

SHORT COMMUNICATIONS

Acta Cryst. (1996). **A52**, 88–90

Debye–Waller factors and Debye temperatures of rubidium halides

T. KUMARA SWAMY, K. SRINIVAS, K. G. SUBHADRA AND D. B. SIRDESHMUKH at *Department of Physics, Kakatiya University, Warangal 506009, India*

(Received 16 June 1995; accepted 10 August 1995)

Abstract

The Debye–Waller factors of the rubidium halides obtained from different theoretical models are critically compared with recent experimental data. The results from the model adopted by Govindarajan [*Acta Cryst.* (1973), **A29**, 576–577] seem to be in better agreement with experimental values than those from other models. The Debye temperatures calculated from the Debye–Waller factors are compared with those from specific heats. A modification recently suggested by Horning & Staudenmann [*Acta Cryst.* (1988), **A44**, 136–142] for the evaluation of the Debye temperature from Debye–Waller factors does not improve the agreement between the two sets.

Introduction

Two applications of experimentally determined Debye–Waller factors are (i) comparison with values derived from lattice dynamical models and (ii) derivation of Debye temperature from the Debye–Waller factors. A critical comparison between the experimental and theoretical Debye–Waller factors has been made by Sen (1964), Pryor (1966) and Linkoaho (1969) for lithium, sodium and potassium halides. Such a critical comparison was not made for the rubidium halides as experimental values were not available except for a single report on RbCl (Jarvinen & Inkinen, 1967). In recent years, several experimental reports have appeared on the Debye–Waller factors of the rubidium halides. Also, the Debye–Waller factors of the rubidium halides have been calculated from several theoretical lattice-dynamical models. Experimental values of Debye–Waller factors can be used to derive the Debye temperature using the relation

$$B = (6h^2/mk\theta_M)\{[\varphi(x)/x] + (1/4)\}, \quad (1)$$

where $x = \theta_M/T$, θ_M being the Debye temperature and the other symbols have the usual meaning (Warren, 1969). Recently, Horning & Staudenmann (1988) have pointed out a modification for polyatomic solids, according to which the Debye temperature should be

$$\theta'_M = \theta_M(p)^{1/2}, \quad (2)$$

where $3p$ is the number of branches in the phonon dispersion relations; for a diatomic solid $p = 2$. Horning & Staudenmann applied this modification to a few alkali halides but could not arrive at a clear conclusion as to whether the modification improves the values in comparison with the specific heat values. In this communication, the experimental values of mean Debye–Waller factors for the rubidium halides are listed and compared with the values obtained from the theoretical models. Further, the Debye temperatures are derived from (1) and (2) and compared with the specific heat values.

Discussion

In Table 1, the experimental values of the Debye–Waller factors are listed. In most of the experimental results, only the mean Debye–Waller factor has been reported. The only rubidium halide for which separate Debye–Waller factors are given is RbCl (Korhonen, 1956; Jarvinen & Inkinen, 1967) but these separate Debye–Waller factors agree with each other within the limits of experimental error. Further, whichever lattice dynamical model is employed, it is found that the Debye–Waller factors of the two ions at room temperature differ by about 10% or less in the rubidium halides. As such, the theoretical values have been converted into mean values to facilitate comparison with experimental values. These theoretical mean values are also given in Table 1.

With regard to the experimental values, there is a single neutron diffraction value for RbF, but with a large error of 18%. In the case of RbCl, there are six values; these vary among themselves by 18%. Among them, four values are rather close, varying by 5%. The other two values by Korhonen (1956) and Srinivas, Atequddin & Sirdeshmukh (1987) are very much lower and may be overlooked. In the case of RbBr, there are two values that differ by 33%. In the case of RbI again there are two values, one from X-ray diffraction and the other from neutron diffraction. These differ by 8% but agree within the limits of error.

The theoretical values have been derived from four models. These are: (i) the 11-parameter shell model with parameters determined from neutron inelastic scattering data (Govindarajan, 1973); (ii) the 11-parameter shell model with parameters determined from elastic constants and dielectric constant data (Gupta, 1975); (iii) the deformation dipole model (Agrawal, Beaver, Weymouth & Hardy, 1975); and (iv) the 7-parameter bond bending force model (Kushwaha, 1981). A careful examination of the theoretical values reveals that the values obtained from different models are of the same order but differ slightly from model to model. The range of variation for a given crystal is from 10 to 15%. Among these values, the values obtained by Govindarajan are systematically larger than those obtained from the other three models.

