state viscosities with data obtained near melting pressures.

In summary, we observe that spin waves do exist in $^3$He-$B$ and that they are by no means overdamped modes. Further, we have shown that within the context of current theory, spin-wave effects can be calculated with reasonable precision. We believe that the (20%) discrepancy between theory and experiment is attributable to the need for a nonzero value of $F_1^a$.

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# Dielectric Anomaly and Improper Antiferroelectricity at the Jahn-Teller Transitions in Rare-Earth Vanadates

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Dielectric measurements have been carried out on the single crystals of $DyVO_4$, $TbVO_4$, and $TmVO_4$ through the Jahn-Teller transition temperatures. An anomalous increase of the dielectric susceptibility with temperature along the $c$ axis was observed for $DyVO_4$, but not for $TbVO_4$ and $TmVO_4$. This behavior is explained as due to the antiferroelectricity driven by the soft $B_{1g}$ strain mode through the "sublattice piezoelectricity."

Some of the zircon-type rare-earth vanadates and arsenides have attracted much interest because of their cooperative Jahn-Teller phase transitions.[1-5] In $DyVO_4$ and $DyAsO_4$, the ($x_1 - x_2$)-type ($B_{1g}$ symmetry) spontaneous strains occur below the transition temperature ($T_D$), while in $TbVO_4$, $TmVO_4$, and $TmAsO_4$, $x_6$-type ($B_{2g}$ symmetry) spontaneous strains occur; thereby softening of transverse acoustic phonons [or the elastic stiffness component $\frac{1}{2}(c_{11} - c_{12})$ for the former group and the component $c_{66}$ for the latter group] takes place.[3-5] The transitions have been regarded as a uniform tetragonal-orthorhombic distortion comprising no internal strain because, according to Raman-scattering experiments,[2] there was no evidence of a soft optical mode either above and below $T_D$. We report here the first observation of the dielectric behavior near the transition temperature in $DyVO_4$, $TbVO_4$, and $TmVO_4$ single crystals and propose a new model —that for $DyVO_4$ at the low-temperature phase there should be an antiferroelectric ordering due to the interaction of some optical modes with the strain mode.

Temperature variations of the dielectric constants were measured for the samples of single

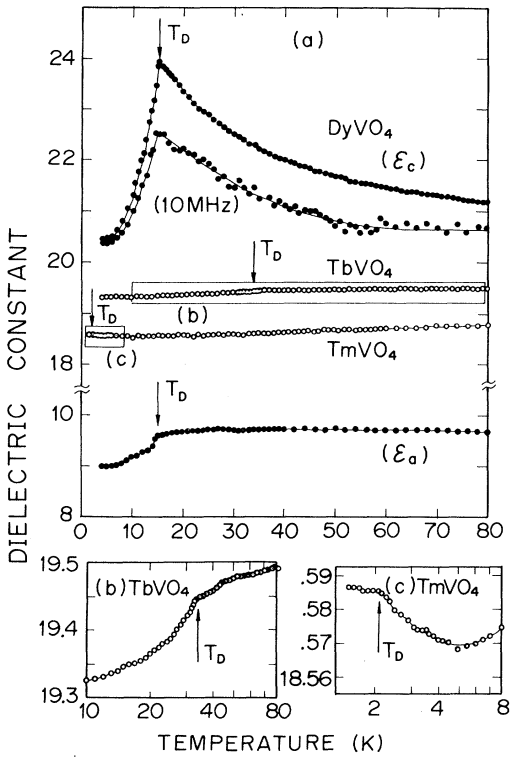


FIG. 1. Temperature variation of the dielectric constants of $DyVO_4$, $TbVO_4$, and $TmVO_4$ along the $c$ and $a$ axes. Measurements were done by a three-terminal capacitance bridge (GR 1615A), at 1 kHz unless otherwise denoted, with relative accuracy of $10^{-4}\sim10^{-5}$.

crystals grown by a floating-zone method. The results of the measurements are summarized in Fig. 1. The important features are as follows: (1) For $DyVO_4$, an anomalous increase in, $\epsilon_c$, the dielectric constant along the $c$ axis, was found with its peak at $T_D\simeq 15.2$ K. In comparison, much smaller anomalies in $\epsilon_c$ were observed for $TbVO_4$ and $TmVO_4$. (2) The temperature variation of $\epsilon_c$ in $DyVO_4$ quite resembles the elastic characteristics[3,4] in such a way that the anomalous part of the inverse dielectric susceptibility is proportional to the value of elastic stiffness $c_{11}-c_{12}$. (3) The dielectric characteristics for $TmVO_4$ also varies, though much smaller in magnitude, concurrently with elastic behavior of the crystal.[5]

