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Anomalous thermal expansion of nonstoichiometric TmSe

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Crystal lattice parameters of a nonstoichiometric and a stoichiometric sample of the intermediate-valent compound TmSe have been measured as a function of temperature by x-ray and neutron diffraction techniques. The thermal expansion behavior of the stoichiometric sample is consistent with this material showing temporal valence fluctuations. The behavior of the nonstoichiometric sample differs from the first, particularly at low temperatures where we have observed an unexpected Schottky anomaly in the thermal expansion. This anomaly may be explained in terms of the random Tm-site vacancies in the lattice which can cause a preferential freezing of Tm^{3+} ions at some sites and Tm^{2+} ions at other sites hindering the process of on-site valence fluctuations.

Much is known about TmSe because of the many and various measurements made on this material.[1] It is a particularly interesting material because it is intermediate valent (IV) under ambient conditions of temperature and pressure and is the only IV material known to order magnetically at lower temperatures.[2] Another interesting feature is that one can vary the average valence of the Tm ions by changing the stoichiometry, i.e., the ratio of Tm to Se atoms in the crystal.[3] Lowering the Tm-to-Se ratio also causes other striking differences in physical properties; for example, the nature of the antiferromagnetic ordering changes from type I to type II and one never quite gets truly long-range ordering.[4,5] The prime motivation for this work was to investigate the nature of the short-range order and the occurrence of any possible lattice distortion in a Tm-deficient nonstoichiometric Tm_xSe sample ($x<1$). To do this, x-ray powder diffraction measurements were carried out on a nonstoichiometric sample ($a=5.684$ Å) in the temperature range 4–300 K. For comparison purposes, neutron and x-ray-powder diffraction measurements on a stoichiometric or nearly stoichiometric sample ($a=5.710$ Å) were also done. We have not detected either ordering of the vacancies or any cooperative lattice distortion in the Tm-deficient sample within the limits of our experimental precision. Any such ordering or lattice distortion would modify the symmetry of the structure and show up in additional superlattice lines or at least in asymmetric broadening of the cubic diffraction peaks, which we have not observed. Thus the short-range order observed earlier by neutron diffraction in the same sample must be of magnetic origin.[5] We have, however, observed an unexpected anomaly in the thermal expansion of the Tm-deficient sample as compared to the stoichiometric sample. This work reports and compares the thermal expansion behavior of the two samples.

Thermal expansion of a crystal lattice principally arises from nonharmonic forces in the lattice. One can derive an expression for the coefficient of thermal expansion from simple statistical mechanics arguments. According to the adiabatic principle, the Helmhotz free energy can be separated into a sum of terms due to ionic lattice vibrations, conduction electrons, crystal-field effects, and the effects of lattice defects, etc. Each effect may have a different temperature dependence allowing one to measure experimentally the various effects. Following Barron *et al.*[6] one arrives at the expression for the volume thermal expansion coefficient β

$$\beta B_T = \frac{1}{VkT^2}(\langle E_i^2\gamma_i^2\rangle - \langle E_i\gamma_i\rangle\langle E_i\rangle)\,, \tag{1}$$

in which

$$\langle E_i\rangle \equiv \sum_i E_i g_i e^{-E_i/kT} \Big/ \sum_i g_i e^{-E_i/kT}\,. \tag{2}$$

$\gamma_i \equiv -\partial \ln E_i/\partial \ln V$ and g_i is the degeneracy of the ith energy level of the system with eigenenergy E_i. V is the volume of the system and k the Boltzmann constant. The bulk modulus B_T varies very slowly with temperature [we have measured values of 371(13) kbar at room temperature and 341(38) kbar at 1.7 K for the stoichiometric sample[7]] and so we will treat it as a constant in the above expression. If the quantum states are very close together in comparison to kT, we can convert the sums to integrals and using the quasiharmonic and Debye approximations one finds

$$\beta = \frac{9Nk\gamma}{B_T V}\left[\frac{T}{\Theta_D}\right]^3 \int_0^{\Theta_D/T} \frac{x^4 e^{-x}dx}{(e^x-1)^2} \tag{3}$$

with γ the Grüneisen parameter being assumed the same for each quantum state. V/N is the volume per formula unit and Θ_D is the Debye temperature. This gives $\beta \sim T^3$ at low temperatures and a linear variation of β with temperature at high temperatures. If we add a term for conduction electrons, we get a linear term in T. Thus at low and high temperatures we find

$$\beta = \frac{\gamma\gamma_{\mathrm{el}}}{VB_T}T + \frac{12\pi^4 Nk}{5VB_T\Theta_D^3}T^3 \quad \text{for } T \ll \Theta_D \tag{4}$$

and

$$\beta = \frac{3Nk\gamma}{VB_T}(1-\Theta_D^2/20T^2) \quad \text{for } T > \Theta_D/2 \ . \tag{5}$$

We have assumed γ to be a constant in each of these ranges.

