Magnetically Controllable Cooperative Jahn-Teller Distortion in $TmAsO_4$

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$TmAsO_4$ undergoes a cooperative Jahn-Teller distortion at 6.0 K. At $T < 6$ K there is a temperature-dependent critical field $\vec{B}_c$ at which a cooperative distortion back to the high-temperature phase occurs. For $B < B_c$, the distortion directions in the basal plane are the (110) and the $(1\bar{1}0)$ directions and are magnetically controllable.

Although the Jahn-Teller effect in the transition-metal ions in solids has been studied extensively,[1] there has been a paucity of such work on the rare-earth ions. Five rare-earth salts have previously been reported to show Jahn-Teller distortions,[2-12] and in each of those the direction of the distortion can be controlled by a magnetic field.[3,4,6,7,10,12] It has also been shown[13,4,10] that a magnetic field increases the Jahn-Teller transition temperature of those salts. We report here the results of an investigation of $TmAsO_4$, in which the non-Kramers Tm^{3+} ion has a free-ion ground state $^3H_6$. $TmAsO_4$ does not order magnetically and it has rather unusual behavior. It not only undergoes a cooperative Jahn-Teller distortion, but its distortion can be prevented by the application of a magnetic field along, or in the vicinity of, the tetragonal axis. To the best of our knowledge such behavior has not previously been observed for any other salt.

Above the cooperative distortion temperature T_{JT}, $TmAsO_4$ has the tetragonal zircon structure[14] with four molecules per unit cell, all magnetically equivalent. The symmetry is $D_{4h}{}^{19}$. The Tm^{3+} ion-site symmetry is D_{2d} at temperatures above T_{JT}, and the Tm^{3+} ions lie on a slightly flattened diamond lattice in which each Tm^{3+} ion has four magnetic nearest neighbors at a distance of 3.83 Å.

We have measured the ac magnetic susceptibility χ of $TmAsO_4$ in zero field in the temperature range 0.3 to 20 K. The χ measured parallel and perpendicular to the tetragonal axis for $T > 6$ K is just that of an ordinary paramagnetic salt with a large $g_\parallel$ but a considerably smaller $g_\perp$. For $T < 6$ K, χ is independent of temperature. This indicates that the ground state for $T < 6$ K is a singlet, whereas that for $T > 6$ K is at least a doublet.

The optical spectra were measured between 1.1 and 77 K and in applied magnetic fields B of 0–36 kG.[15] For $T > 6$ K the spectra showed that the ground state was a doublet and that the first excited state, a singlet, was approximately 80 cm^{-1} above. The Zeeman patterns taken at $T > 6$ K indicated tetragonal symmetry with $g_\parallel = 8.8 \pm 0.2$ and $g_\perp = 5.5 \pm 0.5$ for the ground-state doublet (taking the effective spin $S' = \frac{1}{2}$). For $T < 6$ K the doublet split symmetrically into two singlets whose separation varied with temperature, reaching a value of 9.1 ± 0.1 cm^{-1} at 1.1 K. The transition temperature at which the doublet split into two singlets was estimated to be 6.1 ± 0.3 K. The Zeeman patterns taken at $T < 6$ K are rather unusual. A typical example in which $\vec{B}$ was applied along the tetragonal axis is shown in Fig. 1. At fields greater than some "critical" field, which is a function of temperature, the two lowest levels diverge linearly with field with $g_\parallel' = 9.8 \pm 0.2$ for the lower. The g value for the second singlet could not be determined since that level became depopulated as the region of linear divergence was reached. It is not clear why $g_\parallel'$ is larger than $g_\parallel$ but it may possibly be as a result

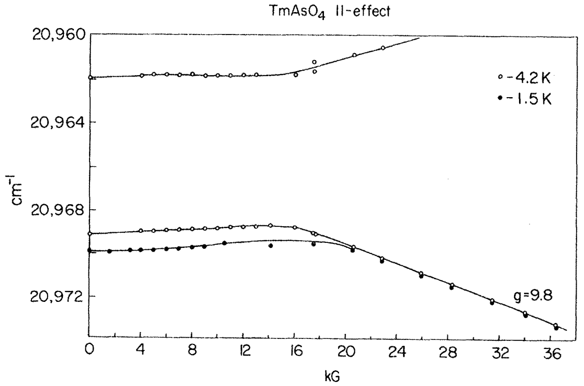

FIG. 1. The parallel Zeeman effect in $TmAsO_4$ for an optical transition from the two lowest levels to a $^1G_4$ at 4.2 and 1.5 K.

of slightly different values of the crystal-field parameters although the symmetry of the crystal field itself is the same. The angular variation of g', away from the direction which was the high-temperature tetragonal axis, was symmetrical with g' a maximum along that axis.

