$E_i = -0.6$ eV in addition to a peak near -1.3 eV, suggesting that the two highest filled bands are split near the edge of the Brillouin zone; such splitting would support the use of Bloch functions in the description of the VB states.[10]

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Phonon Instabilities in $TmVO_4$

R. L. Melcher, E. Pytte, and B. A. Scott
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598
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The lattice instability of $TmVO_4$ near its cooperative Jahn-Teller phase transition is shown to be a competitive process involving distortions of B_{1g} and B_{2g} symmetry. In order to understand the soft-mode behavior, we must consider the spin-lattice coupling of the entire $J=6$ ground multiplet of the Tm^{3+} ion. Axial magnetic fields are found to affect dramatically the soft acoustic-mode behavior.

In this Letter we report experimental and theoretical results concerning the dynamic behavior of acoustic phonons near the tetragonal-to-orthorhombic cooperative Jahn-Teller phase transition in $TmVO_4$ ($T_c = 2.1°K$). The crystallographic point group for $T > T_c$ is D_{4h}, and the Tm^{3+} site symmetry is D_{2d}. Our principal findings are these: (1) The soft acoustic mode [with strain $e(B_{2g}) \equiv e_{12}$ transforming as xy, and elastic constant c_{66}] exhibits considerable structure in its temperature dependence for $T \simeq 40T_c$. This structure is found to be a consequence of the Jahn-Teller interaction of the strain with an excited doublet with E symmetry ($2\Delta \simeq 138$ cm^{-1}) of the Tm^{3+} ground multiplet ($J=6$). (2) The acoustic mode corresponding to the $e(B_{1g}) \equiv (e_{11} - e_{22})/2$ strain transforming as $x^2 - y^2$ [elastic constant $(c_{11} - c_{12})/2$] competes with the B_{2g} strain to determine the space group of the distorted low-temperature phase. This elastic constant $[(c_{11} - c_{12})/2]$ softens by 18.6% (in absolute value as much as c_{66}) as the transition is approached from above. However, at T_c the crystal becomes unstable to the B_{2g} strain and consequently distorts according to a B_{2g} strain. This distortion stabilizes the B_{1g} mode, thereby arresting the softening of $(c_{11} - c_{12})/2$, which is then found in the distorted phase to be both temperature and magnetic field independent. (3) Because the Zeeman splitting of the ground doublet by axial magnetic fields of a few kilo-oersteds is comparable to the Jahn-Teller splitting of this doublet, the elastic properties are found to be extremely sensitive to fields of this type. In particular, c_{66} is zero along the phase boundary in the H-T plane, and $(c_{11} - c_{12})/2$ exhibits a sharp kink at the phase boundary. (4) Elastic modes for which the spin-phonon interaction has no nonvanishing matrix elements between the components of the ground doublet are found to exhibit no anomalous dependence on temperature for $T \gtrsim T_c$. These include c_{44}, c_{33}, and $(c_{11}+c_{12})/2$ corresponding to strains with E_g, A_{1g}, and A_{1g} symmetry, respectively.

The tetragonal crystal field acting on the Tm^{3+} ion in $TmVO_4$ lifts the thirteenfold degeneracy of the $J=6$ ground multiplet into seven singlets and three doublets.[1] The lowest level is a doublet and the first excited state is a singlet at ~54 cm^{-1}. The total splitting of the multiplet is ~350 cm^{-1}. For simplicity we outline initially the necessary theoretical results for a simple doublet (pseudospin $=\frac{1}{2}$) described by Pauli operators $\vec{\sigma}$.[2,3] The Hamiltonian for the coupled spin-lattice system is taken to be[4,5]

$$H=-\frac{1}{2}\sum_{\substack{i=1,2\\ l,l'}} J_i(ll')\sigma_i(l)\sigma_i(l') - \sum_{\substack{i=1,2\\ l}} \eta_i\sigma_i(l)e_i + \frac{1}{2}\sum_{i=1,2} c_i^{\infty} e_i^2, \qquad (1)$$

