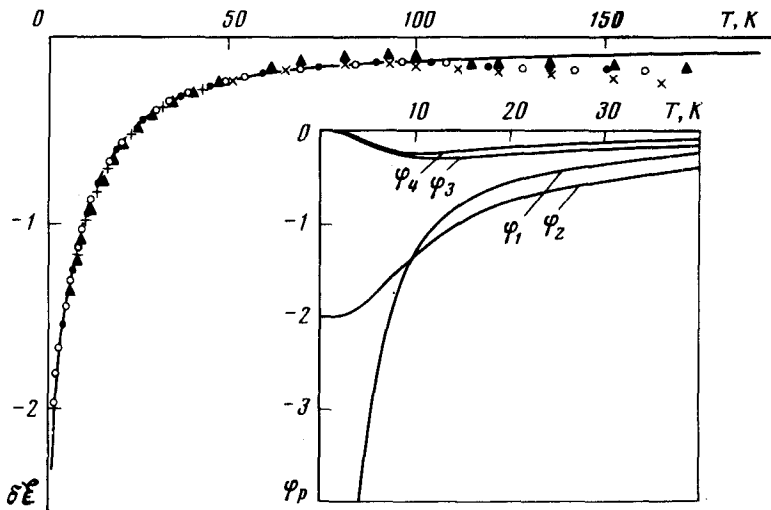


FIG. 2. The temperature dependence of the component of Young's modulus ($\delta\mathcal{E}$) attributable to the strain-induced change of the crystal field in $\text{Tb}_2\text{Ti}_2\text{O}_7$. ●, ○, ▲, and ×—experimental points for the polycrystalline samples taken from different batches; solid curve—calculated for the function $k_1\Phi(T)$.

following expression for the s -th sample:

$$\mathcal{E}^{(s)} = \mathcal{E}_\infty^{(s)} + k_s \Phi(T), \quad (3)$$

where $k_s = \alpha_s^2$, and $\Phi(T)$ is a universal function found in (2). We can infer from this model that the experimental values $\delta\mathcal{E}^{(s)}$ for various polycrystalline samples are described, within a constant k_s , by the temperature function $\Phi(T)$ alone.

As can be seen from Fig. 2, the results for the four samples, given (by the points) in the coordinates $\delta\mathcal{E} = k_1(\mathcal{E}^{(s)} - \mathcal{E}_\infty^{(s)})/k_s$ and T , fit on a single curve which in turn matches the calculated curve $k_1\Phi(T)$ (the solid curve) well. The parameters k_1, e_p were determined from the experimental values of $\mathcal{E}(T)$ for the reference sample ($s = 1$) by the method of least squares with the use of $\Delta = 16$ K from Ref. 1.

We found that at $4 \leq T \leq 100$ K the second term in sum (2) is the dominant term in the temperature dependence of the elastic modulus ($k_1 e_2 = 0.7 \times 10^{11}$ dyn/cm²). The importance of this term increases with decreasing distance between the doublets. At lowest possible temperatures ($T < 4$ K), the key term in the temperature dependence $\mathcal{E}(T)$ is the first term which is proportional to $1/T$ ($k_1 e_1 = 0.06 \times 10^{11}$ dyn/cm²). The third and fourth terms in sum (2) are negligible terms over the entire temperature interval.

In the expression for the elastic modulus, the nonvanishing term, proportional to $1/T$, necessarily leads to a decrease of the elastic modulus to zero at a finite temperature. This behavior corresponds to a Jahn-Teller cooperative structural phase transition induced by an electron-strain interaction.² From the instability condition

$$\mathcal{E}^{(s)} = \mathcal{E}_\infty^{(s)} + k_s \Phi(T_c) = 0 \quad (4)$$

we estimate the critical temperature of $\text{Tb}_2\text{Ti}_2\text{O}_7$ to be $T_c \simeq 0.1$ K.

The experimental studies conducted by us thus show that the anomalous behavior of the elastic modulus of $\text{Tb}_2\text{Ti}_2\text{O}_7$ at low temperatures may be viewed as a manifestation of the Jahn-Teller interactions in this compound, caused by the coupling between the electronic states of a Tb^{3+} ion and the lattice strain.

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