may well be important to include carrier-carrier interactions (direct and via the electron-lattice interaction) in developing a model for the "metal-insulator" transition in these materials.

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Soft Acoustic Mode at the Cooperative Jahn-Teller Phase Transition in $DyVO_4$

R. L. Melcher and B. A. Scott

IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

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The temperature dependence of the elastic constant $\frac{1}{2}(c_{11}-c_{12})$ shows that the B_{1g} acoustic phonon branch is the soft mode at the cooperative Jahn-Teller phase transition in $DyVO_4$. For $T > 2T_D$ (T_D is the transition temperature) the data can be described by mean field theory and show that the dominant driving mechanism for the transition is the coupling of the Jahn-Teller ions to the static elastic strain. However, for $T_D < T < 2T_D$ we find significant deviations from mean field theory due to critical fluctuations.

In this paper we present detailed measurements showing the existence of a soft acoustic mode at a cooperative Jahn-Teller phase transition. The temperature dependence of the elastic constant $c(T) \equiv \frac{1}{2}(c_{11} - c_{12})$ in the high-temperature tetragonal phase of $DyVO_4$ shows that the long-wavelength B_{1g} acoustic phonon branch (wave vector $\vec{q} \parallel \langle 110 \rangle$, particle displacement $\vec{u} \parallel \langle 1\bar{1}0 \rangle$) is soft at the tetragonal-to-orthorhombic phase transition. The data in the tetragonal phase for $T > 2T_D$ are in excellent agreement with the mean field theory of Elliott and co-workers,[1] and Gehring *et al.*[2] However, contrary to conclusions drawn from static stress measurements and an assumed value for $c_{11} - c_{12}$,[2] we find that the dominant driving mechanism for the transition is the coupling of the Jahn-Teller ion (Dy^{3+}) to the static elastic strain. The combined coupling to all dynamic phonon modes (optic and acoustic), including the self-energy correction,[3,4] is found to be negative and therefore impedes the transition. The data for $T_D < T < 2T_D$ show deviations from the mean field theory arising from critical fluctuations. The data in the orthorhombic phase are also not in agreement with the predictions of the mean field theory.

Kanamori[3] originally recognized the importance of static strain coupling to Jahn-Teller ions in leading to structural phase transitions. Pytte[5] has recently pointed out that as a consequence of this coupling there should exist a soft acoustic phonon mode leading to the phase transition.

Pytte and Stevens[6] have shown that the crystal field in $DyVO_4$ causes the angular momentum of

the Dy^{3+} ($J=\frac{15}{2}$) ion to tunnel between equivalent energy minima located along the positive and negative $\langle 100\rangle$ and $\langle 010\rangle$ axes. The ground state of the system consists of a pair of Kramer's doublets separated by $2\epsilon = 9\ cm^{-1}$.[2] Below the transition temperature ($T_D \simeq 14.8°K$) in the orthorhombic phase, the free energy has absolute minima along either the $\langle 100\rangle$ or $\langle 010\rangle$ axis. The energy separation between the two Kramer's doublets increases at low temperature to 27 cm^{-1}. Elliott and co-workers have considered in detail the coupling of the Dy^{3+} ion to both the dynamic phonon modes of the material[4] and to the static elastic strain.[1,2] The symmetry of the low-temperature phase requires that the dominant coupling is to lattice distortions with B_{1g} symmetry. They use the following Hamiltonian for the coupled electron-phonon system[1,2]:

$$\mathcal{H} = \sum_{n,\vec{q}} \{[c_n^{\dagger}(\vec{q})c_n(\vec{q}) + \tfrac{1}{2}]\hbar\omega_n(\vec{q}) + \xi_n(\vec{q})[c_n^{\dagger}(\vec{q}) + c_n(\vec{q})]\sigma_z(\vec{q})\} - \epsilon\sqrt{N}\,\sigma_x(0) - \eta e\sqrt{N}\,\sigma_z(0). \quad (1)$$

