JOURNAL OF MATERIALS SCIENCE **38** (2003) 2001 – 2006

Micro-macro property correlations in alkali halide crystals*

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Correlations are developed between the microscopic parameters, Debye-Waller factor and lattice constant and the macroscopic properties, melting temperature and hardness of alkali halide crystals with NaCl structure. Proper equations are proposed and physical justification is provided for the observed correlations. Further, these properties are correlated with the force constant calculated from the compressibility and these correlations are, again, shown to have physical justification. Finally, a kaleidoscopic relationship is shown to exist between all these properties. © *2003 Kluwer Academic Publishers*

1. Introduction

Butt *et al.* [1, 2] made an attempt to establish micro-macro property correlations in cubic crystals. For this purpose, they chose the Debye-Waller factor on the one hand and the lattice constant, the melting point, the hardness, the Young's modulus and a few other properties. Butt *et al.* [1, 2] drew log-log plots between combinations of these properties and commented on the trends. However, this attempt had some limitations. Firstly, Butt *et al.* [1, 2] did not provide any basis or justification for the observed trends. Secondly, there was no uniformity in the choice of materials. Thus, some correlations were tested only on elemental solids whereas some others were tested on compound crystals. In the latter case, Butt *et al.* [2] included crystals of several structures together which resulted in considerable scattering in the plots. It is known that the constants in any correlations are different for different crystal families. Hence it is preferable to test a correlation on a single structural family at a time.

The present communication reports the results of a more detailed and systematic study of micro-macro property relations. The properties considered are the mean Debye-Waller (or temperature) factor (B), the lattice constant (a), the melting point (T_{m}) and the hardness (H); instead of the Young's modulus we have included the compressibility (ψ). Further, the study is confined only to the alkali halides with NaCl structure.

The approach is to look for definite relationships among B, a, T_{m} and H and to quantify the relations in the form of equations. Several possible relations were considered but, finally, only one relation is proposed between two parameters. The choice is based not just on the best fit but more on our ability to provide physical basis for the proposed relationship in terms of existing theories or well-established empirical relations. Finally, an attempt is made to establish a kaleidoscopic relation between these properties and the interatomic force constant (f) calculated from the compressibility.

The values of B, a, T_{m}, H and ψ are collected in Table I. The discussion in the following sections involves a large number of constants. To minimise confusion, the generic symbol C_i ($i = 1, 2, \ldots$) is used to represent constants occurring in equations proposed by us whereas the generic symbol K_i ($i = 1, 2, \ldots$) is used for constants in other equations. The values of some of the constants are given in the Appendix.

2. Inter-property correlations

2.1. Correlation between temperature factor, lattice constant and melting point

Butt *et al.* [1] plotted the values of B against T_{m} on a log-log scale for elemental solids and obtained an "approximately linear" correlation. They also plotted B vs a^2/T_{m}; this plot appeared better than the B versus T_{m} plot since it could differentiate between the fcc and bcc metals. However, Butt *et al.* [1] did not provide any arguments in favour of one or the other of these two correlations. Butt *et al.* [2] also plotted the values of B and T_{m} on a log-log scale for cubic compound crystals. Here they included crystals of NaCl, CsCl, ZnS and CaF_2 structures in a single plot. The plot shows an approximately linear correlation but with considerable scatter. Butt *et al.* [2] did not draw the B versus a^2/T_{m} plot for the compound crystals as they did for the elements. We have drawn both B versus T_{m} and B versus a^2/T_{m} plots for the alkali halides with NaCl structure. The B versus T_{m} plot (not shown) appears like a hyperbola. On the other hand, the B versus a^2/T_{m} plot (Fig. 1) is a straight line, which passes through the origin.

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*Dedicated to Prof. B. T. M. Willis, Oxford University, in appreciation of his contributions to the physics of atomic thermal vibrations in solids.