The experimental value for RbF is comparable with all three theoretical values. In view of the large error in experimental value for RbF, it is not possible to identify the best theoretical value. In the case of RbCl, as mentioned earlier, four experimental values are close to one another and are also close to the theoretical value obtained by Govindarajan from the 11-parameter shell model. Among them, the value obtained by Jarvinen & Inkinen (1967) is closest to the value obtained by Govindarajan. The values of Korhonen and Srinivas *et al.* are decidedly lower than the other experimental values as well as the theoretical value of Govindarajan. Based on the analysis of RbCl data, the theoretical model of Govindarajan is taken as the

Table 1. Theoretical and experimental values of mean Debye–Waller factor \bar{B} (in \AA^2) for rubidium halides at room temperature

Crystal	Theoretical		Experimental		
	\bar{B}	Reference	\bar{B}	Method	Reference
RbF	1.591	Govindarajan (1973)	<u>1.40 (25)</u>	NDP	Beg <i>et al.</i> (1981)
	1.392	Gupta (1975)			
	1.433	Agrawal <i>et al.</i> (1975)			
RbCl	2.331	Govindarajan (1973)	2.06	XDP	Korhonen (1956)
	1.992	Gupta (1975)	<u>2.33 (10)</u>	XDP	Jarvinen & Inkinen (1967)
	2.168	Agrawal <i>et al.</i> (1975)	<u>2.36 (6)</u>	XDP	Pathak & Trivedi (1973)
	1.983	Kushwaha (1981)	2.34 (12)	XDP	Khaav & Treufeldt (1981)
			2.11 (6)	XDP	Srinivas <i>et al.</i> (1987)
			2.43 (20)	NDP	Ghazi <i>et al.</i> (1989)
RbBr	2.708	Govindarajan (1973)	2.18 (8)	XDP	Srinivas <i>et al.</i> (1987)
	2.361	Gupta (1975)	<u>2.89 (18)</u>	XDP	Kumara Swamy <i>et al.</i> (1994)
	2.451	Agrawal <i>et al.</i> (1975)			
	2.343	Kushwaha (1981)			
RbI	3.265	Govindarajan (1973)	3.36 (14)	XDP	Kumara Swamy <i>et al.</i> (1994)
	2.909	Gupta (1975)	<u>3.19 (11)</u>	NDP	Beg <i>et al.</i> (1979)
	3.003	Agrawal <i>et al.</i> (1975)			
	2.900	Kushwaha (1981)			

best among the four and the experimental data in the other crystals are compared *vis a vis* Govindarajan's values. In the case of RbBr, the value reported by Srinivas *et al.* is much lower than the values obtained from any of the models. On the other hand, the recent value reported by Kumara Swamy, Subhadra & Sirdeshmukh (1994) is closer to Govindarajan's value than the values from other models and is taken to be better. In the case of RbI, again, the recent X-ray value by Kumara Swamy *et al.* is close to the value obtained by Govindarajan. We may, therefore, conclude that, of the four models, the 11-parameter shell model adopted by Govindarajan gives Debye–Waller factors closely agreeing with experimental values. The recommended values are indicated in Table 1 by underlines.

As mentioned earlier, the Debye temperatures (θ_M) can be calculated from (1) with the mean Debye–Waller factor as the input and Horning & Staudenmann (1988) have suggested a modified expression [θ'_M , equation (2)]. We have calculated the Debye temperatures θ_M and θ'_M from the recommended values of the experimental mean Debye–Waller factors given in Table 1. As mentioned above, $p = 2$ for these crystals. These values are given in Table 2 along with the high-temperature limit of the specific heat Debye temperature θ_D reported by Karo (1960).

Table 2 also includes the corresponding values for the alkali halides considered in the paper by Horning & Staudenmann. It is observed that θ_M is generally less than θ_D . On the other hand, θ'_M , which is supposed to improve the agreement with θ_D , is generally larger than θ_D . The differences $(\theta_D - \theta_M)$ and $(\theta_D - \theta'_M)$ and the e.s.d.s for the suite of alkali halides have been evaluated. The RbF results are not included in view of the very large error in the experimental value of \bar{B} . The e.s.d. value of 9 K for $(\theta_D - \theta_M)$ is found to be much less than the e.s.d. value of 27 K for $(\theta_D - \theta'_M)$. Horning & Staudenmann (1988) have concluded that the modification (2) works well for solids composed of atoms with similar masses. But in the case of the alkali halides it is found that, in KCl, RbBr and CsI, the modification (2) suggested by Horning & Staudenmann does not result in any improvement in Debye-temperature values, although the masses are nearly equal; instead, the differences between θ_D and θ'_M are larger compared with the differences

Table 2. Comparison between Debye temperatures from X-ray and neutron diffraction and specific heat Debye temperatures (in K) for alkali halides

θ_M and θ'_M values for rubidium halides are taken from recommended values of \bar{B} in Table 1 and values for other compounds from the paper by Horning & Staudenmann (1988).

E.s.d. = 9 K for $(\theta_D - \theta_M)$; e.s.d. = 27 K for $(\theta_D - \theta'_M)$.

Compound	θ_D	θ_M	θ'_M	$(\theta_D - \theta_M)$	$ (\theta_D - \theta'_M) $
RbF	279	218	308	61	29
RbCl	186	157	222	29	36
RbBr	135	121	171	14	36
RbI	115	99	140	16	25
LiF	645	623	881	22	236
NaCl	290	265	375	25	85
KCl	235	213	301	22	66
KBr	188	148	209	40	21
CsCl	162	151	214	11	52
CsBr	179	118	167	61	12
CsI	101	101	143	0	42

between θ_D and θ_M . Thus, it is concluded that for alkali halides the modification (2) suggested by Horning & Staudenmann (1988) does not lead to any improvement.

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