Here, $c_n^{\dagger}(\vec{q})$ and $c_n(\vec{q})$ are the creation and annihilation operators for phonons of the nth branch with wave vector $\vec{q}$ and energy $\hbar\omega_n(\vec{q})$, $\xi_n(\vec{q})$ is the corresponding electron-phonon coupling constant, $\vec{\sigma}(\vec{q})$ is the effective spin-$\frac{1}{2}$ operator describing the two low-lying Kramer's doublets, ϵ is the high-temperature splitting of the doublets, $2N$ is the number of Dy^{3+} ions, and η is the coupling constant to the static strain $e \equiv \frac{1}{2}(e_{xx} - e_{yy})$. Solving the coupled equations of motion for the long-wavelength B_{1g} acoustic phonons, they find the following expression for the elastic constant in the high-temperature phase:

$$\frac{c(T)}{c_0} = \left[1 - \frac{J(0)+\chi}{\epsilon}\tanh\beta\epsilon\right] \times \left[1 - \frac{J(0)}{\epsilon}\tanh\beta\epsilon\right]^{-1}, \quad (2)$$

where $c(T) = \frac{1}{2}(c_{11} - c_{12})$, c_0 is the value of $c(T)$ in the absence of Jahn-Teller coupling, $\beta = 1/kT$, and $J(0)$ and χ are related to $\xi_n(\vec{q})$ and η by

$$J(0) = \sum_n \frac{2\xi_n^2(0)}{\hbar\omega_n(0)} - \frac{1}{N}\sum_{n,\vec{q}'} \frac{2\xi_n^2(\vec{q}')}{\hbar\omega_n(\vec{q}')}, \quad (3a)$$

$$\chi = (2N/c_0)\eta^2. \quad (3b)$$

The first term in Eq. (3a) represents the coupling to $q=0$ optic phonons (the acoustic-mode contribution to this term vanishes), and the second term represents the subtraction of the self-energy arising from the coupling to both the acoustic- and optic-phonon branches. A measure of $J(0)$ and χ determines the relative importance of phonon versus static-strain coupling in driving the Jahn-Teller phase transition. Whereas χ is necessarily positive or zero, $J(0)$ can be positive, zero, or negative.

Our experiments were performed on a single crystal of $DyVO_4$ grown by the Czochralski method. We used an oriented section having dimensions of ~3 mm along the $\langle 110\rangle$ axes. The adiabatic elastic constant $c(T) \equiv \frac{1}{2}(c_{11} - c_{12})$ was measured with the continuous-wave–resonance technique[7] using 30-MHz AC-cut quartz transducers. The elastic constant was also measured by noting the harmonic number of the mechanical resonance occurring (if any) at a fixed frequency as the temperature was varied. The agreement of the two techniques to within the experimental scatter eliminates the possibility of systematic error in the measurements.

Figure 1 shows the measured value of $c(T) = \frac{1}{2}(c_{11} - c_{12})$ over an extended temperature range. Although the crystal was made single domain below T_D by application of a magnetic field along the $\langle 100\rangle$ axis, measurements in the temperature range $7 < T < 16.4°K$ were not possible because of high absorption. At 16.4°K the value of $c(T)$ is about 7% of the value at room temperature. A rough extrapolation to $c(T) = 0$ (see inset, Fig. 1) shows that the long-wavelength B_{1g} acoustic phonons condense at $T_D \simeq 14.8°K$. At low tempera-

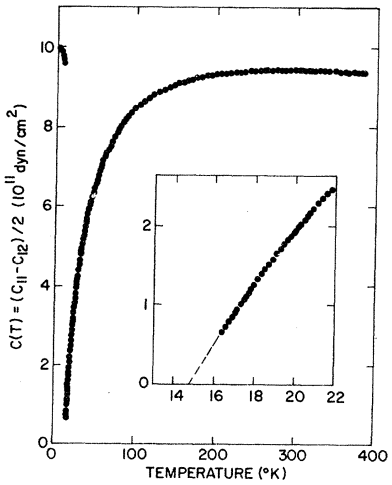

FIG. 1. Measured elastic constant $c(T) = \frac{1}{2}(c_{11} - c_{12})$ versus temperature for $DyVO_4$. Inset shows behavior in neighborhood of the phase transition at $T_D \simeq 14.8°K$.