where $i=1, 2$ correspond respectively to lattice distortions of B_{1g} and B_{2g} symmetry. The pseudospin-strain coupling constant is η_i, and $J_i(ll')$ describes the pseudospin-phonon (both optic and acoustic) interaction.[5] Since both B_{1g} $(i=1)$ and B_{2g} $(i=2)$ lattice distortions enter the Hamiltonian in an entirely symmetric way, the resultant Jahn-Teller distortion of the crystal is a competitive process. Which of the two distortions actually occurs at $T_c=2.1$°K is determined by the magnitude of the respective spin-lattice coupling constants and not by symmetry. A straightforward calculation of the elastic constants in the undistorted phase and in the mean-field approximation leads to

$$c_i(T, H=0)=c_i^{\infty}[1-G_i/(T-\lambda_i)], \quad i=1, 2, \qquad (2)$$

where

$$G_i=2\eta_i^2/c_i^{\infty} \text{ and } \lambda_i=\sum_{l\neq l'} J_i(ll').$$

The adiabatic and isothermal elastic constants are equal.

In Figs. 1 and 2 the experimental behaviors of c_{66} $(i=2)$ and $(c_{11}-c_{12})/2$ $(i=1)$ versus temperature are shown. The frequency of the measurements was 30 MHz. Transverse elastic waves propagating along the [100] and [110] axes, polarized perpendicular to the ⟨001⟩ axis, were used to measure c_{66} and $(c_{11}-c_{12})/2$, respectively. Because of the extremely high attenuation, c_{66} could not be reliably measured below 4.2°K. There was no significant change in the attenuation of the mode corresponding to $(c_{11}-c_{12})/2$ over the entire temperature region. Also shown in Figs. 1 and 2 are the best least-squares fits of the data by Eq. (2) on allowing the parameters c_i^{∞}, G_i, and λ_i to vary. [In Fig. 2 the theoretical result that $(c_{11}-c_{12})/2$ is constant in the distorted phase is used in the fitting procedure.] The best values of the parameters found for c_{66} are $c_2^{\infty}=1.683\times10^{11}$ dyn/cm^2, $G_2=2.56$ cm^{-1}, and $\lambda_2=1.40$ cm^{-1}, from which the transition temperature is calculated to be 1.68°K compared to the actual transition temperature of 2.1°K. For $(c_{11}-c_{12})/2$ the best parameters are $c_1^{\infty}=11.0\times10^{11}$ dyn/cm^2, $G_1=0.276$ cm^{-1}, and $\lambda_1=-0.336$ cm^{-1}, and the transition temperature is an experimentally determined quantity. The good fit of the theory to the data for $T<10T_c$ is an indication that as long as only the lowest-lying doublet is thermally populated, the Hamiltonian [Eq. (1)] adequately describes the behavior.

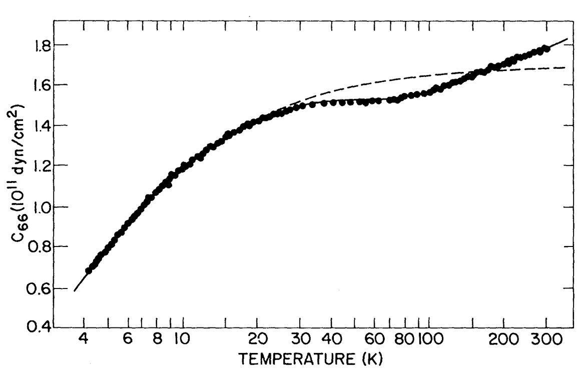

FIG. 1. The temperature dependence of the elastic constant c_{66}. The dashed and solid lines correspond respectively to the best fits of the data by Eqs. (2) and (3). The parameters determined for the fits are given in the text.

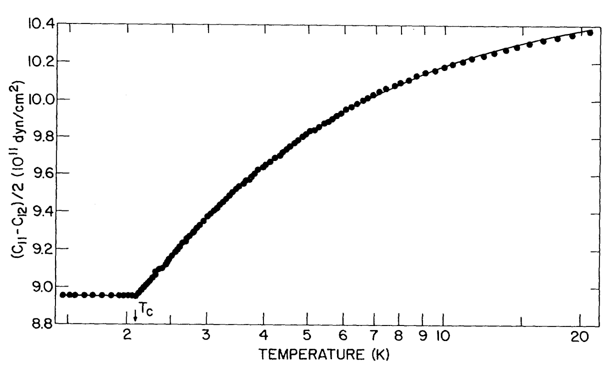

FIG. 2. The temperature dependence of the elastic constant $(c_{11}-c_{12})/2$. The solid curve is the best fit by Eq. (2) with the parameters given in the text.