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TABLE I Values of the mean Debye-Waller factor B (Å^2), hardness H, melting point T_m (K), lattice constant a (Å), compressibility ψ(10^{-12} cm^2/dyne), force constant $f \times 10^3$ (megadynes/cm), lattice energy U (kcal/mole) and molar volume V (cm^3) of alkali halides with rocksalt structure

S. no.	Crystal	B	H	T_m	a	ψ	$f \times 10^3$	U	V
1	LiF	0.76	3.16	1121	4.03	1.49	40.58	242.3	9.826
2	LiCl	(1.38)	(1.96)	883	5.13	3.36	22.91	198.9	20.442
3	LiBr	(1.64)	(1.75)	825	5.50	4.20	19.65	189.8	25.062
4	LiI	(2.12)	(1.53)	742	6.00	5.83	15.44	177.7	32.712
5	NaF	0.91	2.70	1269	4.62	2.15	32.24	214.4	14.970
6	NaCl	1.56	1.89	1074	5.641	4.17	20.30	182.6	27.012
7	NaBr	1.67	1.60	1020	5.973	5.02	17.85	173.6	32.083
8	NaI	2.24	1.45	933	6.473	6.64	14.63	163.2	40.829
9	KF	1.21	(1.96)	1131	5.347	3.28	24.46	189.8	22.977
10	KCl	2.17	1.59	1044	6.239	5.73	16.48	165.8	37.518
11	KBr	2.37	1.45	1007	6.600	6.75	14.67	158.5	43.248
12	KI	2.99	1.29	954	7.066	8.55	12.40	149.9	53.103
13	RbF	1.40	(1.81)	1106	5.640	3.81	22.21	181.4	27.177
14	RbCl	2.18	1.43	988	6.580	6.40	15.43	159.3	43.083
15	RbBr	2.24	1.35	955	6.854	7.69	13.37	152.6	49.261
16	RbI	3.44	1.23	915	7.342	9.48	11.62	144.9	59.584

Values of B for NaBr and NaI from Geeta Krishna *et al.* [3] and rest from Butt *et al.* [4], H from compilation of data by Sirdeshmukh *et al.* [5] (the Vickers hardness values have been converted to the Moh scale), T_m from CRC Handbook [6], 'a' from Wyckoff [7], ψ from Tosi [8], U and V from Sirdeshmukh *et al.* [9]. Values in parenthesis are estimated from the correlations in the text.

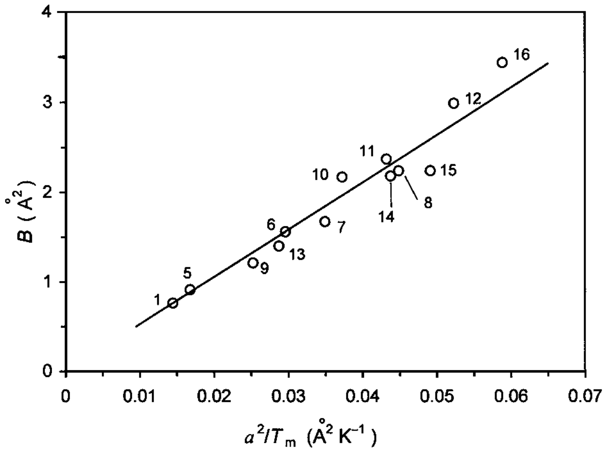

Figure 1 B versus (a^2/T_m). In this and other figures the data points are numbered as given in Table I.

The relationship indicated by this plot is represented by:

$$B = C_1(a^2/T_m) \tag{1}$$

where C_1 is a constant.

It will now be shown that Equation 1 has a physical basis. From the Debye-Waller theory [10], we have

$$B = \frac{6h^2}{mk_B\theta}\left[\frac{\phi(x)}{x} + \frac{1}{4}\right] \tag{2}$$

where h is Planck's constant, m the mean atomic mass, k_B the Boltzmann constant, θ the Debye temperature, and $\phi(x)$ the Debye function given by

$$\phi(x) = \frac{1}{x}\int_0^x \frac{y\,dy}{(e^y - 1)} \tag{3}$$

with $x = \theta/T$, T being the temperature. At high temperatures ($T > \theta$), Equation 2 approximates [11] to

