

use for surface structure determination.¹⁶ An attempt, however, to assess its potential role and to compare it to established surface-structure-determination methods that are based on LEED intensity analysis¹⁷⁻¹⁹ would be premature at this stage. Further calculations and measurements are required.

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Crystal-Electric-Field Effects on the Thermal Expansion of TmSb

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We report a crystal-electric-field effect on the low-temperature thermal expansion of TmSb, manifesting itself as a Schottky-type anomaly. From our results we deduce a volume dependence of the crystal-field level splitting which is in contradiction to point-charge-model expectations.

Because of the crystal-field splitting of the lowest J multiplet of the order of 200 K, rare-earth compounds, such as the rare-earth pnictides, are ideally suited to study effects of the crystal electric field (CEF) on various physical properties in these substances. In particular, TmSb has often been quoted as a model crystal-field-only paramagnetic substance.^{1,2} Experimentally determined thermodynamic properties such as the magnetic susceptibility,¹ specific heat, and elastic constants³ can very well be accounted for by using a crystal-field energy-level scheme de-

termined from neutron-scattering experiments.² TmSb crystallizes in the cubic NaCl structure and the Tm^{3+} $J=6$ CEF splitting gives a Γ_1 singlet ground state followed by a Γ_4 triplet at 25 K and a Γ_5 triplet at 56 K, the other excited levels lying higher than 110 K. These higher levels are neglected in our considerations throughout this work.⁴

In this Letter we would like to show the first experimental evidence of a CEF effect on the thermal expansion. We have chosen TmSb because of its properties mentioned above and because elec-

tron and phonon contributions have a small influence in the temperature range in which CEF effects on the other properties of this material are observed. The two single crystals investigated, with dimensions of $2.5 \times 0.5 \times 0.5 \text{ mm}^3$, were cut from the same batch as those used for measurements of the elastic constants.³ The length changes were measured with a capacitance dilatometer.

In Fig. 1 we show the experimental results of the linear thermal expansion coefficient α along the $\langle 100 \rangle$ axis of a TmSb single crystal, as a function of temperature between 1.5 and 16 K. Above 1.5 K, α is negative, passing through a minimum of $-1.8 \times 10^{-6} \text{ K}^{-1}$ at 9 K. Above 14 K α then becomes positive. We can interpret this result in terms of a CEF effect by noting that the specific heat c_p and the volume thermal expansion coefficient β are thermodynamic derivatives of the free energy F , namely $c_p = -T(\partial^2 F / \partial T^2)$ and $\beta = -\kappa(\partial^2 F / \partial V \partial T)$, where κ is the adiabatic compressibility and V is the volume. For the

CEF contribution of c_p and β we can write

$$c_p = (1/kT^2)[\langle E^2 \rangle - \langle E \rangle^2], \quad (1)$$

$$\beta = (\kappa/\Omega kT^2)[\langle E^2 \gamma \rangle - \langle E \rangle \langle E \gamma \rangle], \quad (2)$$

where Ω is the molar volume. Quantities of the form

$$\langle X \rangle = \sum_i X_i \exp(-E_i/kT) / \sum_i \exp(-E_i/kT)$$

denote statistical averages over the CEF levels E_i , and $\gamma_i \equiv -\partial \ln E_i / \partial \ln V$ is the Grüneisen parameter for the crystal field level E_i . Note that for cubic crystals $\beta = 3\alpha$. Comparing Eqs. (1) and (2) we find that β is proportional to c_p (a) if only two CEF levels are considered or (b) if all the γ_i are equal. Such assumptions lead to the broken line in Fig. 1(a), where the experimental specific heat c_p was fitted to the low-temperature part of α . Good agreement is obtained up to 9 K but rather drastic deviations are observed at higher temperatures. From this fit we deduce a Grüneisen parameter $\gamma = \alpha\Omega/\kappa c_p = -1.15$, where for α , Ω , κ , and c_p the known experimental values are used. At low temperatures, this γ is equal to γ_1 , arising from the volume dependence of the lowest energy splitting $\Gamma_1 - \Gamma_4$. The deviations above 10 K clearly indicate that the Grüneisen parameter γ_2 for the next higher level at 56 K is different from γ_1 . The broken line in Fig. 1(b) is a fit obtained with $\gamma_1 = -1.30$ and $\gamma_2 = +1.05$.⁵ The fitted value of γ_1 is in fair agreement with the experimental γ value mentioned above. The salient features of the experimental data are well reproduced by taking into account these CEF effects only and thus represent a Schottky-type anomaly in the low-temperature thermal expansion of TmSb.^{6,4}

For normal metals the electronic contribution to the thermal expansion is of the order $10^{-9}T$ and can thus be neglected in our case.⁷ Above 10 K, however, additional thermal expansion due to phonons has to be expected. The temperature dependence of the thermal expansion due to lattice vibrations can be written in the form

$$\alpha_{\text{ph}} = bT^3 + dT^5 + \dots \quad (3)$$

In the Debye approximation $b = (\gamma_G \kappa / \Omega) 1.944 \times 10^{10} / \Theta_D^3$,⁸ where γ_G is typically of the order of unity and $\Theta_D = 237 \text{ K}$ in our case.³ At 15 K this gives a contribution of approximately $1 \times 10^{-7} \text{ K}^{-1}$ to α , a rather small effect. The anharmonic T^5 term is more difficult to estimate but is known⁷ to be noticeable for $T > \Theta_D/40$. The solid line in Fig. 1(b) represents a fit to the experimental da-

