

## LETTERS TO THE EDITOR

## PASKIN'S THEORY WITH PHONON-PHONON INTERACTION

ACCORDING to the Debye theory, the Debye characteristic temperature  $\Theta$  should be a constant. In practice however  $\Theta$  is found to vary with temperature especially at high temperatures. This is due to the fact that anharmonic terms in the potential energy function of a substance are important.

Paskin<sup>1</sup> first showed that if the temperature variation of  $\Theta$  is due only to the volume expansion of the material

$$\frac{\Theta(T)}{\Theta(T_0)} = \left(\frac{V_{T_0}}{V_T}\right)^\gamma \quad (1)$$

where  $T_0$  is a reference temperature, say room temperature, and  $\gamma$  is the Grüneisen parameter.

According to the Debye theory, the Debye-Waller factor  $2M$  is given by

$$2M = \frac{12h^2 \sin^2 \theta T}{mk\lambda^2 \Theta^2(T)} \quad (2)$$

Combining eqns. (1) and (2) we have

$$2M = \frac{12h^2 \sin^2 \theta}{mk\lambda^2 \Theta^2(T_0)} \left(\frac{V_T}{V_{T_0}}\right)^{2\gamma} \quad (3)$$

Thus  $2M$  is seen to be proportional to the reduced temperature  $T' = T(V_T/V_{T_0})^{2\gamma}$ . As the intensity  $I$  of a given x-ray line is proportional to  $\exp(-2M)$ , it follows that

$$\ln \frac{I_T}{I_{T_0}} = -\frac{12h^2 \sin^2 \theta}{mk\lambda^2 \Theta^2(T_0)} (T' - T_0') \quad (4)$$

From eqn. (4) it is evident that if the temperature variation of Debye  $\Theta$  is due solely to the volume expansion, the plot of  $\ln(I_T/I_{T_0})$  versus  $T$  should be a straight line. Paskin has shown that this is true for NaCl and KCl.

Tolpadi<sup>2</sup> has modified Paskin's theory by taking into consideration the anharmonicity not only due to volume expansion but also due to self-energy of the crystal which depends on the phonon-phonon interaction. An isobaric Grüneisen parameter is defined as

$$\gamma_p = \gamma_v + \gamma_T \quad (5)$$

where  $\gamma_v$  and  $\gamma_T$  are the isochoric and isothermal Grüneisen parameters along (100), (110) and (111) directions respectively.

The temperature variation of  $\Theta$  is then given by the formula

$$\frac{\Theta(T)}{\Theta(T_0)} = \left(\frac{V_{T_0}}{V_T}\right)^{\bar{\gamma}_p} \quad (7)$$

where  $\bar{\gamma}_p$  contains the anharmonic effects due to phonon-phonon interaction and volume expansion of the crystal.

Recently the authors<sup>3</sup> have determined accurate values of Debye  $\Theta$  of Ag and Al by x-ray diffraction using a diffractometer, scintillation counter and a specially designed furnace having a large volume of uniform temperature. The details of experimental procedure are given by Pathak and Vasavada<sup>4</sup> and Pathak and Trivedi<sup>5</sup>.

TABLE I  
Debye temperatures

Temperature (°K)	(°K)			
	Ag		Al	
	a	b	a	b
300	195	195	400	400
350	193	193	394	395
400	191	190	388	390
450	189	188	382	386
500	187	186	376	381
550	185	184	368	377
600	183	182	361	372
650	180	180	353	376

(a) Using eq. (7).

(b) Pathak and Shah<sup>3</sup> (Chipman's method).

Table I shows the values of  $\Theta$  for Ag and Al obtained in our investigation<sup>3</sup> together with those calculated from eq. (7). The parameter  $\bar{\gamma}_p$  is found to be slightly temperature dependent. Between 300 and 650°K  $\bar{\gamma}_p$  varies from 3.3 to 3.6 for Ag and from 3.9 to 4.5 for Al. The values of  $\bar{\gamma}_p$  used in the calculation of  $\Theta$  from eq. (7) are those given by Tolpadi<sup>2</sup>. It is seen that agreement between theory and experiment is excellent for Ag but not for Al. This shows that higher order anharmonic terms in

the potential energy function of Al play an important role.