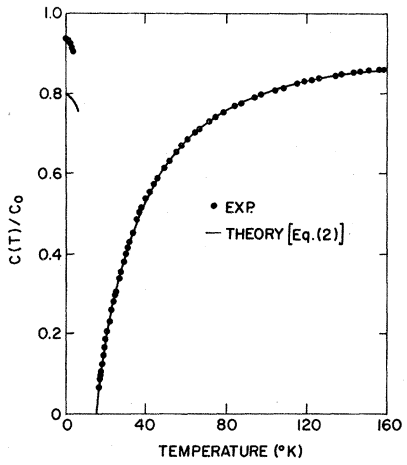

FIG. 2. Data (solid circles) on a reduced plot showing best fit with Eq. (2) (solid line) for the temperature range $16.4 < T < 150$°K ($1.1 < T/T_D < 10$). The values of the parameters used are given in Eqs. (4).

tures, $T \ll T_D$, the elastic constant is magnetic field dependent [a field of 10 kOe applied along the ⟨010⟩ axis increases $c(T)$ by ~1% at 4.2°K]. In zero field, $c(T)$ increases approximately 1% when the temperature is reduced to below the antiferromagnetic phase transition ($T_N = 3$°K).

In Fig. 2 the data are fitted by Eq. (2) over the temperature range $16.4 \leq T \leq 150$°K. A least-squares criterion was used to determine the best fit on varying the parameters c_0, $J(0)$, and $J(0) + \chi$. The "best" set of parameters for this temperature range are

$$c_0 = 10.63 \times 10^{11} \text{ dyn/cm}^2, \quad (4a)$$

$$J(0) = -3.6 \text{ cm}^{-1}, \quad (4b)$$

$$J(0) + \chi = +11.1 \text{ cm}^{-1}. \quad (4c)$$

To determine the range of validity of the mean field theory, we have fit the data with Eq. (2) over several temperature ranges as summarized in Table I. Over all temperature ranges considered, an excellent fit to the data can be obtained by varying the parameters c_0, $J(0)$, and $J(0) + \chi$. The "best" values of these parameters vary somewhat, depending upon the temperature range used in the fitting procedure. However, as shown in rows 3, 4, and 5 of Table I, the parameters are essentially independent of the temperature range considered if the data for $T < 2T_D$ are omitted. The meaning of this is discussed below.

Using expressions given in Refs. 1 and 2, and the parameters obtained from fitting the high-temperature data, we have calculated the expected values of the low-temperature ($T \to 0$) elastic constant. These values are given in the last column of Table I. Our experimental value (Fig. 1) at 1.5°K is $(9.95 \pm 0.1) \times 10^{11}$ dyn/cm^2. This is some 17% higher than the values calculated in rows 1 and 2 of Table I, and 8 to 10% higher than that given in rows 3, 4, and 5. We do not believe that this large discrepancy can be ignored. We suggest that the discrepancy indicates a failure of this mean field theory to account for the elastic behavior of this material in the low-temperature phase.

Several conclusions can be drawn from the present experiment concerning the driving mechanism for the Jahn-Teller distortion in $DyVO_4$:

(1) For all temperature ranges considered, the mean field calculation for the high-temperature phase [Eq. (2)] is in excellent agreement with experiment for the "best" values of the parameters c_0, $J(0)$, and $J(0) + \chi$.

TABLE I. Least-squares fitting procedures used to compare the measured values of $c(T) = \frac{1}{2}(c_{11} - c_{12})$ with Eq. (2).[a,b]

Temperature range of fit	Parameters c_0[c] (10^{11} dyn/cm^2)	Parameters $J(0)$ (cm^{-1})	$J(0) + \chi$ (cm^{-1})	Root-mean-square difference in $c(T)/c_0$	Calculated $c(T=0)$ (10^{11} dyn/cm^2)
$16.4 \leq T \leq 150$	10.63	−3.6	+11.1	3.2×10^{-3}	8.44
$22.5 \leq T \leq 150$	10.59	−3.1	+11.3	2.0×10^{-3}	8.53
$33 \leq T \leq 150$	10.38	−0.014	+12.7	2.7×10^{-3}	9.07
$45 \leq T \leq 150$	10.41	−0.014	+12.85	1.3×10^{-3}	9.13
$60 \leq T \leq 150$	10.42	−0.021	+12.85	1.1×10^{-3}	9.14

[a] In order to save computer time, only 27 data points were used in a fit. Tests were made to ascertain that the point selection did not affect the results.