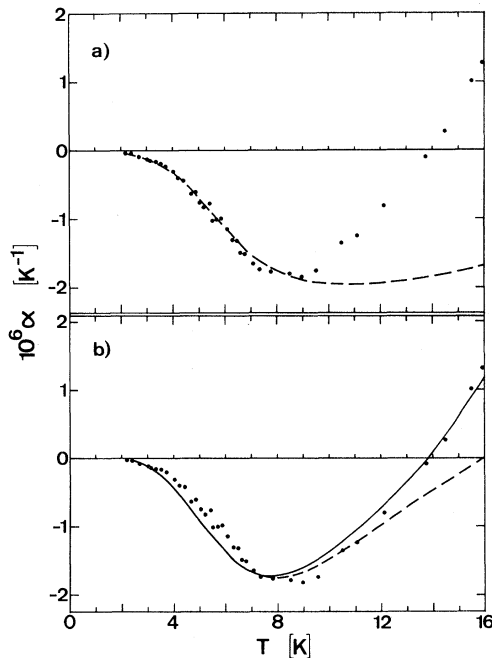


FIG. 1. Temperature dependence of the linear thermal expansion coefficient α along the $\langle 100 \rangle$ axis of TmSb. (a) Full circles, experiment; broken line, experimental specific heat values from Ref. 3 fitted to the low-temperature part of α , with a single Grüneisen parameter $\gamma_1 = -1.15$. (b) Full circles, experiment [as in (a)]; broken line, calculated fit with two Grüneisen parameters $\gamma_1 = -1.30$ and $\gamma_2 = +1.05$, using the CEF level scheme of Ref. 2; solid line, same as broken line, including a phonon contribution $bT^3 + dT^5$, with $b = 3 \times 10^{-11} \text{ K}^{-4}$ and $d = 1 \times 10^{-12} \text{ K}^{-6}$.

ta by taking into account CEF effects *and* phonon contributions outlined above. For the T^5 term we obtain $d = 1 \times 10^{-12}$ which is of reasonable magnitude.

An alternative expression for Eq. (2) can be obtained from the microscopic Hamiltonian⁹

$$H_{me} = \epsilon_V \left[\sum_i B_{O_4} \alpha (O_4^0 + 5O_4^4)_i + B_{O_6} \alpha (O_6^0 - 21O_6^4)_i \right], \quad (4)$$

where ϵ_V denotes the volume strain $\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}$, O_4 and O_6 are the CEF operators, and $B_{O_4} \alpha$ and $B_{O_6} \alpha$ are magnetoelastic coupling constants. Equation (4) leads to volume-dependent CEF levels and, accordingly, to the Grüneisen parameters γ_i .

The Grüneisen parameter γ of the Γ_1 - Γ_4 level splitting is, as deduced above, approximately -1.25 . In the framework of the point-charge model one expects a value of around $+\frac{5}{3}$ arising from the dominant R^{-5} dependence of the CEF potential. In their neutron-scattering study of TmSb, Birgeneau *et al.*² have pointed out that the point-charge-model predictions are less successful in the case of TmSb than for Pr^{3+} compounds. Nevertheless, this considerable discrepancy between experiment and the point-charge estimate is somewhat surprising since the dominant term of the CEF parameters, $A_4 \langle r^4 \rangle$, and also the magnetoelastic coupling constants³ follow point-charge-model predictions rather closely.

This behavior, however, offers an alternative explanation of the recently measured pressure dependence of the low-temperature magnetic susceptibility of TmSb.¹⁰ At low temperatures, the CEF susceptibility for such a Van Vleck system is given by

$$\chi_c = 2g^2 \mu_B^2 \frac{|\langle \Gamma_1 | J_z | \Gamma_4 \rangle|^2}{k_B (E_{\Gamma_4} - E_{\Gamma_1})}. \quad (5)$$

With neglect of a possible stress dependence of the matrix element $\langle \Gamma_1 | J_z | \Gamma_4 \rangle$, the relative stress or pressure dependence of χ_c is given by

$$\partial \ln \chi_c / \partial p = - \partial \ln (E_{\Gamma_4} - E_{\Gamma_1}) / \partial p = - \kappa \gamma_1. \quad (6)$$

With a value of $\gamma_1 = -1.25$ we calculate $\partial \ln \chi_c / \partial p = +2.3 \times 10^{-3} \text{ kbar}^{-1}$, close to the measured $\partial \ln \chi / \partial p = +3.0 \times 10^{-3} \text{ kbar}^{-1}$. We therefore conclude

that the pressure dependence of the exchange parameter J is not the essential feature to explain the pressure derivative of χ , at least not in the case of TmSb.

In conclusion we may say that we have observed a Schottky-type anomaly in the low-temperature thermal expansion of TmSb. From our measurements we calculate a pressure dependence of the energy splitting between the lowest two levels which is in contradiction with the point-charge model, but accounts for the main part of the earlier reported pressure dependence of the magnetic susceptibility.

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