The observed anomaly in $\epsilon_c$ of $DyVO_4$ around the Jahn-Teller phase transition cannot be ascribed to the electrostrictive effect which always attends at the structural phase transition with the relation $\Delta\gamma_i=2q_{ii}(x_i)_s$. However, the observed $\Delta\gamma_3$ and spontaneous strain $(x_3)_s$ were found not to obey the above relation but to give much larger $q_{33}$ by factors of $10^2$–$10^3$ compared with $q_{11}$ ($\sim 2\times10^9$ m/F). Moreover, there is no such precursing effect in the lattice distortion $(x_3)_s$ as that in $\Delta\gamma_3$ above $T_D$. The Jahn-Teller ordering of the magnetic ions is not directly responsible for the dielectric anomaly, because this "ferroquadrupolar" ordering[2] does not seem to alter the dielectric polarizabilities of the electronic orbitals along the $c$ axis.

To explain these properties we would have to introduce couplings among some optical-phonon modes and the strain modes. First, we postulate that the zircon-type crystal lattice can be conceived as composed of two sublattices which are composed, respectively, of two molecular units (denoted hereafter by $A$ and $B$). In each sublattice, the constituent rare-earth ions are surrounded tetrahedrally by the oxygen ions, each of which in turn is a menber of the neighboring $VO_4$ tetrahedra. It is important to note that, although the whole lattice has the symmetry $4/mmm$, the symmetry of each sublattice is $\bar{4}2m$ which belongs to the piezoelectric class. Hence, the sublattice polarization can afford to couple with the homogeneous lattice strain through an effective piezoelectric tensor $a_{ijk}$ of the form (1-axis$\perp m$, 2-axis$\perp m$, 3-axis $\parallel c\parallel\bar{4}$)

$$\begin{pmatrix} 0 & 0 & 0 & 0 & a_{15} & 0 \\ 0 & 0 & 0 & -a_{15} & 0 & 0 \\ a_{31} & -a_{31} & 0 & 0 & 0 & 0 \end{pmatrix}.$$

Since the sublattices are enantiomorphic to each other, we can put $a_{ijk}{}^A=-a_{ijk}{}^B$. Therefore, the antiferroelectric polarization (or the $B_{1g}$ external phonon mode[6] amplitude) along the $c$ axis, $\tilde{P}=P_A-P_B$, can couple with the lattice strain $x=x_1-x_2$ through the sublattice piezoelectric (or the "linear piezo-optic"[7]) coupling constant $a=a_{31}{}^A=-a_{31}{}^B$; i.e., we should expect an interaction term of the form $a\tilde{P}x$. It is to be noted that, for $TbVO_4$ and $TmVO_4$, there is no piezo-optic component which linearly couples the soft strain $x_6$ with $\tilde{P}$. Analogously, the uniform polarization, $P=P_A+P_B$ (or the $A_{2u}$ external phonon mode amplitude), is assumed to couple with, so to speak, the "staggered" strain[8] $\tilde{x}$ [or the $A_{2u}$ internal phonon mode amplitude, cf. Fig. 2(b)]; i.e., the free energy should contain also a term of the form $aP\tilde{x}$.

We now construct, taking also the dielectric terms due to the collinear sublattice polarizations into account,[9,10] a Helmholtz free energy of the following form,[11] in which the strain $x$ is the phase-transition parameter and only the coeffi-

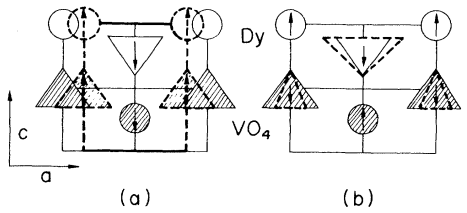


FIG. 2. The sublattice structure and the two types of the polarization-strain-coupled motion of $DyVO_4$ projected onto the $a$-$c$ plane. One sublattice is specified by hatching; the polarization is denoted by arrows and the strain motion, by dashed lines. (a) The $B_{1g}$-symmetry motion, where the staggered polarization $\tilde{P}$ couples with the uniform strain $x$. The $A_{2u}$-symmetry motion, where the uniform polarization $P$ couples with the staggered strain $\tilde{x}$.