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2. Tolpadi, S., *Ind. J. Pure and Appl. Phys.*, 1975, 13, 504.
3. Pathak, P. D. and Shah, N. P., *Ind. J. Phys.*, 1979, 53A, 283.
4. — and Vasavada, N. G., *Acta Cryst.*, 1970, A26, 655.
5. — and Trivedi, J. M., *Ibid.*, 1973, A29, 45.

### SOME STUDIES ON ASTROPHYSICALLY SIGNIFICANT BN MOLECULE

In further continuation of our programme on the calculation of transition probability parameters for astrophysically significant diatomic molecules it is proposed in this communication to report the results of such studies on the (A-X) transition of BN molecule.

Apart from the discovery<sup>1</sup> of the emission spectrum due to (A<sup>3</sup>π-X<sup>3</sup>π) transition of BN molecule, which occurs in the region 3850-3400 Å, no further studies either on theoretical side or on experimental side have been made on this transition. Accurate rotational constants are already available for this band system<sup>1</sup>. Thus it is worthwhile to report the Franck-Condon (FC) factors and *r*-centroids for the (A-X) transition of BN molecule.

The usual procedure of using R-K-R-V wavefunctions, that we have adopted<sup>2,3</sup> is not applicable in the present situation because of the lack of availability of the experimental data on vibrational analysis on this band system to higher vibrational quantum numbers. FC factors and *r*-centroids computed on the IBM 1130 computer using Frasher and Jarman<sup>4,5</sup> and the graphical method of Nicholls and Jarman respectively are given in Table I.

A careful observation of the FC factors given in Table I shows that out of the ten bands observed experimentally the (3,1) band bears the lowest value. Further, there are some bands having FC-factors values greater than that corresponding to (3,1) band; the non-appearance of such of the bands is due to the lack of appropriate experimental conditions like temperature, pressure and excitation mechanisms.

As for the computed *r*-centroids, for this red degraded band system, there is (i) an expected increase

TABLE I

Franck-Condon (FC) factors and *r*-centroids for the (A<sup>3</sup>π-X<sup>3</sup>π) transition of BN molecule

<i>v'</i> , <i>v''</i>	FC-factors	<i>r</i> -centroids	Wavelength (Å)
0,0	0.7646	0.308	3599.2
0,1	0.2108	1.399	3803.2
0,2	0.0232	1.492	..
0,3	0.0013	1.582	..
0,4	0.0000	1.674	..
0,5	0.0000	1.775	..
1,0	0.1975	1.232	3439.7
1,1	0.3315	1.412	3625.6
1,2	0.3315	1.412	3829.3
1,3	0.0629	1.501	..
1,4	0.0050	1.590	..
1,5	0.0002	1.680	..
2,0	0.0327	1.164	..
2,1	0.2873	1.245	3467.4
2,2	0.1749	1.333	3653.2
2,3	0.3802	1.423	3856.1
2,4	0.1122	1.511	..
2,5	0.0120	1.599	..
3,0	0.0045	1.108	..
3,1	0.0802	1.177	3496.3
3,2	0.2998	1.259	3681.8
3,3	0.0512	1.347	..
3,4	0.3748	1.434	..
3,5	0.1649	1.521	..
4,0	0.0005	1.016	..
4,1	0.0158	1.120	..
4,2	0.1279	1.191	..
4,3	0.2529	1.273	..
4,4	0.0036	1.360	..
4,5	0.3323	1.446	..
5,0	0.0001	1.024	..
5,1	0.0026	1.073	..
5,2	0.0340	1.133	..
5,4	0.0207	1.288	..

of *r*-centroids with increasing wavelength and (ii) a constancy of the difference

$$\Delta \bar{r} = \bar{r}_{v',v''} - \bar{r}_{v'+1, v''+1}$$

Moreover, the potentials are not very anharmonic and wide because of the fact that  $(\bar{r}_{v'} + \bar{r}_{v''})/2 \approx r_{e,0}$ .