Specific heats of Tl_3AsSe_3, Tl_3SbS_3, AgTlS, and AgTlSe between 1 and 50 K

H. Akbarzadeh and P. H. Keesom
Department of Physics, Purdue University, West Lafayette, Indiana 47907

H. Kuwamoto
Rockwell International Science Center, Thousand Oaks, California 99360
(Received 12 October 1982)

The specific heats of Tl_3AsSe_3, Tl_3SbS_3, AgTlS, and AgTlSe have been measured between 1 and 50 K. The Debye temperatures are, respectively: 140, 145, 160, 140 K. Above 2.5 K an additional contribution is noticed which indicates low-lying optical modes.

Ternary chalcogenides crystals have become very important for acousto-optic devices[1,2] and, as a consequence, their optical, acoustic, and electrical properties have been investigated extensively in the last decade. Since no low-temperature calorimetric data have been reported, we have investigated the specific heat of some crystals which had previously been prepared for some of the other measurements. The samples included Tl_3AsSe_3 and Tl_3SbS_3 crystals, which are rhombohedral containing three formula units in a $R3m$ unit cell,[3] and also AgTlS and AgTlSe crystals, which are orthorhombic having four formula units in a *Pnam* unit cell.[4]

The details of the growth procedure for good quality crystals have been previously discussed.[5] Stoichiometric mixtures were sealed in a quartz ampoule and prereacted to a boule. This boule was then etched with 0.3 at. % Br-methanol and placed in another quartz ampoule with a narrow tip. The vertical Bridgman-Stockbarger method produced large crystals. Specific-heat measurements have been carried out, using slices of about 1–2-g specimen, by the standard heat pulse method.[6] The addenda correction was 2% at 2 K increasing to 3% at 50 K. Two unencapsulated germanium thermometers were used to measure the temperature. They were compared with the vapor pressures of ^{3}He and ^{4}He and above 4 K with a thermometer calibrated by Cryocal. We corrected the temperature scales to agree as good as possible with the newer temperature scale T_{76}.[7]

At low temperatures all four crystals are insulators and so only the lattice vibrations will contribute to the specific heat. At sufficiently low temperatures this contribution will be the Debye T^3 term so we plotted semilogarithmically C/T^3 vs T^2. The lower limit of the Debye temperature Θ_0 can be calculated using

$$\frac{C}{T^3}=\gamma\left(\frac{12\pi^4 R}{5\Theta_0^3}\right)=\frac{1944\gamma}{\Theta_0^3} \tag{1}$$

given in units of J/mole K^4, where R is the gas constant and γ is the number of atoms in a formula unit.

The Debye temperatures are shown in Table I. Considering $\Theta_0=140$ K for Tl_3AsSe_3 and using $\Theta_0=\hbar V_0(6\pi^2 N)^{1/3}/k$, $N=3.57\times10^{22}$ atoms/cm^3 (N is the number of atoms/cm^3) we obtain a sound velocity, $V_0=1.4\times10^5$ cm/sec, which is about 18% larger than follows from the weighted average of V^{-3} using the sound velocities $V_L=2.1\times10^5$ cm/sec, $V_S=1.05\times10^5$ cm/sec.[8]

At higher temperatures C/T^3 increases, goes through a maximum, and then decreases. This indicates contributions by optical modes to the specific heat. These optical modes can be investigated by Raman and infrared measurements, but such data are apparently not reported in the literature. Thus, from the specific heat, it is possible to give a first estimate of the lowest optical mode. If the lowest optical mode is approximately independent of the wave vector it can be represented by an Einstein oscillator. Adding an Einstein mode to the Debye acoustical modes leads to a maximum in C/T^3 at a temperature $T_{max}\simeq\nu_E/3$ (ν_E in cm^{-1}).[9] For a compound having n atoms per unit cell, there will be 3 acoustical and $3n-3$ optical modes, and the expression for the

TABLE I. Debye temperatures and Einstein frequencies.

Compound	Θ_0 (K) Calorimetric	ν_E (cm^{-1}) Calorimetric
Tl_3AsSe_3	140	18
Tl_3SbS_3	145	21
AgTlS	160	24
AgTlSe	140	26

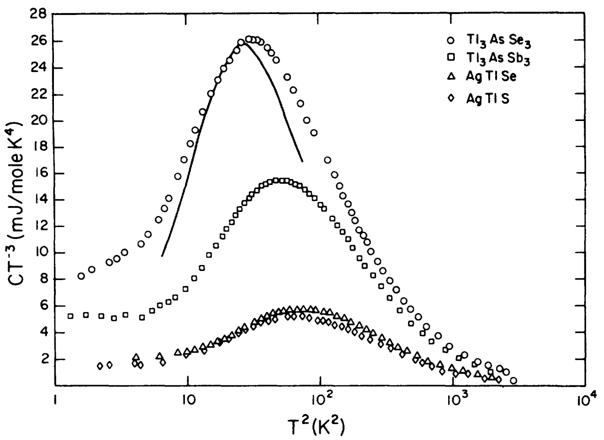

FIG. 1. Semilogarithmic plots of CT^{-3} vs T^2 are shown for all the four compounds. The solid line shows for Tl_3AsSe_3 calculated data discussed in the text.

specific heat is written

$$nC_{\rm expt}=3R\gamma D\left[\frac{\Theta_D}{T}\right]+R\gamma\sum_{i=1}^{3n-3}E\left[\frac{\Theta_{E_i}}{T}\right], \quad (2)$$

where $\Theta_D=\Theta_0(1/n)^{1/3}$, $\Theta_{E_i}=1.44\nu_{E_i}$, ν_E is the Einstein frequency in cm^{-1}. We have collected these Einstein frequencies in Table I. The calculated data for Tl_3AsSe_3 with six optical modes with the frequency $\nu_E=3T_{\max}=18$ cm^{-1} and using Eq. (2) are shown as a solid line in Fig. 1. The agreement is reasonable between 2–6 K, but for higher temperatures there is a large deviation from the experimental data, and higher-frequency modes are required to reproduce the experimental results.

ACKNOWLEDGMENT

This work was supported in part by the National Science Foundation Materials Research Laboratory under Grant No. DMR77-23798.

[1]J. D. Feichtner and G. W. Roland, Appl. Opt. 11, 993 (1972).

[2]J. D. Feichtner, M. Gottleib, and J. J. Conroy, SPIE J. 82, 106 (1976).

[3]H. Y-P. Hong, J. C. Mikkelsen, Jr., and G. W. Roland, Mater. Res. Bull. 9, 365 (1974).

[4]J. C. Tedenac, B. Gardes, G. Brun, E. Philippot, and M. Maurin, J. Solid State Chem. 33, 429 (1980).

[5]H. Kuwamoto (unpublished).

[6]Gul Dad Khattak, P. H. Keesom, and S. P. Faile, Solid State Commun. 26, 441 (1978).

[7]M. Duriex, W. R. G. Kemp, C. A. Swenson, and D. N. Astron, Metrologia 15, 65 (1978).

[8]M. Gottlieb, T. J. Isaacs, J. D. Feichtner, and G. W. Roland, J. Appl. Phys. 45, 5145 (1974).

[9]W. N. Lawless, Ferroelectrics 17, 341 (1975).