$$B = \frac{6h^2T}{mk_B\theta^2} \tag{4}$$

Further, from Lindemann's theory, we have

$$\theta = K_1(T_m/mV^{2/3})^{1/2} \tag{5}$$

where K_1 is a constant and the molar volume V is given by

$$V = K_2a^3 \tag{6}$$

Combining Equations 4, 5 and 6, we get

$$B = \left(6h^2TK_2^{2/3}/k_BK_1^2\right)(a^2/T_m) \tag{7}$$

which is the same as Equation 1 which was proposed empirically. The constant C_1 in Equation 1 is now given by

$$C_1 = \left(6h^2TK_2^{2/3}/k_BK_1^2\right) \tag{8}$$

2.2. Correlation between hardness and melting point

The relation between hardness and melting point is now considered. In Fig. 2, the values of H are plotted against (T_m/a^3). The plot is linear but with an intercept on the H axis. Hence, the following relation is proposed:

$$H - C_2 = C_3(T_m/a^3) \tag{9}$$

where C_2 and C_3 are constants. A similar relation between H and T_m was proposed by Bodnar *et al.* [12] empirically for crystals with the chalcopyrite structure.

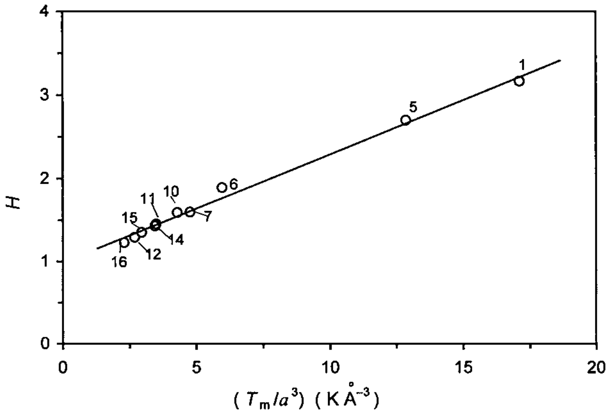

Figure 2 Hardness H versus (T_m/a^3).

It will now be shown that Equation 9 evolves out of well-established relations. The Madelung formula for Debye temperature is

$$\theta = K_3 \psi^{-1/2} m^{-1/2} V^{1/6} \tag{10}$$

where K_3 is a constant for a family of related crystals. Plendl *et al.* [13] has pointed out that for a family of isostructural crystals, the hardness is linearly related to the reciprocal of compressibility. Plotting H against ψ^{-1} for the alkali halides with NaCl structure (Fig. 3), we get the relation

$$H - K_4 = K_5 \psi^{-1} \tag{11}$$

where K_4 and K_5 are constants. Combining Equations 5, 6, 10 and 11, we get

$$H - K_4 = \left(K_1^2 K_5 / K_2 K_3^2\right)(T_m/a^3) \tag{12}$$

which is the same as Equation 9 with

$$C_2 = K_4 \tag{13}$$

$$C_3 = \left(K_1^2 K_5 / K_2 K_3^2\right) \tag{14}$$

It is interesting to observe that the constants C_2 and K_4 obtained from two independent properties are indeed equal within statistical limits.

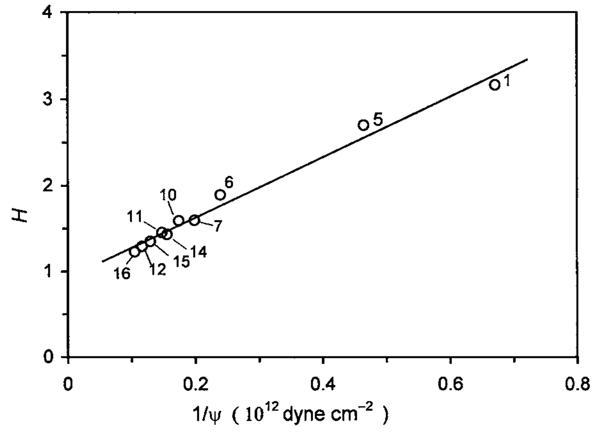

Figure 3 Hardness H versus ($1/\psi$).