cient $c^{\tilde{P}}$ is temperature-dependent:

$$F(P,\tilde{P},x,\tilde{x}) = F_1(P,\tilde{x}) + F_2(\tilde{P},x), \tag{1}$$

$$F_1(P,\tilde{x}) = \tfrac{1}{2}\gamma^{\tilde{x}}P^2 + aP\tilde{x} + \tfrac{1}{2}\tilde{c}^{P}\tilde{x}^2, \tag{1a}$$

$$F_2(\tilde{P},x) = \tfrac{1}{2}\tilde{\gamma}^{x}\tilde{P}^2 + a\tilde{P}x + \tfrac{1}{2}c^{\tilde{P}}x^2, \tag{1b}$$

where $\gamma^{\tilde{x}}$ is the inverse susceptibility at constant staggered strain $\tilde{x}$, and $\tilde{\gamma}^{x}$ is the inverse "staggered" susceptibility which connects $\tilde{P}$ with its conjugate "staggered" field $\tilde{E}$: $E_A = -E_B$.[12] The symbol $\tilde{c}^{P}$ stands for the "staggered" elastic stiffness which connects $\tilde{x}$ with its conjugate "staggered" stress $\tilde{X}$.

Following some transformation procedures, the function $F$ can be converted into the elastic Gibbs function of the form

$$G(P,\tilde{P})_{X,\tilde{X}=0} = \tfrac{1}{2}\gamma^{\tilde{X}}P^2 + \tfrac{1}{2}\tilde{\gamma}^{X}\tilde{P}^2, \tag{2}$$

where the inverse susceptibilities under constant stresses are

$$\gamma^{\tilde{X}} = \gamma^{\tilde{x}} - a^2/\tilde{c}^{P}, \tag{3a}$$

$$\tilde{\gamma}^{X} = \tilde{\gamma}^{x} - a^2/c^{\tilde{P}}. \tag{3b}$$

The actually observed elastic constant, which is temperature-sensitive and vanishes as the temperature approaches $T_D$, is

$$c^{\tilde{E}} = c^{\tilde{P}} - a^2/\tilde{\gamma}^{x}, \tag{4}$$

which appears in the electric Gibbs function derived from Eq. (1b). From Eqs. (3b) and (4), the inverse "staggered" susceptibility at constant stress is

$$\tilde{\gamma}^{X} = (\tilde{\gamma}^{x})^2(\tilde{\gamma}^{x}c^{\tilde{E}} + a^2)^{-1}c^{\tilde{E}}. \tag{5}$$

The lattice softenings can arise from a softening of either $\tilde{\gamma}^{x}$ or $c^{\tilde{P}}$ in Eq. (3b). In our case, the latter softens primarily. Thus, $\tilde{\gamma}^{X}$ vanishes concurrently with $c^{\tilde{E}}$ as $T$ approaches $T_D$; i.e., the antiferroelectric ordering or the $B_{1g}$ external-mode condensation should take place below $T_D$, although the $B_{1g}$-mode frequency, the square of which is proportional to the inverse "clamped" staggered susceptibility $\tilde{\gamma}^{x}$, should remain constant.

Furthermore, since the restoring force working on the oxygen octahedron in the staggered strain motion [see, Fig. 2(b)] is regarded as composed of joint contribution from both outside and inside the $VO_4$ octahedron, we assume that

$$\tilde{c}^{P} = c^{\tilde{P}} + \Delta, \tag{6}$$

where $\Delta$ corresponds to the $A_{2u}$ internal phonon mode contribution. Then, the inverse susceptibility actually observed for uniform field is, from Eqs. (3), (4), and (6), given by

$$\gamma^{\tilde{X}} = \left[\frac{\tilde{\gamma}^{x}\gamma^{\tilde{x}}\Delta + (\gamma^{\tilde{x}} - \tilde{\gamma}^{x})a^2}{a^2 + (c^{\tilde{E}} + \Delta)\tilde{\gamma}^{x}}\right] + \left[\frac{\tilde{\gamma}^{x}\gamma^{\tilde{x}}}{a^2 + (c^{\tilde{E}} + \Delta)\tilde{\gamma}^{x}}\right]c^{\tilde{E}}$$

$$\simeq k + k'c^{\tilde{E}}. \tag{7}$$

This relation was found to hold at all temperatures by fitting the observed characteristics of $\gamma^{\tilde{X}}$ to that of $c^{\tilde{E}}$, with constants $k = 4.9\times10^{9}$ m/F and $k' = 7.6\times10^{-3}$ m$^4$/C$^2$.

