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## Elastic Properties of DySb near the Magnetic and Structural Phase Transition\*

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The shear elastic constants  $c_\theta = (c_{11} - c_{12})/2$  and  $c_{44}$  have been measured in DySb.  $c_{44}$  shows a small softening of about 0.6% at the phase transition, while  $c_\theta = (c_{11} - c_{12})/2$  exhibits a 58% drop. The large change in  $c_\theta = (c_{11} - c_{12})/2$  occurs over a temperature range of more than 200 °K. The dominant mechanism for the softening of the elastic constant  $c_\theta = (c_{11} - c_{12})/2$  is a Jahn-Teller strain coupling. Strong-biquadratic pair interactions are present which compete with the strain coupling.

There has been much interest recently in the magnetic and structural phase transition in DySb.<sup>1-3</sup> The system was originally thought to undergo successive magnetic and structural transitions at 9.5 and 11.5 °K, respectively. However, a recent study of the magnetic properties<sup>3</sup> revealed a single first-order magnetic and structural phase transition which occurred at 9.5 °K. This work left unresolved the question of the microscopic origin of the transition. As was suggested, sound-velocity measurements should help to resolve this point. In this paper (i) we report the results of the first measurement of the shear elastic constants  $c_\theta = \frac{1}{2}(c_{11} - c_{12})$  and  $c_{44}$  through the phase transition<sup>4</sup> and (ii) we present the results of our fit to the elastic constant  $c_\theta$ .

We find that the  $E_g(\Gamma_{31}^+)$  strain coupling to the dysprosium ions is the dominant mechanism for the softening of the elastic constant  $c_\theta$ . By itself,

this coupling would produce a cooperative first-order Jahn-Teller phase transition at about 6 °K. However, the elastic constant  $c_\theta$  does not continue to soften past 9.5 °K because the exchange interactions present in DySb cause the system to undergo a first-order phase transition at 9.5 °K.

We studied two samples<sup>5</sup> of DySb, both of which were originally rectangular in shape, with the sides being normal to [100] axes. The corners of each sample were polished flat to obtain faces normal to the [110] axis, with the resulting faces being approximately 1.5 mm on a side. Sample I was 2.1 mm in length, while sample II was 1.8 mm. The sound-velocity changes were measured using a pulse-echo phase-comparison technique which is described in detail elsewhere.<sup>6</sup>

In Fig. 1 we show the change in the elastic constant  $c_\theta$  as function of temperature from 3.5 to 360 °K for sample I. Sample II gave essentially

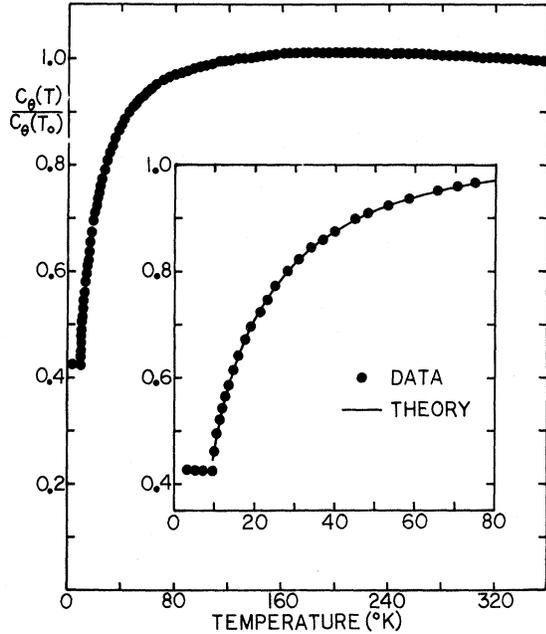


FIG. 1. Change in  $c_\theta(T) = \frac{1}{2}(c_{11} - c_{12})$  as a function of temperature.  $c_\theta(T_0 = 325^\circ\text{K}) = (7.4 \pm 0.4) \times 10^{11}$  erg/cm<sup>3</sup>; propagation direction, [110]; frequency, 20 MHz. Inset shows fit to Eq. (4) by using  $(g_\theta)^2 = 14 \times 10^{-4}$  K,  $I_\theta = -4 \times 10^{-4}$  K, and  $c_\theta = 1.056 c_\theta(325^\circ\text{K})$ . The uncertainty in the data is approximately given by the size of the data points.