For $T \gtrsim 10T_c$, Fig. 1 shows serious qualitative discrepancies between theory and experiment for c_{66}. Such behavior has not been previously observed at Jahn-Teller transitions.[6] This cannot be explained on the basis of a two-level system, or by effects resulting from lattice anharmonicity. The discrepancy can be eliminated by treating the spin-lattice coupling of the entire $J=6$ Tm^{3+} ground multiplet. For the energies of the levels within the multiplet we take the values measured by Knoll for Tm^{3+} in YVO_4.[1] By symmetry there are no nonzero matrix elements of the spin-lattice interaction for B_{1g} or B_{2g} distortions which involve any of the singlet levels. These then enter only as statistical factors in the calculation. Each of the three doublets (E_g symmetry) with energies 0, $\simeq 138\ \mathrm{cm}^{-1}$, and $\simeq 340\ \mathrm{cm}^{-1}$ possesses nonzero spin-lattice matrix elements. We consider here only the two lowest-lying doublets, the third doublet being thermally depopulated at the temperatures of interest. The elastic constants are calculated to have the following form:

$$c_i = c_i^\infty\left[1 - \sum_{m=1}^{3} \frac{G_{im}A_m}{1-\lambda_{im}A_m}\right], \quad i=1,2, \tag{3}$$

where $A_1 = 2/ZT$, $A_2 = A_1\exp(-2\beta\Delta)$, and $A_3 = 4[1-\exp(-2\beta\Delta)]/2\Delta Z$. Z is the partition function for the thirteen-level system, $2\Delta \simeq 138\ \mathrm{cm}^{-1}$ is the energy of the excited doublet,[1] and $\beta = 1/kT$. The three terms on the right-hand side of Eq. (3) for $m=1$, 2, and 3 correspond respectively to the contributions from matrix elements between the components of the ground doublet, the excited doublet, and between the two doublets. Using $G_{i2}/G_{i1} = \lambda_{i2}/\lambda_{i1}$ and $G_{i3}/G_{i1} = \lambda_{i3}/\lambda_{i1}$, $i=1, 2$, two of the parameters in Eq. (3) can be eliminated. The best five-parameter fit of Eq. (3) to the data for c_{66} is shown as the solid curve in Fig. 1. An excellent fit is obtained for $c_2^\infty = 1.933\times10^{11}$ dyn/cm^2; $G_{21} = 1.85\ \mathrm{cm}^{-1}$; $\lambda_{21} = -0.742\ \mathrm{cm}^{-1}$; $G_{22}/G_{21} = 40.8$; $G_{23}/G_{21} = 5.90$. From these values and Eq. (3) the calculated transition temperature is 2.06°K compared to the experimental value of $T_c = (2.1 \pm 0.05)$°K. This good agreement is an excellent check on the validity of the fit, and shows that there is a non-negligible contribution to the transition temperature (and to c_2^∞) from the doublet at 2Δ.[7] Similar effects are expected to be important in $TmAsO_4$ which possesses very low-lying excited states.[8] Moran *et al.*[9] and Lüthi *et al.*[10] have used the full J multiplet structure of DySb and TmCd, respectively, to interpret their results on the soft mode in these materials although the structure observed here was not found.