[b] In all cases the constraint $\epsilon = 4.5$ cm^{-1} was imposed. For $kT \gg \epsilon$, Eq. (2) is independent of ϵ.

[c] In all cases it was assumed that c_0 was independent of temperature. This is valid for temperatures much less than the Debye temperature.

(2) The parameters so determined are essentially independent of the temperature range of the fit as long as the data for $1 \lesssim T/T_D \lesssim 2$ are excluded. This is a clear indication that the mean field theory is valid for $T/T_D \gtrsim 2$. From rows 3, 4, and 5 of Table I, the best mean field parameters are

$$c_0 = (10.40 \pm 0.02) \times 10^{11} \text{ dyn/cm}^2, \quad (5a)$$

$$J(0) = -0.015 \pm 0.01 \text{ cm}^{-1}, \quad (5b)$$

$$J(0) + \chi = 12.8 \pm 0.1 \text{ cm}^{-1}. \quad (5c)$$

From the low-temperature splitting of the two Kramer's doublets, the value $J(0) + \chi = 13.5$ cm^{-1} has been obtained.[2] Using the static-strain measurements of Will, Schäfer, and Goebel.,[8] and expressions derived in Ref. 1, we calculate $\chi = 12$ cm^{-1}. Fixing all the independently known parameters [$J(0) + \chi = 13.5$ cm^{-1}, $\chi = 12$ cm^{-1}, and $\epsilon = 4.5$ cm^{-1}] and adjusting only c_0, a reasonable fit of the data for $T > 2T_D$ by Eq. (2) can be achieved. From such a fit we obtain $c_0 = 10.31 \times 10^{11}$ dyn/cm^2 and calculate $c(T = 0) = 9.29 \times 10^{11}$ dyn/cm^2. The rms deviation is, however, 4.7×10^{-3} as compared with 2.7×10^{-3} when only ϵ is fixed and the other parameters are varied (see Table I).

(3) From our result $\chi \gg J(0)$ [Eqs. (5)], we conclude that the coupling to the static elastic strain is the dominant driving mechanism for the transition. Because of the self-energy correction included in the definition of $J(0)$ [Eq. (3a)], no conclusion can be drawn concerning the pressence or absence of static internal strains in the low-temperature phase. To the extent that $J(0)$ is negative for $T > 2T_D$ (see Table I), we can conclude that the self-energy corrections cannot be neglected as is done in a simple linearization of the problem.

(4) The difference between the best mean field parameters [Eqs. (5)] and the parameters obtained by fitting over the entire temperature range $T > T_D$ [Eqs. (4)] is an indication that critical fluctuations become important as the transition is approached (i.e., for $T_D < T < 2T_D$). Since the fluctuations are not included in the mean field calculation, the agreement over the entire temperature range $T > T_D$, using the parameters given in Eqs. (4), must be considered fortuitous. Such fortuitous fits can easily occur when several adjustable parameters are available. Since the parameters $J(0)$, χ, c_0 are temperature independent, their values as obtained by fitting Eq. (2) to the data must be independent of the temperature range of the fit if one is to conclude that Eq. (2) is valid. As the discussion of Eqs. (5) above points out, this is true for $T > 2T_D$ but not for $T_D < T < 2T_D$. Therefore, we conclude that the mean field approximation breaks down as a result of short-range order in the temperature range $T_D < T < 2T_D$.

We should point out that in a similar system, $NiCr_2O_4$, a 50–60% softening in $\frac{1}{2}(c_{11} - c_{12})$ has recently been observed over a limited temperature range near a cooperative Jahn-Teller phase transition.[9] In other recent work, Gorodetsky, Lüthi, and Wanklyn[10] have measured c_{33}, c_{44}, and c_{55} in $DyVO_4$. They find changes in these constants of approximately 1% due to the Jahn-Teller transition. However, their restricted sample geometry prevented them from measuring the soft mode $\frac{1}{2}(c_{11} - c_{12})$.

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