identical results. The elastic constant is seen to decrease with decreasing temperature over a wide range, starting in the vicinity of 200 °K and reaching a minimum of 0.42 of  $c_\theta(325^\circ\text{K})$  at 9.5 °K.<sup>4</sup> At the transition we observe a sharp increase of 0.2% followed by a slow increase down to 3.5 °K. The elastic constant would be expected to return to near its high-temperature value below the transition if the sample was in a single-domain state. Our samples were not clamped to form such a state, therefore our results for  $T < T_N$  represent an average elastic constant over many domains.

The measurement of  $c_{44}$  also showed a softening of the elastic constant as the transition was approached. For this case, the over-all effect was only 0.6%, in contrast to the large change in  $c_\theta$ . We find  $c_{44} = (2.6 \pm 0.1) \times 10^{11}$  erg/cm<sup>3</sup> at 325 °K.

The separation of the background elastic constant changes from those due to the coupling to the soft mode is relatively difficult for  $c_\theta$  because the softening extends to temperatures near 300 °K. Normally, the high-temperature elastic constant is fitted to a polynomial in temperature and this function is extrapolated down to 0 °K. A similar extrapolation for DySb is difficult since we were unable to obtain reliable data above 360 °K. A

test of various functions which gave reasonable fits to the data above 300 °K showed that the intercept at 0 °K should be in the range between 1.03–1.07 times  $c_\theta(325^\circ\text{K})$ . As will be seen later, we allowed the background elastic constant to be a variable parameter in our fit to the data and found a 0 °K intercept of 1.06 $c_\theta(325^\circ\text{K})$  which is in excellent agreement with the above estimates.

Most work on the softening of elastic constants near cooperative Jahn–Teller phase transitions has been limited to pseudospin- $\frac{1}{2}$  manifolds<sup>7</sup> and triplet states.<sup>8</sup> The ground state of the Dy<sup>3+</sup> ions is  $J = \frac{15}{2}$  which is split in a cubic crystal field by about 175 °K.<sup>3</sup> In the temperature range 10–300 °K over which the elastic constant  $c_\theta$  softens, several crystal field levels will be occupied and it is necessary to consider the entire  $J = \frac{15}{2}$  manifold.

To calculate the free energy of the Dy<sup>3+</sup> ions we consider a Hamiltonian which contains single-ion and pair interactions appropriate to the cubic phase of DySb. We approximate the pair interactions by using the molecular-field approximation (MFA). As the distortion attendant to the transition at 9.5 °K is uniform,<sup>1</sup> the thermal expectation values of the operators are the same at all Dy<sup>3+</sup> sites (modulo a sign for odd-rank terms). The molecular-field Hamiltonian for DySb is (per ion)

$$\mathcal{H} = \sum_l B_l O_{\Gamma_1}^l - \sum_{\alpha, l} (\Omega c_\alpha / N)^{1/2} \epsilon_\alpha \times \left( g_0^{\alpha, l} O_\alpha^l + \sum_{\alpha', l'} d_{\alpha' l'}^{\alpha l} \langle O_{\alpha'}^l \rangle O_{\alpha''}^{l'} \right) - \sum_{\alpha l l'} I_{\alpha l l'}^{\alpha''} \langle O_{\alpha'}^l \rangle O_{\alpha''}^{l'}, \quad (1)$$

where  $O_\alpha^l$  represents an operator of the  $l$ th rank referring to the Dy<sup>3+</sup> ions which transforms according to  $\alpha$ th representation of the cubic group. The first term represents the cubic crystal field which splits the  $J = \frac{15}{2}$  level of Dy<sup>3+</sup> by about 175 °K.<sup>3</sup> The second term contains the single- and two-ion magnetoelastic couplings to the macroscopic strain  $\epsilon_\alpha$ .<sup>9</sup> For odd-rank interactions the pair-coupling term  $I_{\alpha l l'}^{\alpha''}$  has only contributions from exchange (to lowest order). The even-rank terms have contributions from the electric multipole interaction, from indirect Coulomb couplings via the antimony ions and conduction electrons, and from the direct, indirect, and superexchange interactions. For the rocksalt structure of DySb,  $k=0$  optical phonons cannot contribute to  $I_{\alpha l l'}^{\alpha''}$  because they have odd parity. The  $k=0$  acoustic-phonon coupling is replaced by the strain  $\epsilon_\alpha$  and the only contribution phonons make to the coupling  $I_{\alpha l l'}^{\alpha''}$  comes from a self-energy correction.<sup>7,10</sup>