Other things such as crystal-field effects, vacancies or other crystal defects may split the low-lying energy levels so that when kT is of the order of the level splitting a repopulation of the states begins and anomalies in the thermal expansion and specific heat may arise. These are Schottky anomalies. If we assume two levels with energies 0 and E, and with respective degeneracies g_0 and g_1, we find after substitution into Eq. (1) that

$$\beta = \frac{A}{T^2}e^{-E/T}\left[1+\frac{g_1}{g_0}e^{-E/T}\right]^{-2} + BT + CT^3 \ . \tag{6}$$

The last two terms in Eq. (6) are the contributions from the conduction electrons and the phonons at low temperatures. We will use Eqs. (4)–(6) for analyzing the experimental results.

The two samples used in this experiment consisted of powered polycrystalline material and had lattice parameters 5.684 and 5.710 Å, respectively, at ambient temperature. The former is thus nonstoichiometric, while the latter can be considered as stoichiometric, or nearly so. The characteristics of both these samples have been given in an earlier paper.[8] The x-ray powder diffraction measurements were done on a Seeman Bohlin powder diffractometer equipped with a quartz monochromator calibrated against the $K\alpha_1$ line of chromium. The temperature accuracy was ±5 K above 100 K and ±0.5 K below 10 K. Full spectra were measured on the nonstoichiometric sample at 5 temperatures between 2.5 and 300 K, but only the (420) peak was measured at the other temperatures and at all the temperatures for the stoichiometric sample. The lattice parameter was calculated from the position of the center of the (420) diffraction peak with a relative precision of $\sim 10^{-4}$. The neutron measurements involved a high-resolution powder diffractometer using the wavelength 1.907 Å and were done only on the stoichiometric sample. Neutron diffraction spectra consisting of 5 to 7 nuclear peaks with all even Miller indices were taken at 15 different temperatures between 1.5 and 300 K. A nonlinear Gaussian fitting was employed to accurately determine the centers of the peaks and a zero offset correction of about 0.017(8)° in θ brought the lattice parameter calculated from all the peaks into coincidence with an accuracy of ±0.0008 Å. The temperature accuracy was of the order of ±0.1 K at low temperatures to ±1 K at the higher temperatures.

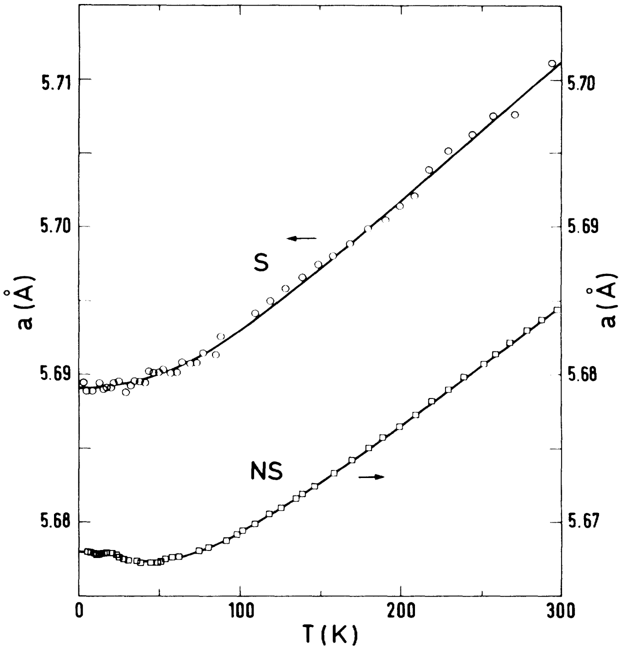

FIG. 1. Temperature dependence of the lattice parameters of stoichiometric (S) and nonstoichiometric (NS) TmSe. Solid lines are results of least-squares fits to the experimental data. See text for details.

The results of the lattice parameter measurements are shown in Fig. 1. We have shifted the x-ray data uniformly by a few mÅ to make them correspond with the neutron work which agrees very well with precision x-ray measurements at room temperature on these samples.[8] This is reasonable since no zero offset correction was made on the x-ray data. The temperature dependence of the lattice parameter appears quite normal for the stoichiometric sample but the reversal in the slope of the nonstoichiometric sample data below 40 K indicates something unusual in this material.

