# DETERMINATION OF THE DEBYE TEMPERATURE $\theta_\infty$ AND THE ANHARMONIC COMPONENT OF THE SPECIFIC HEAT OF SCANDIUM, YTTRIUM, AND LANTHANUM

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Using experimental values of the specific heat of Sc, Y, and La in the temperature range 4-300°K, we have calculated the Debye temperature in the high-temperature limit and the anharmonic component of the specific heat at constant volume.

The rare-earth metals (REM) and their analogs scandium and yttrium are being more and more widely used in various fields of modern technology. The solution of numerous practical problems involving the use of REM, the fabrication of alloys, the synthesis of compounds, and understanding factors depending on the peculiarities of their physical properties, etc. require study of the thermodynamic properties of the REM.

The specific heats of scandium, yttrium, and lanthanum were studied in the temperature range 4-300°K (Fig. 1). The errors in the absolute measurements of the specific heat $C_p$ of doubly distilled scandium [1], yttrium [2], and lanthanum [3] made by pulsed heating of the sample under adiabatic conditions [4] did not exceed 4% in the very low temperature range, and 1% in the 300°K range.

The values of $C_v$ were determined from the relation

$$C_v = C_p(1 - AC_pT), \tag{1}$$

where $A = V\beta^2/\varkappa C_p^2$.

At 300°K the compressibilities of scandium, yttrium, and lanthanum are $1.752 \times 10^{-12}$, $2.4 \times 10^{-12}$, and $4.12 \times 10^{-12}$ cm²/dyn, respectively [5]. The values of the temperature dependence of the coefficient of volume expansion β of scandium, yttrium, and lanthanum were taken from [6-8]. Using these data, we found the values of the coefficient A in Eq. (1) were $10.84 \times 10^{-7}$, $9.85 \times 10^{-7}$, and $1.67 \times 10^{-7}$ mole/J for Sc, Y, and La, respectively. The difference $C_p - C_v$ for scandium and yttrium at 300°K was 0.8% of the total specific heat at that temperature. It was a quarter as large for lanthanum as for scandium and yttrium.

The specific heat $C_v$ in the temperature range $T < \theta$ can be expressed as the sum of the lattice and electronic components.

$$C_v = C_L + C_E. \tag{2}$$

$C_L$ is the sum of the harmonic and an harmonic components [9, 10]

$$C_L = C_{v,h} + C_{v,a} = 3R\left(1 - \frac{1}{12}\frac{\hbar^2 <\omega^2>}{k_B^2 T^2}\right) + A'T. \tag{3}$$

In the Debye model

$$<\omega^2> = \frac{3k_B^2}{5\hbar^2}\theta_\infty^2. \tag{4}$$

We determined the Debye temperature $\theta_\infty$ and the anharmonic contribution to the specific heat at constant volume by analyzing the experimental specific heat data (Fig. 1) at temperatures for which $C_{v,h}$ is larger than 0.5 (3R) [11].

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TABLE 1. Temperature Dependence of Electronic Specific Heat of Scandium, Yttrium, and Lanthanum (J/°K·mole)