For temperatures above the Néel point the isothermal and adiabatic elastic constants are equal. The isothermal elastic constant is easier to cal-

culate and is defined as

$$c_{\gamma\phi}(T) = \frac{1}{\Omega} \left( \frac{\partial^2 F}{\partial \epsilon_\gamma \partial \epsilon_\phi} \right)_{(\epsilon), T}, \quad (2)$$

where the derivatives are taken holding all other strains and the temperature constant. The free energy  $F$  for the system is

$$(1/N)F = -kT \ln \text{Tr} e^{-\mathcal{H}/kT} + \frac{1}{2} \left[ (\Omega/N) \sum_{\alpha} c_{\alpha} \epsilon_{\alpha}^2 + \sum_{\alpha} (\Omega c_{\alpha}/N)^{1/2} \epsilon_{\alpha} \sum_{\alpha' \alpha''} d_{\alpha' \alpha''}^{\alpha} \langle O_{\alpha'}^i \rangle \langle O_{\alpha''}^{i'} \rangle + \sum_{\alpha i i'} I_{\alpha}^{i i'} \langle O_{\alpha}^i \rangle \langle O_{\alpha}^{i'} \rangle \right], \quad (3)$$

where the Hamiltonian  $\mathcal{H}$  is that given by Eq. (1). The term proportional to the volume  $\Omega$  represents the elastic-strain energy of the lattice. For temperatures  $T > T_N$  we find the cubic elastic constant  $c_{\theta} = \frac{1}{2}(c_{11} - c_{12})$  is given by<sup>11</sup>

$$\frac{c_{\theta}(T)}{c_{\theta}} = \frac{T - [(g_{\theta}^0 + \frac{1}{2} d_{\theta}^0 \langle O_{\Gamma_1}^4 \rangle)^2 + I_{\theta}] \chi_{\theta\theta}(T)}{T - I_{\theta} \chi_{\theta\theta}(T)}, \quad (4)$$

where

$$\chi_{\theta\theta}(T) = \int_0^1 dx \langle O_{\theta}^2(x) O_{\theta}^2 \rangle = \int_0^1 dx \{ \text{Tr} e^{-\mathcal{H}_0/kT} e^{x\mathcal{H}_0/kT} O_{\theta}^2 e^{-x\mathcal{H}_0/kT} O_{\theta}^2 \} / \text{Tr} e^{-\mathcal{H}_0/kT},$$

$\mathcal{H}_0$  represents the cubic-crystal-field term<sup>3</sup>  $B_4 O_{\Gamma_1}^4 + B_6 O_{\Gamma_1}^6$ ,  $O_{\theta}^2 \equiv 3J_z^2 - J(J+1)$ ,  $g_{\theta}^0 \equiv g_0^{\theta,2}$ , and  $I_{\theta} \equiv I_{\theta}^2$ . Here we have considered only the lowest-rank cubic harmonic  $O_{\theta}^2$  which transforms according to the  $E_g^{\theta}(\Gamma_{31}^+)$  representation of the cubic group. We estimate that this term gives the largest magnetoelastic coupling<sup>2</sup>; however, fourth- and sixth-rank cubic harmonics with  $E_g^{\theta}$  symmetry exist and should be considered in a more complete treatment. The only two-ion magnetoelastic coupling to contribute for  $T > T_N$  is the one with one operator proportional to  $O_{\Gamma_1}^4 = O_4^4 + 5O_4^4$  or its sixth-rank equivalent. The variation of these thermal averages is very small over the temperature interval in which we fit the data and we consider the entire quantity  $(g_{\theta}^0 + \frac{1}{2} d_{\theta}^0 \langle O_{\Gamma_1}^4 \rangle) \equiv g_{\theta}$  as one parameter.

