

X-ray determination of the mean amplitudes of vibration and Debye temperatures of some rare earth monochalcogenides

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Abstract. The x-ray diffraction intensities of Bragg reflections have been measured at room temperature for thulium selenide, samarium sulphide, samarium selenide and samarium telluride. On the basis of a common amplitude approximation, the Debye-Waller factor, the mean amplitude of vibration and the Debye temperature have been evaluated. The values of the Debye temperatures and mean amplitudes of vibration are $176 \pm 16^\circ\text{K}$, $0.185 \pm 0.017 \text{ \AA}$ (TmSe), $155 \pm 7^\circ\text{K}$, $0.244 \pm 0.012 \text{ \AA}$ (SmS), $153 \pm 14^\circ\text{K}$, $0.221 \pm 0.020 \text{ \AA}$ (SmSe) and $151 \pm 20^\circ\text{K}$, $0.204 \pm 0.027 \text{ \AA}$ (SmTe).

Keywords. Lattice dynamics; Debye temperature; rare earth chalcogenides.

1. Introduction

In recent years the rare earth chalcogenides have attracted considerable attention due to their interesting electronic structure and the consequent electric, magnetic and optical properties. Jayaraman *et al* (1974) have determined the bulk modulus of some rare earth monochalcogenides. However, in general, there is a dearth of data regarding the basic properties of lattice dynamical interest (Smirnov 1972). The present study was aimed at the determination of the Debye temperatures and mean amplitudes of atomic vibrations of four rare earth monochalcogenides at room temperature from x-ray diffraction intensities. The substances studied are TmSe, SmS, SmSe and SmTe.

2. Experimental

2.1. Measurement of intensities

A Phillips PW 1051 x-ray diffractometer with an argon-filled GM counter was used to obtain the relative intensities of Bragg reflections from powder samples. Filtered $\text{CuK}\alpha$ radiation was used. A 2θ scan with a goniometer speed of $\frac{1}{4}^\circ$ per minute was adopted.

The material was reduced to fine powder by slow grinding and packed in an aluminium holder by light pressing. This procedure minimises effects of extinction and preferred orientation (Blattner *et al* 1972). X-ray intensities can be affected

by the surface roughness and porosity of the sample. However, the error due to this factor is about 2% at $2\theta=20^\circ$ and is less at higher angles (Suortti 1972). All the reflections recorded in the present work have $2\theta>20^\circ$.

The relative intensities were recorded over a 2θ range of 2° on either side of a peak and the background was eliminated by a straight line scheme. The integrated intensities were corrected for dead-time effects using the method suggested by Chipman (1969) with a dead-time of 150 μ s. The intensities were also corrected for TDS by the method suggested by Chipman and Paskin (1959). The absorption correction is independent of the Bragg angle for a flat powder sample and for the geometry of the diffractometer. All measurements were made at room temperature.

2.2. Analysis of intensity data

The effect of temperature on the intensities of x-ray reflections has been discussed in detail by James (1967). The integrated intensity of a Bragg reflection may be written as

$$I_0 = C \cdot I_c \cdot \exp [-2B(\sin \theta/\lambda)^2] \quad (1)$$

where I_0 is the measured intensity corrected for factors discussed in section 2.1, C is the scale factor, B the Debye-Waller factor and λ the wavelength. The calculated intensity I_c is given by

$$I_c = LP \cdot J \cdot F^2 \quad (2)$$

where LP is the Lorentz-polarisation factor, J the multiplicity factor and F the structure factor. For the sodium chloride structure, the structure factors are given by

$$F = 4(f_M \pm f_N) \quad (3)$$

where f_M and f_N are the atomic scattering factors for the two atoms and the + and - signs apply to all-even and all-odd reflections respectively.

Strictly speaking, for diatomic crystals, two Debye-Waller factors should be employed, one for each atom. However, a single mean Debye-Waller factor has been used in view of the following:

- (i) Huiszoon and Groenewegen (1972) have shown from lattice dynamics that in cubic crystals the Debye-Waller factors become mass-independent at temperatures above the Debye temperatures.
- (ii) The assumption of a common Debye-Waller factor has been made by several workers. Mention may be made of the work of Houska (1963) on ZrC, Baldwin and Tompson (1964) on CaO, Sedivy *et al* (1968) on TaC and Colella *et al* (1969) on UC. The mass ratios in these crystals are 7.6, 15, 2.5 and 20. The mass ratios of crystals studied in this work, including SmS, are within this range.
- (iii) The number of reflections measured is not large enough for an accurate determination of separate Debye-Waller factors.

