

LETTERS TO THE EDITOR

DEBYE TEMPERATURE AND GRÜNEISEN CONSTANT OF SOME CUBIC CRYSTALS WITH PEROVSKITE STRUCTURE

DURING the last few years, extensive studies have been made on the experimental and theoretical aspects of structural phase transitions occurring in compounds of perovskite structure. However, very little information is available about the Debye temperature, θ and Grüneisen constant, γ , of these compounds. These parameters are of great importance in the study of a large number of problems involving lattice vibrations and anharmonic effects in solids. Data on elastic constants of some of the perovskite structure compounds have become available only recently and it is now possible to evaluate these parameters.

There exist a number of methods for calculating Debye temperature from elastic constant data¹⁻². Different averaging schemes for the shear modulus have been proposed³⁻⁵ for use in Anderson's² method

of calculating θ_{agg} . The averaging scheme proposed by Verma and Aggarwal⁵ has been found superior to other schemes in that the values of θ_{agg} thus computed for a number of cubic elements⁵ and compounds⁵⁻⁷ are in closer agreement with the corresponding exact values obtained by numerical integration of the cubic secular equation¹. The Debye temperatures of twelve perovskite compounds have been calculated by Anderson's method with Verma-Aggarwal approximation (VAA) for the shear modulus and also by numerical integration. The results are presented in Table I. The input data, single-crystal elastic coefficients, c_{ij} , and density, ρ , used in these calculations are also listed in Table I. The Debye temperatures have been calculated to a greater number of significant figures than is warranted by the accuracy of the experimental input data. This has been done to bring out small differences, if any, between the computed values by the two methods. It is seen from Table I that VAA values are in excellent agreement with exact

TABLE I
Experimental data for c_{ij} and ρ , Zener anisotropy η and Debye temperature θ

Crystal	c_{11}	c_{12}	c_{44}	ρ (g/cm ³)	η	θ (°K)	
	(10 ¹¹ N/m ²)					VAA	Exact
TiCdF ₃ ^a	1.028	0.385	0.177	7.3109	0.550	226.53	226.44
RbCdF ₃ ^a	1.096	0.373	0.204	4.9716	0.564	292.66	292.51
KMnF ₃ ^b	1.2037	0.3715	0.2761	3.42	0.664	416.99	416.84
KNiF ₃ ^c	1.582	0.485	0.403	3.9866	0.735	477.05	476.96
CsCdF ₃ ^a	1.078	0.405	0.250	5.6392	0.743	284.28	284.26
RbMnF ₃ ^d	1.045	0.332	0.300	4.30	0.842	364.74	364.72
KCoF ₃ ^e	1.32	0.52	0.35	3.8212	0.875	434.03	434.03
KZnF ₃ ^e	1.345	0.527	0.381	4.0242	0.932	437.08	437.07
KMgF ₃ ^e	1.3801	0.4366	0.4983	3.15	1.056	556.21	556.20
RbCoF ₃ ^e	1.296	0.554	0.415	4.7577	1.119	397.15	397.14
SrTiO ₃ ^f	3.156	1.027	1.215	5.116	1.141	684.82	684.78
BaTiO ₃ ^g	1.7278	0.8196	1.0823	6.035	2.383	493.59	492.80

^aRousseau, M., Gesland, J. Y., Julliard, J. and Nouet, J., *Phys. Rev.*, 1975, B12, 1579.

^bSimmons, G. and Wang, H., *Single Crystal Elastic Constants and Calculated Aggregate Properties: A Handbook*, The M.I.T. Press, Cambridge, 1971.

^cRousseau, M., Nouet, J. and Zarembowitch, A., *J. Phys. Chem. Solids*, 1974, 35, 921.

^dEastman, D. E., *Phys. Rev.*, 1967, 156, 645.

^eReschikova, L. M., *Sov. Phys.—Solid State*, 1969, 10, 2019.

^fWachtman Jr, J. B., Wheat, M. L. and Marzullo, S., *J. Res. N.B.S.*, 1963, 67A, 193.

θ except for BaTiO_3 , where the anisotropy, η ($\eta = 2c_{44}/c_{11} - c_{12}$) is large. The Debye temperatures were also calculated (but not shown in Table I) using other commonly used averaging schemes, viz., AMA, GMA and HMA⁴. It was found that the values of θ_{avg} were ordered according to $\theta_{\text{AMA}} \geq \theta_{\text{GMA}} \geq \theta_{\text{HMA}} \geq \theta_{\text{VAA}} \geq \theta_{\text{exact}}$. Hence the relative error for the three other averaging schemes is larger as compared to VAA.

The Grüneisen constant is usually determined experimentally from the relation⁸

$$\gamma = 3\alpha V / \beta C_p \quad (1)$$

where the symbols have their usual meaning.

Due to lack of experimental data on the values of α , β and C_p for the twelve perovskite compounds, eqn. (1) cannot be used to obtain the value of γ . The Grüneisen constant has also been defined as⁸

$$\gamma = -d(\log \theta) / d(\log V) \quad (2)$$

or

$$\log \theta = -\gamma \log V + C \quad (3)$$

where V is the molar volume and C a constant.