We have evaluated  $\chi_{\theta\theta}(T)$  by using the entire  $J = \frac{15}{2}$  manifold of  $\text{Dy}^{3+}$  and have used Eq. (4) to fit the data. As we have not taken into account anharmonic lattice effects we are restricted in our analysis to temperatures for which the lattice constant remains fixed. From Lévy's data<sup>1</sup> this restricts us to  $T < 80^\circ\text{K}$ . Good fits to the data for  $9.5 < T < 80^\circ\text{K}$  are found by using Eq. (4) with the following parameters:

$$(g_{\theta}^0)^2 = (14.5 \pm 1.0) \times 10^{-4} \text{ }^\circ\text{K},$$

$$I_{\theta} = -(5 \pm 2) \times 10^{-4} \text{ }^\circ\text{K},$$

$$c_{\theta} = (1.060 \pm 0.007) c_{\theta}(325^\circ\text{K})$$

$$= (7.8 \pm 0.4) \times 10^{11} \text{ erg/cm}^3.$$

At the Néel point,  $\chi_{\theta\theta}(T_N) = 4703$ . In Fig. 1 we show our best fit using the parameters  $(g_{\theta}^0)^2 = 14 \times 10^{-4} \text{ }^\circ\text{K}$ ,  $I_{\theta} = -4 \times 10^{-4} \text{ }^\circ\text{K}$ , and  $c_{\theta} = 1.056 c_{\theta}(325^\circ\text{K})$ . We have determined the first-correction term to the molecular-field result, Eq. (4), due to short-range order.<sup>11</sup> This term has contributions from bilinear exchange as well as biquadratic and higher-degree pair interactions. We find that to within the experimental error this term does not appreciably better the fits obtained by using Eq. (4).

The value of  $(g_{\theta}^0)^2$  can be compared to the value obtained from  $\Omega c_{\theta} \epsilon_{\theta}^2 / N \langle O_{\theta}^2 \rangle^2$ , where the strain and expectation value must be evaluated at the same temperature. By using the data on  $\epsilon_{\theta}(T)$  of Lévy<sup>1</sup> and the  $c_{\theta}$  found in our experiment we find  $(g_{\theta}^0)^2 = 21 \times 10^{-4} \text{ }^\circ\text{K}$ . This value is larger than that found from the elastic data for  $T > T_N$ . The difference can be explained by the presence of additional two-ion magnetoelastic contributions  $d_{\alpha' \alpha''}^{\alpha}$  to the energy, Eq. (1), present only for  $T < T_N$ . Due to the cubic symmetry above  $T_N$ ,  $g_{\theta}$  has only a small contribution from the two-ion magnetoelastic coupling from fourth- and sixth-cubic invariants. Below  $T_N$  additional terms coming from anisotropic-bilinear exchange and biquadratic interactions contribute to the two-ion magnetoelastic energy. Due to the formation of domains for  $T < T_N$  these terms cannot be extracted from our data.

The negative sign for the parameter  $I_{\theta}$  indicates that the pair interactions compete with the dominant strain coupling  $(g_{\theta}^0)^2$ . The electric quadrupole-quadrupole contribution to the pair coupling is<sup>12</sup>  $I_{\theta} = 3.8 \times 10^{-4} \text{ }^\circ\text{K}$ . It favors a parallel alignment of quadrupoles along a [100] axis. Therefore the unexplained coupling is  $I_{\theta}^{\text{unexpl}} \approx -9 \times 10^{-4} \text{ }^\circ\text{K}$  which is comparable but of opposite sign to the coupling  $(g_{\theta}^0)^2$ . The self-energy correction term due to the phonon coupling is sizeable only if this coupling is very short ranged, i. e., if this term is equal in magnitude to the interaction energy due to phonon coupling. Unfortunately no data are available on this coupling. Because the  $k = 0$  optical and acoustic phonons cannot contribute to  $I_{\theta}$  for a rocksalt structure, the only remaining interactions that contribute are direct- and indirect-exchange and indirect Coulomb interactions via the anion and conduction electrons. Therefore, the elastic data in no way rules out the existence of large  $[I_{\theta}^{\text{unexpl}} \langle O_{\theta}^2 \rangle^2]_{T_N} \approx -5 \text{ }^\circ\text{K}$  biquadratic pair interactions via conduction and anion electrons in  $\text{DySb}$ .<sup>2</sup>