The value of $\Delta$ is estimated as $\sim 6.5\times10^{11}$ N/m$^2$, by using $k/k' \simeq \Delta$ which is derived from Eq. (7). Since $c^{\tilde{P}} \simeq c^{\tilde{E}} \simeq 1\times10^{11}$ N/m$^2$ for $DyVO_4$ at room temperature,[3,4] $\tilde{c}^{P} \sim 7.5\times10^{11}$ N/m$^2$ from Eq. (6). This is in agreement with the stiffness value of $\sim 1\times10^{12}$ N/m$^2$ calculated approximately from the one-dimensional Debye cutoff frequency which is estimated from the $A_{2u}$ internal-mode frequency in $YVO_4$ (=455 cm$^{-1}$ at room temperature).[13]

So far the temperature variation of any optical-phonon mode frequency in $DyVO_4$ has not been reported.[2] In view of the Lyddane-Sachs-Teller relation, however, we anticipate that the $A_{2u}$ external mode which is infrared-active should be temperature-dependent around $T_D$. The attempt to observe the double hysteresis loop around $T_D$ was not successful. The calculated threshold field for the forced transition based upon the model is larger by two orders of magnitude than that of $PbZrO_3$.

In the case of $TbVO_4$ and $TmVO_4$, the Jahn-Teller–driven elastic softening occurs mainly for $c_{66}$, which will explain the reason why the dielectric anomaly due to the piezo-optic coupling was not observed in these crystals. For $TmVO_4$, however, there is also a small variation[5] of $c_{11}$-$c_{12}$

around $T_D$, which will be responsible for the tiny anomaly of $\epsilon_c$.

The intervention of the extra short-range interaction between the phonon modes represented by the piezo-optic coupling may also be responsible for the unexplained high-temperature tail in the heat capacity data in $DyVO_4$ and $DyAsO_4$ around $T_D$,[14] and also for the discrepancy between the observed $T_D$ values and the theoretical ones predicted by the molecular-field theory.

In conclusion, the dielectric anomaly observed at the Jahn-Teller transition temperature in $DyVO_4$ may be understood as a direct consequence of the onset of an antiferroelectric ordering[8] which is driven by the softening $B_{1g}$ strain mode, i.e., as an optical-mode condensation without its softening. By following and extending the conventional terminology,[15] this phenomenon may suitably be called as the improper (or indirect) antiferroelectricity.

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[8]Throughout this Letter, the terms "staggered" and "antiferroelectricity" are referred to as the state in which the displacement alternates its direction from one sublattice to another *within a unit cell;* i.e., it is associated, contrary to the convention, with a Fourier component at zero wave vector, not with that at the zone boundary.

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## COMMENTS

# $p_\perp$ Dependence of Heavy-Particle Production

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I emphasize the close similiarity in the inclusive production of genuine heavy resonances compared to nonresonant hadron pairs. For small $x$ and not too big $p_\perp$ a simple relation describes both with proper mass dependence of the $p_\perp$ slope. Data on $J$-production support this picture.

In a recent measurement by Aubert *et al.*[1] at Brookhaven National Laboratory all pair combinations of $\pi^\pm$, $K^\pm$, and $p^\pm$ were detected with a double-arm spectrometer.[2] The cross sections for the simultaneously measured nine neutral two-body final states ($\pi^+\pi^-, \pi^+K^-, \ldots$) show a band structure[1] when plotted against their invariant mass, $m$. For production at rest in the c.m. system, i.e., $x = 2p_\parallel{}^*/\sqrt{s} \simeq 0$ and $p_\perp \simeq 0$, cross sections in all channels decrease like $\exp(-5m)$ over the measured range of $1.5 \leq m \leq 5.5$ GeV/$c^2$. No simple relations such as the frequently[3] used $\exp(-a \cdot p_\perp)$ or $\exp(-b \cdot p_\perp{}^2)$ describe these data because $a$ or $b$ will depend on $m$. However, all