The spectra for $\vec{B}$ applied in the basal plane showed no strictly linear behavior and no "critical" field for $B < 36$ kG, the highest field attainable, although the curvature in the region of 25–36 kG was small. Both singlet levels decreased in energy with increasing field in a manner which can be accounted for by the admixing of higher-lying levels. Taking the region 25 to 36 kG to be sufficiently linear to determine the g factor for the lower level, its angular variation in the basal plane was measured at 1.5 K. It had a $\pi/2$-rad peridocity with $g \simeq 3.5$ when $\vec{B}$ was applied perpendicular to a crystal face, and with $g \simeq 6.0$ when $\vec{B}$ was at an angle of $\pi/4$ rad to the crystal face. The angular variation in the basal plane had a cusplike behavior such as that observed previously in TbPO$_4$,[10] TbVO$_4$,[6] DyVO$_4$,[4] and DyAsO$_4$.[16] This indicates that there is a sudden change in the distortion direction and that the distortion direction prefers to lie at small angles ($\pi/4$ rad or less) to the direction of the applied field. The distortion directions in the basal plane are the (110) and the (1$\bar{1}$0) directions, the same as that observed in TbVO$_4$,[6] but $\pi/4$ rad away from that observed in DyAsO$_4$[16,7] and DyVO$_4$.[4] The angular dependence of the g factor in the basal plane indicates that the symmetry of the distorted phase is no higher than orthorhombic.

Measurements of dM/dB vs $\vec{B}$ were made in the range 0.3–10 K using the ac-mutual-inductance technique, where the ac measuring field and the dc field were applied either parallel or perpendicular to the tetragonal axis. Some typical results are shown in Fig. 2. These results show clearly the dramatic changes in dM/dB at the various critical fields which are those for the cooperative Jahn-Teller transitions from the distorted phase back to the undistorted tetragonal phase. The critical field for the transition is a very strong function of temperature.

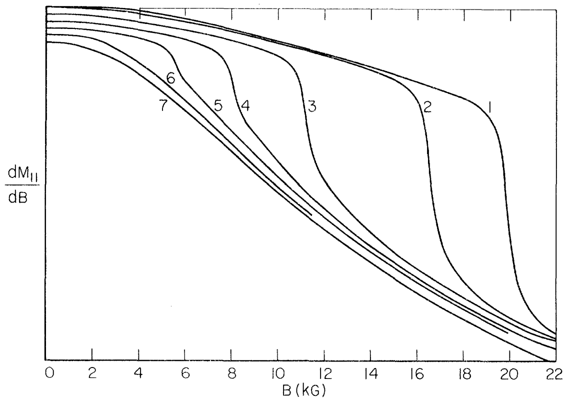

FIG. 2. Curves of dM/dB vs $\vec{B}$ ($\vec{B}$ parallel to the tetragonal axis) in kilogauss for several temperatures. The ordinate scale is arbitrary and the zero positions of the different curves have been arbitrarily shifted for clarity. The temperatures at which the various curves were obtained were as follows: (1) $T = 1.13$ K; (2) $T = 4.19$ K; (3) $T = 5.34$ K; (4) $T = 5.69$ K; (5) $T = 5.86$ K; (6) $T = 6.00$ K; and (7) $T = 6.12$ K.