For the calculation of structure factors, the atomic scattering factors for Tm, Sm and Te were taken from Cromer and Waber (1965) and those for S and Se from the International Tables. This choice was made in accordance with Cromer's (1965) recommendations. The atomic scattering factors were corrected for dispersion (Cromer and Liberman 1970).

Equation 1 may be written in logarithmic form as:

$$\log (I_0/I_c) = \log C - 2B(\sin \theta/\lambda)^2. \quad (4)$$

From a least squares treatment the values of B can be obtained. We also have from the Debye-Waller theory

$$B = (6h^2/\bar{m}kT) W(x) \quad (5)$$

where \bar{m} is the mean mass, T the temperature at which the intensities are measured and h and k have the usual significance. The function $W(x)$ is given by

$$W(x) = [\phi(x)/x^2] + (1/4x) \quad (6)$$

where $x = (\theta/T)$ and $\phi(x)$ is an integral. The values of $W(x)$ for a wide range of x are tabulated by Benson and Gill (1966). From eqs 4, 5 and 6, the Debye temperature can be evaluated. The mean root mean square amplitude of vibration $(\bar{u}^2)^{1/2}$ can be obtained from

$$B = (8\pi^2/3)\bar{u}^2 \quad (7)$$

3. Results

The plots between $\log (I_0/I_c)$ and $(\sin \theta/\lambda)^2$ for the four compounds, TmSe, SmS, SmSe and SmTe are shown in figure 1. The values of the Debye-Waller factors, the Debye temperature and the mean amplitude of vibration are given in table 1.

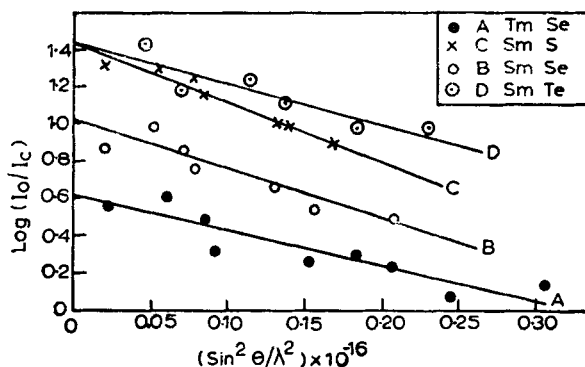


Figure 1. Plots of $\log (I_0/I_c)$ and $(\sin \theta/\lambda)^2$ for TmSe, SmS, SmSe and SmTe.

Table 1. Values of the mean Debye-Waller factor (B), the average r.m.s. amplitude of vibration $(\bar{u}^2)^{1/2}$ and the Debye temperature (θ_M) of the rare earth chalcogenides.

Compound	B (\AA^2)	$(\bar{u}^2)^{1/2}$ (\AA)	θ_M ($^\circ\text{K}$)
TmSe	0.899 ± 0.167	0.185 ± 0.017	176 ± 16
SmS	1.565 ± 0.148	0.244 ± 0.012	155 ± 7
SmSe	1.288 ± 0.239	0.221 ± 0.020	153 ± 14
SmTe	1.095 ± 0.289	0.204 ± 0.027	151 ± 20

The present measurements are the first x-ray measurements of the Debye temperatures of these substances. A value of $176 \pm 16^\circ\text{K}$ has been obtained for TmSe from the present x-ray study. This is lower than the value of 200°K quoted by Smirnov (1972) from low temperature specific heats. For the Debye temperature of SmS, Smirnov (1972) and Bader *et al* (1972) quote values of 269°K and 260°K from specific heats. Goryachev and Kutsenok (1972) obtained a value of 730°K from lattice potential calculation. The present value of $155 \pm 7^\circ\text{K}$ is closer to the specific heat values than to the lattice potential values. For SmSe, Smirnov (1972) quotes a value of 206°K from specific heats. Here also the present x-ray value of $153 \pm 14^\circ\text{K}$ is lower than the specific heat value. There seems to be no report on the Debye temperature of SmTe by any method. The present value of $151 \pm 20^\circ\text{K}$ is of the same order as for the other Sm compounds.

The present x-ray values are very much lower than the specific heat values. It must be noted that the specific heat values correspond to low temperatures whereas the x-ray measurements are at room temperature. Also while comparing the x-ray values and specific heat values, exact agreement between the two is not to be expected. The averaging of the frequency distribution is different in the two cases and, in general, x-ray values of Debye temperatures are smaller than the specific heat values (Blackman 1955, Barron *et al* 1964, Blattner *et al* 1972, Sharma 1972, Batterman and Chipman 1962, Sirdeshmukh and Rao 1973). The present x-ray values conform to this trend.

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