We have analyzed the high-temperature data for both the samples using the equation

$$a(T) = a_0 + a_1 T + a_2 T^2 \ , \tag{7}$$

where the coefficients a_i's were determined by a least-squares fitting of the data to the equation. Upon differentiating Eq. (7) with $\beta = 3\alpha = (3/a)da/dT$, we arrive at Eq. (5) allowing us to physically interpret the parameters a_i's. For the nonstoichiometric sample, however, we first smoothed the data by averaging each point with the average of the two nearest-neighboring points. This helped to smooth out effects of scatter in the data. Use of Eqs. (7) and (5) gives $\Theta_D = (20a_0/a_2)^{1/2}$ and $\gamma = a_2 a^2 B_T/4k$. An average of a over the temperature range is chosen and using the value of B_T at high temperature[7] we get the Grüneisen parameter γ. B_T is assumed to be essentially the same for the two samples.[3] The results are shown in Table I. For the low-temperature range, using the data for the stoichiometric sample we

TABLE I. Summary of physical parameters for stoichiometric (S) and nonstoichiometric (NS) TmSe obtained from least-squraes fits of Eqs. (4)–(6) to experimental data.

Sample	a(300 K) (Å)	a(0 K) (Å)	α(300 K) (10^{-5} K^{-1})	$\gamma_{\rm HT}$	Θ_D (K)	$\gamma_{\rm el}$ (mJ mol^{-1} K^{-2})	$\Theta_S=E/k$ (K)	g_1/g_0
NS	5.6846(3)	5.6680(5)	1.44	1.87(9)	217(40)	~175	68(2)	1.9(5)
S	5.7109(3)	5.6891(6)	1.67	2.18(7)	212(38)	~300		

made a linear fit of the lattice parameter to

$$a(T)=b_0+b_1T+b_2T^2 \tag{8}$$

and again with $\beta=3\alpha=(3/a)da/dT$ gives an equation of the form of Eq. (4). We required that the coefficient of thermal expansion from the low- and high-temperature fittings coincide with approximately the same slope at the crossover point near 75 K. Now $\gamma\gamma_{\rm el}=3b_1a^2B_TN_A/2$, where N_A is Avogadro's number. Not knowing the Grüneisen parameter at low temperature, we assume[9] $\gamma_{\rm LT}\simeq\frac{1}{2}\gamma_{\rm HT}$. This then yields a $\gamma_{\rm el}\simeq300$ mJ/mole K^2 in good agreement with the more direct evaluation of this quantity from specific-heat data.[10] The Debye temperature is not realizable from the T^3 term because of the accuracy of our data. It is not easy to find an appropriate function to fit the low-temperature lattice parameter data of the nonstoichiometric sample; so we fitted selected ranges of this data with a parabola and calculated a value for the linear thermal expansion coefficient, α, at the center of each. It was necessary to use 9–11 points at a time to properly smooth the data. We then get the results shown in Fig. 2. These results were then analyzed with Eq. (6) to determine a value for the Schottky level splitting and the ratio of the degeneracy of the ground and the excited state. From the linear term we find $\gamma\gamma_{\rm el}$. Since the values of γ for the two samples are quite alike at 300 K, we assume that they are likewise similar at low temperatures and conclude that the $\gamma_{\rm el}$ is only one-half as large in the nonstoichiometric sample as in the stoichiometric sample. All the results are given in Table I and the variation of the linear thermal expansion coefficients for the two samples over the entire temperature range is shown in Fig. 3. The intensities of the higher-order Bragg peaks do not show, for either samples, any anomalous decrease as the temperature is lowered. We have not thus observed any indication of a possible lattice softening at low temperature.

To interpret the above results, we begin by discussing the results for the stoichiometric sample. We find that the thermal expansion is consistent with an interpretation of TmSe as being an IV system in which the lattice is soft or unstable with respect to volumetric changes which gives both a large value of the compressibility[7] and, correspondingly, of the thermal expansion at room temperature. The Debye temperature is in the range of values estimated from other measurements[10] and again is characteristic of a reasonably soft lattice. The most interesting result is the existence of the large linear term in the low-temperature thermal expansion, characteristic of a large density of states at the Fermi surface which is one of the identifiers of the IV state. There is not much difference between the stoichiometric and the nonstoichiometric sample at high temperatures in terms of the Grüneisen parameter or the

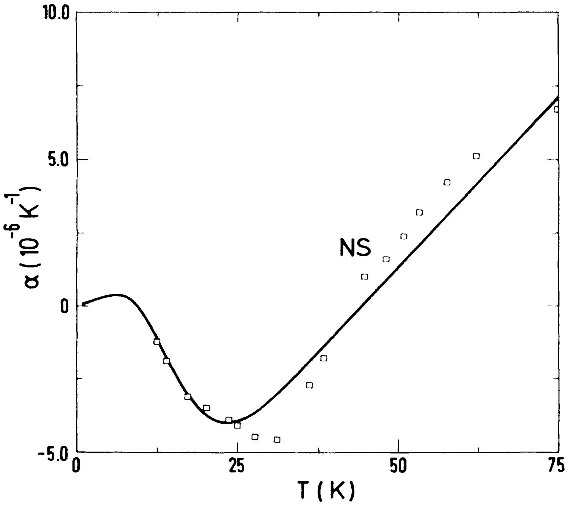

FIG. 2. Linear thermal expansion coefficient of nonstoichiometric TmSe as a function of temperature. Solid line is a least-squares fit of Eq. (6) to the experimental data.