Although the distortions in TmAsO$_4$ are static in character, there must still be enough dynamic distortion, even at 0.3 K, for the system to sample effectively the states available to it and then transform into the lowest free-energy state of the crystal. The states of the system that are sampled are the Zeeman states and those due to the cooperative distortion. That is, *there is a sampling as to whether the distortion which splits the doublet, or the Zeeman splitting of the ground-state doublet of the tetragonal phase, gives the lower free energy for the system.* The critical fields B_c are just those values of the magnetic field at which the system lowers its free energy by distorting from the low-temperature phase back to the tetragonal phase and going into the Zeeman-split states of the tetragonal phase, which have a larger splitting for higher fields than for the distortion at that particular temperature. In fact, if one uses the measured g' value and takes the value of $\vec{B}$ at which dM/dB has its maximum slope, then one may calculate the splitting of the doublet due to the cooperative distortion at that temperature. The calculated splitting may be compared with that determined optically. Excellent agreement is found. For example, at 1.1 K, B_c is 19.9 kG which corresponds to a splitting of 9.1 cm^{-1}, which is precisely the value determined optically in zero field at that temperature.

The critical fields and, hence, the splittings of the doublet are shown as a function of temperature in Fig. 3. The temperature dependence is as expected for second-order phase transitions where the critical fields which are characteristic of the transition are proportional to an order parameter. The temperature dependence is similar to that of the sublattice magnetization of antiferromagnets and the spontaneous magnetization of ferromagnets. It is well known that the molec-

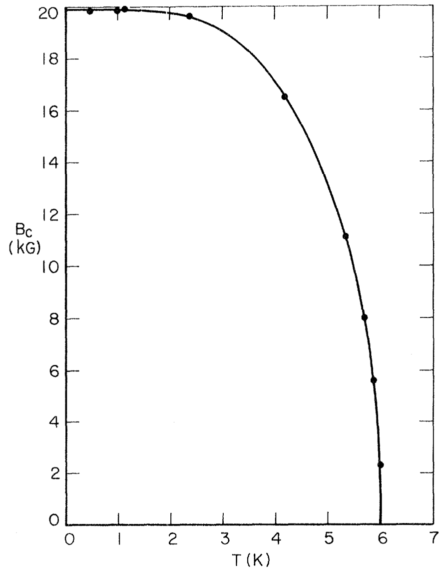

FIG. 3. A comparison of the critical fields (and, hence, the splittings of the two singlets), determined experimentally by the measurements of dM/dB as a function of $\vec{B}$ ($\vec{B}$ parallel to the tetragonal axis), for the cooperative Jahn-Teller distortion from the low-temperature (probably orthorhombic) phase to the high-temperature tetragonal phase with the predictions of the molecular-field theory. The solid circles are the data points, and the solid curve is the molecular-field prediction.

ular-field approximation describes such systems in a qualitative way. In the molecular-field theory, the order parameter Δ/Δ_0 for spin-$\frac{1}{2}$ systems is simply $\Delta/\Delta_0 = \tanh(T_c\Delta/T\Delta_0)$ where $2T_c = \Delta_0$, the splitting of the doublet in zero field at zero temperature. The solid line in Fig. 3 is that predicted by the molecular-field theory, where it has been normalized to agree with the experimental values at 0.4 and 6.00 K. The transition temperature predicted by the theory, with the use of the measured value of Δ_0, is 6.5 K, however, and not 6.0 K. This is not surprising since the molecular-field approximation generally predicts a transition temperature which is too high when the coordination number is not large, because short-range order, or statistical-fluctuation effects near T_c are ignored. As may be seen from Fig. 3, the fit of the theory after normalization is in quantitative agreement with experiment. This is to be contrasted with $\mathrm{DyVO_4}$ and $\mathrm{TbVO_4}$ where the fit was only qualitative.[11,17]

Elliott *et al.*[18] have derived a theory for the cooperative Jahn-Teller distortions in rare-earth systems based on a harmonic-oscillator Hamiltonian for the crystal and an electron-lattice coupling which is small compared to typical phonon zero-point energies. The electron-lattice interaction can be described by a Hamiltonian such as $H_{\mathrm{JT}} = \sum_{\Gamma i} A^{\Gamma} O_i^{\Gamma} Q_i^{\Gamma}$ containing couplings between symmetry-lowering strain operators Q_i^{Γ} and electronic operators O_i^{Γ} of symmetry Γ, both operating on the ith rare-earth ion. A^{Γ} is the coupling constant. The strain operators can be transformed into phonon coordinates, and the equations of motion for the coupled system can be solved. If only the static aspects of the problem are considered, i.e., if the Q_i^{Γ} are determined by only the static displacements of the zero positions of the phonon coordinates, then, as shown by Harley, Hayes, and Smith,[17] the problem reduces to a simple molecular-field type of theory, and the Q_i^{Γ} become proportional to the mean values of the electronic operators. Then the effective molecular-field Hamiltonian for a single rare-earth site becomes $H_{\mathrm{JT\,eff}} = \sum_{\Gamma} \lambda^{\Gamma} \langle O^{\Gamma}\rangle O^{\Gamma}$, where λ^{Γ} is the molecular-field constant. All the $\langle O^{\Gamma}\rangle$ are zero above T_{JT}, but below T_{JT} the free energy of the system is lowered by a distortion such that at least one $\langle O^{\Gamma}\rangle$ is nonzero. Since this is a molecular-field theory, a second-order transition is predicted and, indeed, is what has been observed experimentally.