The unusual structure in the temperature dependence of c_{66} for $T \gtrsim 10T_c$ can therefore be definitely attributed to the Jahn-Teller coupling of the strain wave with the doublet at 2Δ. The strength of this coupling is found to be some 40 times greater than that of the ground doublet. That this is not unreasonable can be seen from the fact that the ground doublet consists predominantly (i.e., 80–90%) of $|J_z = \pm 5\rangle$ states.[1] There are no nonzero matrix elements of the Jahn-Teller interaction between pure $|J_z = \pm 5\rangle$ states. Therefore, the interaction for the ground doublet is anomalously weak (note the low transition temperature), and the large ratio $G_{22}/G_{21} = 40.8$ is not surprising. In addition to the uncertainty in the values of the parameters expected of a fit of this type, additional uncertainty arises due to the unavoidable neglect of the effect of lattice anharmonicity on the high-temperature behavior of c_{66}. However, this is expected to be a minor effect since even at $T \approx 300$°K, $c_{66}(T)$ is clearly dominated by the Jahn-Teller coupling.

The behavior of $(c_{11} - c_{12})/2$ for $T > 35$°K is dominated by lattice anharmonicity. Therefore, the slight upward curvature found for $75 < T < 250$°K (not shown here) can only tentatively be ascribed to the influence of the doublet at 2Δ. The stabilizing effect on this mode $[e(B_{1g})]$ of the B_{2g} distortion at $T_c = 2.1$°K is clearly shown in Fig. 2. Measurements made in the presence of an axial magnetic field (not shown here) show that $(c_{11} - c_{12})/2$ is constant independent of H and T at all points in the H-T plane corresponding to the distorted phase. This is in agreement with the predictions of the mean-field theory.

The influence of an axial magnetic field on the elastic properties of $TmVO_4$ can be readily calculated by including the Zeeman interaction in the Hamiltonian. For low temperatures ($T \ll 2\Delta$), and not too large fields, only the Zeeman splitting of the ground doublet ($g_c \simeq 10.1$[2]) need be considered. Under these conditions the expression for the field dependence of the elastic constants in the undistorted phase is given by

$$c_i = c_i^\infty\left[1 - \frac{G_{i1}\tanh(g_c\mu_0H_0/2kT)}{\frac{1}{2}g_c\mu_0H_0 - \lambda_{i1}\tanh(g_c\mu_0H_0/2kT)} - \frac{G_{i3}}{\Delta - \lambda_{i3}}\right], \quad i=1,2. \tag{4}$$

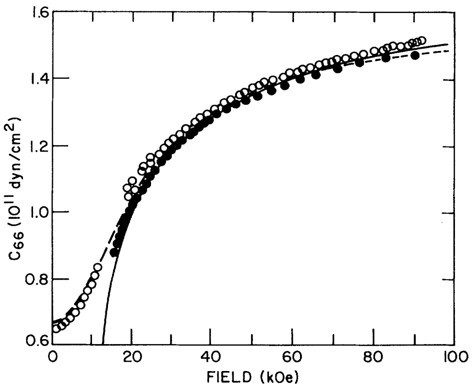

FIG. 3. The field dependence of c_{66} at $T=4.2$°K (open circles) and $T=1.5$°K (solid circles) for $H \parallel \langle 001 \rangle$. The dashed and solid curves are the expected theoretical behavior for the two cases. There are no adjustable parameters.

Since no new parameters are introduced by the Zeeman interaction, and since all the other parameters of the theory have been determined by the temperature dependence of the elastic constants, the field dependence of c_{66} and $(c_{11}-c_{12})/2$ is completely determined with no adjustable parameters. In Fig. 3 the field dependence for c_{66} at 4.2 and 1.5°K is shown. The dashed (4.2°K) and solid (1.5°K) curves are calculated using the parameters determined by the five-parameter fit to the temperature dependence of c_{66} (Fig. 1, solid curve). The excellent agreement is remarkable considering the absence of any parameters (including the vertical scale) and the ~1% absolute accuracy of the experiments. Some deviation at high fields can be attributed to the Zeeman splitting of higher-lying states for which the g factors are unknown. Similar data for $(c_{11}-c_{12})/2$ (not shown here) exhibit equally remarkable agreement with theory.

In conclusion, we have shown for the first time the unambiguous influence of higher-lying states on the soft-mode behavior near a cooperative Jahn-Teller phase transition. Also, we have shown that the mode softening is a competitive process between the two symmetry-allowed lattice distortions. The mean-field theory adequately describes both the temperature dependence and field dependence of the elastic properties. The latter can be predicted without any adjustable parameters from the former.

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