$\text{DySb}$  is an induced-quadrupole-moment system and requires either a threshold-biquadratic pair interaction or bilinear exchange to have a phase transition. From the free energy Eq. (3) and the best-fit parameters we find<sup>13</sup> that the strain cou-

pling  $(g_\theta)^2$  alone produces a first-order Jahn-Teller phase transition at 6 °K. When we include the competing biquadratic coupling  $I_\theta$  we find no phase transition at all down to  $T = 0.3$  °K (our numerical calculations only go down to this temperature). However, the elastic constant  $c_\theta$  does not continue to soften past 9.5 °K because of the bilinear interactions present in DySb. These interactions do not contribute appreciably to the softening of the elastic constant [except for short-range effects, i. e., as corrections to Eq. (4)] but they do cause the system to undergo a first-order phase transition at 9.5 °K.

Finally, by using the values of  $g_\theta$  and  $I_\theta$  determined from the elastic data and taking into account the contributions to  $g_\theta$  that appear below the transition, we have been able to fit<sup>13</sup> the low-temperature data on the magnetization, susceptibility, specific heat,<sup>3</sup> and anisotropic distortion.<sup>1</sup>

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## Divergence of the Correlation Length along the Critical Isotherm\*

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Three plausible postulates (rigorous for Ising systems) are shown to lead to three new inequalities: (i)  $(2-\eta)\mu_\phi \geq (\delta-1)/\delta$ , (ii)  $\mu_\phi \geq 2/\delta(d-2+\eta)$ , and (iii)  $d\mu_\phi \geq (\delta+1)/\delta$ , concerning  $\mu_\phi$ , the critical-point exponent characterizing the divergence along the critical isotherm of the correlation length  $\xi_\phi(T, H) \equiv [\sum_{\vec{r}} |\vec{r}|^{2\phi} C_2(T, H, \vec{r}) / \sum_{\vec{r}} C_2(T, H, \vec{r})]^{1/2\phi}$ . Result (iii) for  $\mu_\phi$  is an analog, for the critical isotherm, of the Josephson inequalities. If we make the plausible but unproved assumption that  $\mu_\phi$  is independent of  $\phi$ , inequality (i) becomes an equality!

The divergence of a "correlation length" at the critical point ( $T = T_c$ ,  $H = 0$ ) is a hallmark of cooperative phenomena near phase transitions, as it reflects the fact that the correlation function,  $C_2(T, H, \vec{r}) \equiv \langle s_0^\alpha s_{\vec{r}}^\alpha \rangle - \langle s_0^\alpha \rangle^2 \equiv \Gamma_2(T, H, \vec{r}) - [\Gamma_1(T, H)]^2$ , (1)

is becoming extremely long range.<sup>1</sup> We define a family of correlation lengths  $\xi_\phi(T, H)$  through the relation<sup>2</sup>

$$[\xi_\phi(T, H)]^{2\phi} \equiv \frac{\sum_{\vec{r}} |\vec{r}|^{2\phi} C_2(T, H, \vec{r})}{\sum_{\vec{r}} C_2(T, H, \vec{r})}, \quad (2)$$

where  $\xi_1(T, H) \equiv \xi(T, H)$  is commonly called the correlation length. The corresponding critical-point exponents are  $\nu'_\phi$ ,  $\mu_\phi$ , and  $\nu_\phi$  for the three paths (paths 1-3) defined in Table I; again the conventional exponents  $\nu$ ,  $\nu'$ ,  $\mu$  correspond to the case  $\phi = 1$ .

The path-1 and path-3 exponents have been studied considerably more than the path-2 exponents.<sup>1,2</sup> It is the purpose of this paper to show that one can readily obtain analogs for path 2 of two of the classic exponent inequalities for paths 1 and 3 (relations IIa and II d of Table I). More-