| T, K | Sc | Y | La | T, K | Sc | Y | La |
|---|---|---|---|---|---|---|---|
| 10 | 0,100 | 0,107 | 0,105 | 140 | 0,868 | 0,812 | 0,476 |
| 15 | 0,153 | 0,163 | 0,163 | 150 | 0,915 | 0,870 | 0,510 |
| 20 | 0,206 | 0,220 | 0,190 | 160 | 0,960 | 0,912 | 0,528 |
| 25 | 0,262 | 0,262 | 0,175 | 170 | 1,020 | 0,969 | 0,561 |
| 30 | 0,315 | 0,300 | 0,165 | 180 | 1,080 | 1,008 | 0,594 |
| 35 | 0,360 | 0,325 | 0,157 | 190 | 1,120 | 1,045 | 0,608 |
| 40 | 0,400 | 0,340 | 0,160 | 200 | 1,180 | 1,100 | 0,640 |
| 45 | 0,441 | 0,355 | 0,171 | 210 | 1,240 | 1,155 | 0,651 |
| 50 | 0,470 | 0,360 | 0,185 | 220 | 1,300 | 1,188 | 0,660 |
| 60 | 0,528 | 0,408 | 0,204 | 230 | 1,360 | 1,219 | 0,667 |
| 70 | 0,574 | 0,455 | 0,238 | 240 | 1,420 | 1,248 | 0,672 |
| 80 | 0,608 | 0,504 | 0,272 | 250 | 1 450 | 1,300 | 0,700 |
| 90 | 0,639 | 0,558 | 0,306 | 260 | 1,510 | 1,326 | 0,702 |
| 100 | 0,680 | 0,610 | 0,340 | 270 | 1,570 | 1,360 | 0,702 |
| 110 | 0,725 | 0,660 | 0,374 | 280 | 1,620 | 1,400 | 0 700 |
| 120 | 0,768 | 0,708 | 0,408 | 290 | 1,680 | 1,421 | 0,696 |
| 130 | 0,819 | 0 767 | 0,442 | 300 | 1,740 | 1,470 | 0,690 |

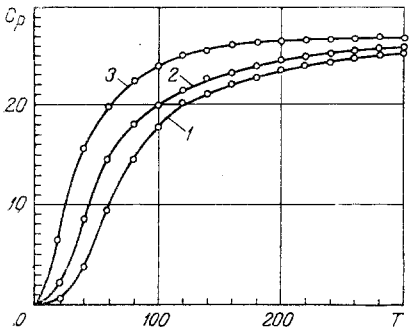


Fig. 1. Specific heat $C_p$ of 1) scandium; 2) yttrium; 3) lanthanum in J/°K·mole. T is in °K.

In determining the electronic specific heat $C_E$ from liquid-helium temperatures to room temperatures we took account of the contributions to the specific heat from the conduction electrons and the electron–phonon interaction [12]. At very low temperatures for which the Debye $T^3$ law is satisfied for the lattice specific heat, and the electronic component of the specific heat $C_E$ predominates over the lattice component, the electronic component is separated out by using the relation

$$C = aT^3 + \gamma_0 T. \tag{5}$$

The values of the coefficient $\gamma_0$ of the electronic component of the specific heat of scandium, yttrium, and lanthanum determined in the temperature range 4-10°K are 9.6, 9.9, and 8.9 mJ/°K·mole, respectively. The values of the electronic component of the specific heat of the metals investigated in the temperature range 10-300°K are listed in Table 1.

The lattice component of the specific heat $C_L$ of these metals in the temperature range 4-300°K was determined by Eq. (2). The Debye temperature $\theta_\infty$ in the high-temperature limit was found graphically (Eq. (3)) from the slope of the $(\Delta C_{v,h} - 3R)/T$ vs $T^{-3}$ curves in the temperature range $0.7 < T/\theta_\infty < 1.3$ (Fig. 2). The slopes of the straight lines in Fig. 2 are $-1.196 \times 10^5$, $-0.7081 \times 10^5$, and $-1.92 \times 10^4$ J·°K/mole for scandium, yttrium, and lanthanum, respectively, which correspond to $\theta_\infty$ equal to 310, 240, and 130°K. In contrast with the Debye temperature, $\theta_0$ determined in the range of liquid-helium temperatures, which is characteristic of very low-energy modes, $\theta_\infty$ is characteristic of all phonon modes. $\theta_\infty$ characterizes the average frequency of the whole phonon spectrum.

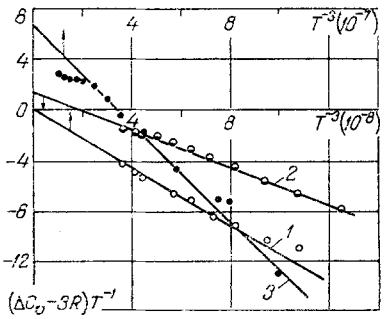


Fig. 2. $(\Delta C_V - 3R)/T$ as a function of $T^{-3}$ for 1) scandium; 2) yttrium; 3) lanthanum. $(\Delta C_V - 3R)/T$ is in mJ/°K²·mole, and $T^{-3} \times 10^{-7}$ is in °K⁻³.

