X-ray determination of the Debye-Waller factors and Debye temperatures of europium monochalcogenides

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Abstract. X-ray powder diffractograms of EuS and EuTe have been recorded. The integrated intensites have been measured and corrected for TDS. From an analysis of the intensity data, Debye-Waller factors and Debye temperatures have been evaluated.

1. Introduction

The rare earth monochalcogenides with sodium chloride structure are interesting as mixed valence systems. The properties of europium chalcogenides were reviewed by Wachter (1979). There is very little work on the Debye-Waller factors and Debye temperatures of these crystals, which are parameters of lattice dynamical interest. The Debye-Waller factors of EuSe were obtained from X-ray diffraction intensities by Subhadra and Sirdeshmukh (1980). Similar information on the other europium chalcogenides is not available. The Debye temperatures were estimated from elastic constants by Shapira and Reed (1972). In the present paper, the Debye-Waller factors and Debye temperatures of EuS and EuTe obtained from X-ray data are reported.

2. Experimental

The europium chalcogenides were available in the form of small crystallites. They were ground slowly in an agate mortar into fine powder. The precautions taken in sample preparation and the methods of correcting the observed intensities for background and TDS have been discussed in an earlier paper (Subhadra and Sirdeshmukh 1977; hereinafter referred to as I). The X-ray reflections were recorded with copper radiation on a JEOL JDX-8P powder diffractometer fitted with a scintillation counter.

   The procedure for evaluation of the individual Debye-Waller factors and the mean Debye-Waller factor has been discussed by Srinivas and Sirdeshmukh (1984, hereinafter referred to as II). For the evaluation of structure factors the atomic scattering factors were taken from the International Tables for X-ray Crystallography (1968) for S and from Cromer and Waber (1965) for Eu and Te. The atomic scattering factors were corrected for anomalous dispersion (Cromer and Liberman 1970). The recorded

reflections for EuS included reflections of the h, k, l all-even and all-odd types. This facilitated the evaluation of the individual Debye-Waller factors (see II). In EuTe, only the all-even reflections were available for intensity analysis and therefore the analysis was limited to the evaluation of the mean Debye-Waller factor. The determination of the Debye temperature (θ_M) from the mean Debye-Waller factor $(\bar{B})$ is done as described in I and II.

3. Results and discussion

The values of the Debye-Waller factors for EuS and EuTe are given in table 1; values for EuSe from our earlier work (Subhadra and Sirdeshmukh 1980) are also included. Experimental data on several crystals with NaCl structure reveal that the Debye-Waller factor for a heavier atom is less than that for a lighter atom, although there are some exceptions (Menz 1968; Linkaoho 1969). Both in EuS and EuTe, the Debye-Waller factor for the heavier Eu atom is smaller than that for the lighter chalcogen atom. The difference between the Debye-Waller factors for the two ions is larger in EuS than that in EuSe. The difference between the atomic masses is also larger in EuS than in EuSe. The mean Debye-Waller factor $\bar{B}$ increases in the sequence EuS–EuSe–EuTe.

The Debye temperatures (θ_M) of the europium chalcogenides determined from the Debye-Waller factors are given in table 1. For comparison, the values obtained from elastic constants (θ_E) and from specific heats (θ_D) are also quoted from Wachter (1979); the values for EuO are also included. θ_E and θ_D values generally agree well (Gschneidner 1964) but, in these crystals, there is some difference, particularly in EuSe and EuTe. This could be due to the difference in the temperatures at which these two values have been determined. Further, Shapira and Reed (1972) point out that analysis of low temperature specific heat data is difficult in these crystals due to the presence of a magnetic contribution. The present θ_M values are much smaller than the θ_E values. Recently, Horning and Staudenmann (1988) have pointed out that θ values determined from X-ray intensities should be corrected by a factor $p^{1/2}$ where p is the number of vibrating units in the molecule. For crystals with NaCl structure, p is 2. The θ_M values corrected by a factor $2^{1/2}$ are given in table 1 as θ_M'. The agreement between θ_M' and θ_E is reasonably good.

Bansigir (1968) showed that $\log(\theta)$ vs $\log(V)$ plots are linear for a family of related crystals and that the slope of such a plot gives the average Gruneisen constant for the family of crystals. For the $\log(\theta)$ vs $\log(V)$ plot for the europium chalcogenides, the unit cell volume calculated from the lattice constants is used. The θ's used are θ_M'

Table 1. Lattice constants (a A), Debye-Waller factors *(B A^2) and Debye temperatures (θ K) of europium chalcogenides.

Crystal	a	B_1	B_2	B	θ_D	θ_E	θ_M	θ_M'
EuO	5·141	—	—	—	353	350	—	—
EuS	5·968	0·39 ± 0·11	1·12 ± 0·28	0·90 ± 0·14	262	276	205 ± 16	290
EuSe	6·195	1·22 ± 0·13	1·37 ± 0·20	1·27 ± 0·15	176	232	153 ± 9	216
EuTe	6·598	—	—	1·43 ± 0·20	140	189	134 ± 10	189

* B_1 refers to Eu, B_2 to S and Se and B is the mean Debye-Waller factor.

except for EuO where θ_E value is used. The plot is linear and yields a value of 0.9 ± 0.2 for the Gruneisen constant. Gruneisen constants for the europium chalcogenides calculated from thermal expansion and compressibility data listed by Wachter (1979) have values in the range $1.3-1.5$. Thus there is an order-of-magnitude agreement in the two values. Considering the approximations in Bansigir's method (for a critical discussion, see Sirdeshmukh and Rao 1973), this agreement seems to be satisfactory and indicates that the Debye temperature values are consistent with other thermal parameters of these crystals.

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