Our experiments have shown that $\mathrm{TmAsO_4}$ is a very interesting and rather unusual compound. It undergoes a cooperative Jahn-Teller crystallographic phase transition at 6 K from a high-temperature phase of tetragonal symmetry to what is probably an orthorhombic (either D_2 or C_{2v}) phase below 6 K. When a magnetic field is applied, at $T < 6$ K, parallel to or in the vicinity of the high-temperature tetragonal axis, the distortion is removed at some critical field, which is a function of temperature. The critical field for the transition is that field at which the Zeeman effect of the degenerate doublet would have produced a splitting equal to the splitting produced by the distortion. There appears to be excellent agreement between theory and experiment. When the field is applied perpendicular to the tetragonal axis and to the crystal face at $T < 4.2$ K, we observe no cooperative Jahn-Teller distortion back to a tetragonal phase. This is as expected for our range of fields, however, since B_c is calculated to be 44.1 kG at 4.2 K. We do observe a magnetically rotatable distortion in the basal plane, however, which behaves similarly to that observed previously in $\mathrm{DyVO_4}$,[4] $\mathrm{TbVO_4}$,[6] and $\mathrm{DyAsO_4}$.[12,7]

It would be interesting to study the strains present in TmAsO$_4$ either by using Raman scattering or by studying the effects of applied stress on its magnetic and optical properties. An x-ray diffraction study would be very useful for determining directly the crystal symmetry below 6 K. Another very interesting experiment would be an adiabatic nuclear demagnetization of ^{169}Tm in TmAsO$_4$, a Van Vleck paramagnet, in which full advantage could be taken of the large electronic moment with its large coupling to the nucleus present at $T < 1$ K in high magnetic fields.

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Photoemission Energy-Level Measurements of Chemisorbed CO and O on Ni†

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Photoemission energy distributions at high photon energies permit one-electron measurements of the electronic energy levels and level widths of chemisorbed gases on clean metal surfaces at fractional monolayer coverages. Chemisorbed CO on Ni exhibits energy levels at 7.5 and 10.7 eV below the Fermi level E_F while chemisorbed O on Ni shows a 2-eV width level at 5.5 eV below E_F. Upon increased oxygen exposure, a surface oxide of Ni is formed which exhibits valence bands about 8.5 eV wide.

Many studies have been reported on the configurations of adsorbed gases on surfaces and on adsorbate binding energies; however, relatively little work has been reported on the electronic energy levels of such adsorbates. Techniques which have been used include ion-neutralization spectroscopy (INS)[1] and field-emission spectroscopy.[2] In this Letter we describe the application of ultraviolet photoemission spectroscopy (UPS) to measurements of electronic energy levels of adsorbed gases on clean metal surfaces. Chemisorbed CO on Ni exhibits energy levels at 7.5 and 10.7 eV below the Fermi level E_F with energy widths of about 2 and 1 eV, respectively. We tentatively identify the -7.5-eV level with the carbon lone pair $\sigma 2p$ molecular orbital involved in bonding to the Ni. Compared with gaseous CO, this level is shifted upwards in energy by about 1.5 eV (relative to the vacuum level). Likewise, the -10.7-eV level is identified as the $\pi 2p$ bonding molecular orbital of CO and is shifted upwards by about 1.2 eV. Chemisorbed oxygen shows a single level of width 2 eV centered at 5.5 eV below E_F. As the oxygen exposure is increased from about 1×10^{-6} Torr sec to 25×10^{-6} Torr sec, this -5.5-eV level broadens into a