It is thus possible using eqn. (3) to determine the average value of γ for a group of crystals if they have the same structure and bond type. This relation has been found valid for alkali halides⁹, alkali metals, rare earth elements¹⁰ and semiconductors belonging to groups $A^{III}B^V$ and $A^{II}B^{VI}$. In order to check whether γ is a constant for the group of perovskite structure compounds shown in Table I, $\log \theta$ is plotted against $\log V$ as shown in Fig. 1. The slope of the linear plot as obtained by least square fit is 2.2 which is the value of γ for this group of crystals. It may, however,

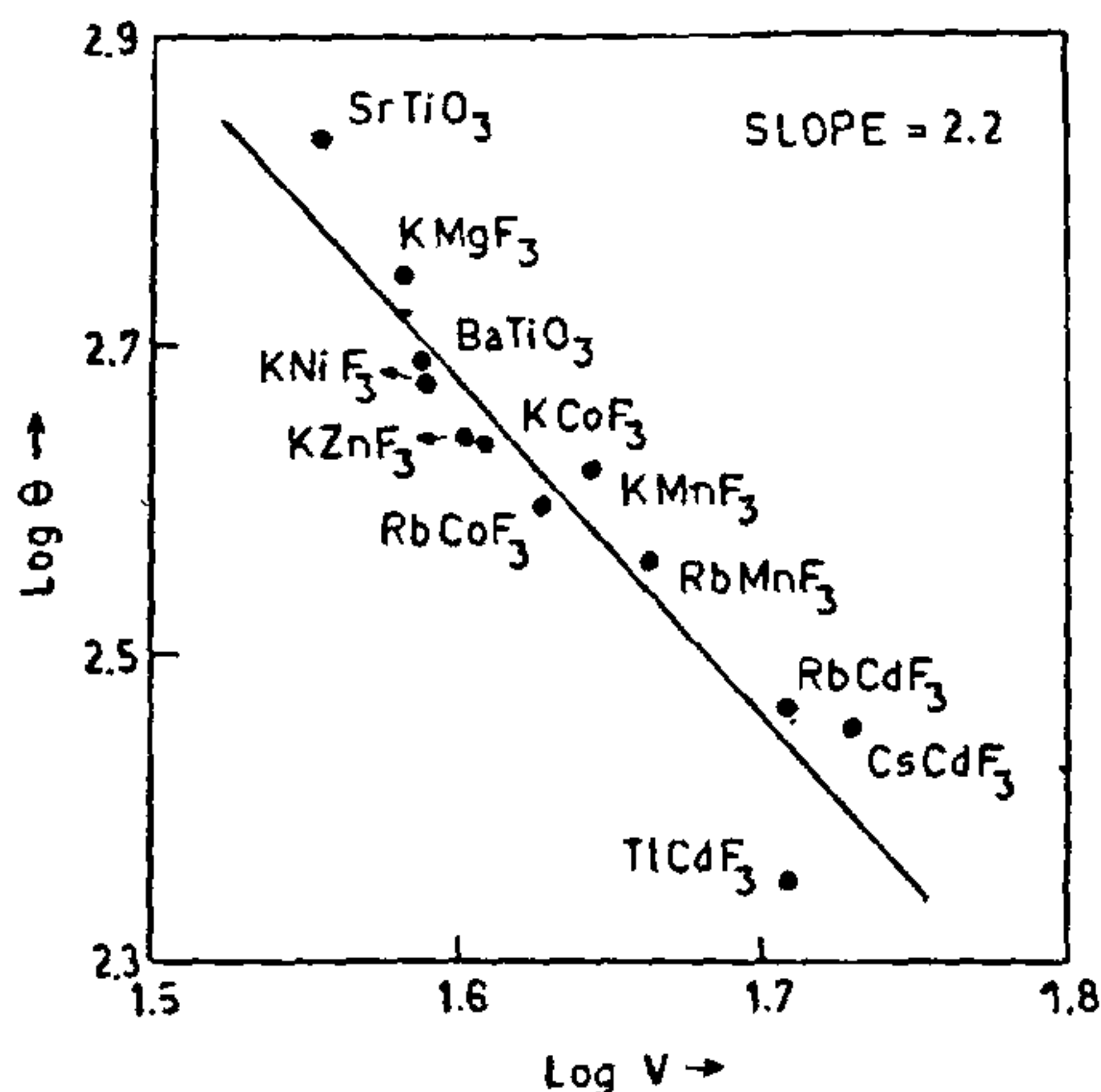


FIG. 1. Log (Debye temperature) versus log (molar volume) plot for perovskite structure crystals.

be mentioned that the Grüneisen constant like Debye temperature is also an average parameter and its value depends upon the averaging procedure adopted.

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ON THE A-X SYSTEM OF THE CuBr MOLECULE

THE copper bromide molecule is known to have four band systems lying in the visible region. The emission spectrum of this molecule was first recorded by Mulliken¹. Ritzel² later on recorded the same bands in absorption. He subsequently made a detailed vibrational analysis of the bands and arranged them in three systems A, B, C, all having the ground state as the common lower level. The D system was later discovered by Rao and Rao³ in 1964. The rotational analysis of the molecule is complicated due to the presence of four isotopic species (⁶³Cu ⁷⁹Br, ⁶³Cu ⁸¹Br, ⁶⁵Cu ⁷⁹Br, ⁶⁵Cu ⁸¹Br with abundance ratio 2 : 2 : 1 : 1). Taking the isotopic species ⁶³Cu ⁸¹Br Rao and Rao⁴ analysed the rotational structure in the C¹Σ-X¹Σ system of this molecule. The rotational structure in the D-X system was recently analysed by Rai *et al.*⁵. In the present communication we report the results of our analysis of the A-X system.

The spectrum of the A-X system of the CuBr molecule was excited in a hollow cathode tube of pyrex glass. The electrodes were of nickel and were kept 8 cm apart. A spec pure sample of CuBr (Riedel make) was used. For a steady intense glow about 1,000 volts d.c. and 0.1 ampere of current was necessary. The bands were found to be developing with