In the first approximation the anharmonic component of the specific heat $C_{V,a}$ of the crystal lattice is proportional to the temperature [10]. The value of the coefficient A' in the expression for $C_{V,a}$ is determined by the intercept on the axis of ordinates of the straight line plots of $(\Delta C_{V,h} - 3R)/T$ vs $T^{-3}$ (Fig. 2). The values of A' for Sc, Y, and La were 0, 1.3, and 7.0 mJ/°K²·mole, respectively.

## NOTATION

$\theta_\infty$, Debye temperature in the high-temperature limit; $\theta_o$, Debye temperature for T = 0°K; T, absolute temperature; $C_p$, specific heat at constant pressure; $C_V$, specific heat at constant volume; A, A', coefficients of the anharmonic contribution to the specific heat at constant pressure and constant volume respectively; V, molar volume; β, temperature coefficient of volume expansion; $\varkappa$, compressibility; $C_L$, $C_E$, lattice and electronic components of the specific heat; $C_{V,h}$, specific heat at constant volume in the harmonic approximation; $C_{V,a}$, anharmonic component of the specific heat at constant volume; $\langle\omega^2\rangle$, second moment of the frequency distribution function; $\hbar$, Planck's consntat; $k_B$, Boltzmann's constant; R, gas constant; $\gamma_o$, $\alpha$, coefficients of electronic and phonon components of the specific heat respectively.

## LITERATURE CITED


1. N. N. Sirota, T. E. Zhabko, N. S. Orlova, et al., "Investigation of the thermophysical properties of Sc, Y, and La in the low-temperature range, and Sc and Ti in the range of the α–β phase transition," Abstracts of Papers at the Seventh All-Union Conference on the Thermophysical Properties of Materials [in Russian], FAN, Tashkent (1982), p. 253.
2. N. N. Sirota and Zh. M. Tomilo, "Specific heat and thermodynamic functions of yttrium in the range 5-300°," Dokl. Akad. Nauk BSSR, 26, 405 (1982).
3. N. N. Sirota, Zh. M. Tomilo, and N. A. Kofman, "Specific heat of lanthanum in the temperature range 2.6-300°K," Vopr. At. Nauki i Tekh. Obshchaya Yad. Fiz., No. 2(23), 66 (1983).
4. N. N. Sirota, Zh. K. Petrova, and N. A. Kofman, "Temperature dependence of heat capacity of cadmium and zinc chalcogenides," Proc. First International Conference on Calorimetry and Thermodynamics, Polish Sci. Publ., Warsaw August 31-September 4 (1969), p. 215.
5. C. Kittel, Introduction to Solid State Physics, Wiley, New York (1976).
6. T. E. Zhabko, "Thermal motion of titanium and scandium atoms in the temperature range 80-360°K, Vestsi Akad. Nauk BSSR, Ser. Fiz.-Mat. Navuk, No. 4, 114 (1982).
7. R. W. Meyerhoff and J. F. Smith, "Anisotropic thermal expansion of single crystals of thallium, yttrium, beryllium, and zinc at low temperature," J. Appl. Phys., 33, 219 (1962).
8. Thermal Expansion of Solids [in Russian], Nauka, Moscow (1974).
9. G. Leibfried, The Microscopic Theory of Mechanical and Thermal Properties of Crystals [Russian translation], Gos. Izd-vo Fiz.-Mat. Literatury, Moscow (1963).
10. G. Leibfried and W. Ludwig, The Theory of Anharmonic Effects in Crystals [Russian translation], IL, Moscow (1963).
11. S. D. Bader and G. S. Knapp, "Calorimetric determination of electron–phonon mass enhancement of α-uranium," Phys. Rev. B, 11, 3348 (1975).
12. G. Grimvall, "Temperature dependent effective masses of conduction electrons," J. Phys. Chem. Solids, 29, 1221 (1968).