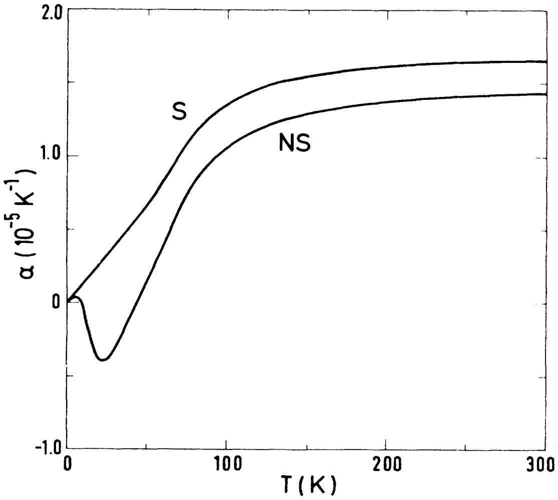

FIG. 3. Linear thermal expansion coefficients of stoichiometric (S) and nonstoichiometric (NS) samples of TmSe as a function of temperature.

Debye temperature. The thermal expansion coefficient is slightly smaller for the nonstoichiometric sample. These results are all in agreement with the compressibility of these two materials being very similar at room temperature.[3] We, therefore, conclude that at high temperature the physical properties of the stoichiometric and the nonstoichiometric sample are quite similar.

For the nonstoichiometric sample we observe, in the low-temperature region, a negative thermal expansion below 43 K which has the form of a Schottky anomaly for a two-level system separated by 68 K with about 1.9 as the ratio of the degeneracies for the excited and the ground state (Table I). The lower value of γ_{el} for the nonstoichiometric sample in comparison to the stoichiometric sample indicates a drop in the density of states at the Fermi surface. It has been proposed recently from ^{77}Se NMR measurements[11] that at low temperatures there is a random static distribution of integral valent Tm^{2+} and Tm^{3+} ions in the nonstoichiometric sample with the pseudo-$4f$ level being near but not pinned at the Fermi level. This would slow down the fluctuations and reduce the density of states at the Fermi level, all consistent with our findings.

One can speculate as to the origin of the Schottky-like anomaly. It could arise from a crystal-field effect but there are no other corroborating evidences to support such an argument. Inelastic neutron scattering studies have found no crystal-field splitting in either of the samples studied here.[12,13] Another possibility which might cause a ground-state splitting would be the effect of vacancies on the system.[6] These vacancies could be as numerous as 2% in the stoichiometric or nearly stoichiometric sample and can reach 5–6% in the Tm-deficient nonstoichiometric sample.[14] Suppose there is a splitting in the energy such that the Tm atoms with all neighboring Tm sites occupied are in a lower or ground state and those with one or more neighboring vacancies in TM sites being in the first excited state with an energy splitting of $E = k\Theta_S$. Assuming a completely random distribution of the vacancies, one obtains from statistics the relative degeneracy of the excited to the ground state as 1.94 (for 5.5% vacancies) for the nonstoichiometric sample but only 0.32 for the stoichiometric sample. The value of 1.94 is a surprisingly good agreement with the value of g_1/g_0 we find experimentally. Since the magnitude of the Schottky anomaly is proportional to g_1/g_0, the effect would be 6 times smaller in the stoichiometric sample and thus not observable in our measurements. This large concentration of random vacancies could also prevent a true long-range magnetic order to develop in the Tm-deficient sample, as confirmed by neutron diffraction measurements.[5] The vacancy-free and vacancy-neighboring sites are sites of different local lattice strain and could be, at low temperatures where the energy splitting is of the order of or less than kT, preferentially occupied by Tm^{2+} and Tm^{3+} ions which have different ionic sizes. This would then cause a progressive spatially random freezing, on the Tm sites, of the two integral valent states of Tm as the temperature falls below Θ_S and hinder valence fluctuation, all in agreement with recent ^{77}Se NMR measurements on the same sample.[11] Such a random distribution of two different magnetic states on the Tm sublattice is a possible explanation of the absence of long-range magnetic order in the Tm-deficient sample. Since the observed[11] average Tm valence in the nonstoichiometric sample is $2.7+$, we are led to believe that the Tm^{3+} ions occupy the preponderant vacancy-neighboring sites and are in the higher-energy state. Indeed the observed value of 1.9 for g_1/g_0 leads to an average Tm valence of $2.66+$. This, however, means that the presence of vacancies promotes the $3+$ valence state of Tm, in agreement with the observed fact that the valence state of Tm approaches $3+$ as one moves away from stoichiometry in the Tm-deficient samples.[14]

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