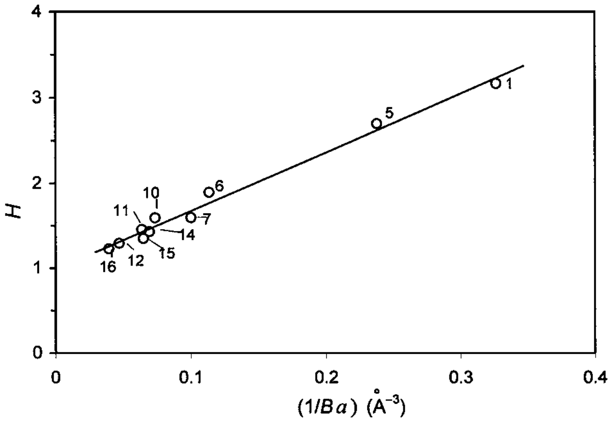

Figure 4 H versus ($1/Ba$).

2.3. Correlation between hardness and temperature factor

Butt *et al.* [1] plotted B against H on a log-log scale for elemental crystals and observed a linear correlation. Butt *et al.* [1] did not examine the correlation in cubic compound crystals. We plotted the values of H for the alkali halides against B and $1/Ba$. The H versus B plot (not shown) resembles a hyperbola. On the other hand, the H versus ($1/Ba$) plot (Fig. 4) is linear. This last correlation may be represented by

$$H - C_4 = C_5(1/Ba) \tag{15}$$

where C_4 and C_5 are constants.

It is easy to see that Equation 15 has a physical basis. If we combine Equations 1 and 9, we get

$$H - C_2 = C_1 C_3 (1/Ba) \tag{16}$$

This is the same as Equation 15 with

$$C_4 = C_2 \tag{17}$$

and

$$C_5 = C_1 C_3 \tag{18}$$

It is seen from Figs 3 and 4 that $C_4 = C_2 \approx K_4$. Equation 15 thus has a physical basis inasmuch as it is the result of combining Equations 1 and 9 which have been shown to have a physical basis. Hence it is preferred over the linear relation between H and $1/B$.

3. A kaleidoscopic relation between *B, H, T_m* and *f*

In the above sections, relations are shown to exist between B, H and T_m. If several properties are interrelated, it is natural to expect each of them to be independently related to some common physical parameter. Several parameters like the ionicity, electronegativity difference etc. were tested for possible correlations. Finally, the interatomic force constant f is chosen as the parameter with which these three properties could be independently related.

3.1. Evaluation of f

The potential energy of a bond may be expressed as

$$U(r) = (f/2)(r - r_0)^2 \tag{19}$$

where $U(r)$ is the potential energy, r is the bond length, r_0 its equilibrium value and f the force constant. It is shown by Waser and Pauling [14] that the force constant can be calculated from

$$f = (9V_0/Nr^2\psi) \tag{20}$$

where N is the number of equivalent nearest neighbour bonds in the unit cell of volume V_0 and ψ is the compressibility. The values of the force constant are given in Table I.

3.2. Relation between f and H

In Fig. 5, the values of H are plotted against f/a. This is a linear plot making an intercept on the H-axis. This linear relationship can be represented by

$$H - C_6 = C_7(f/a) \tag{21}$$

We shall now substantiate this relationship. Using physical reasoning, Plendl and Gielisse [15] have shown that the volumetric lattice energy, (U/V) is linearly related to the hardness. The relationship is expressed as

$$U/V = K_6(H - K_7) \tag{22}$$

where K_6 and K_7 are constants. Plendl and Gielisse [15] have given different values for the two constants for different hardness ranges. In doing so, Plendl and Gielisse [15] have included crystals of various structures. We have reevaluated the constants exclusively for the alkali halides with NaCl structure; the linear plot is shown in Fig. 6. The values of U and V used for this purpose are given in Table I. Using physical reasoning and substituting for U and V in terms of quantities like the force constant, lattice constant, the frequency of vibration etc., Plendl and Gielisse [15] have shown that

$$U/V = K_8(zf/a) \tag{23}$$

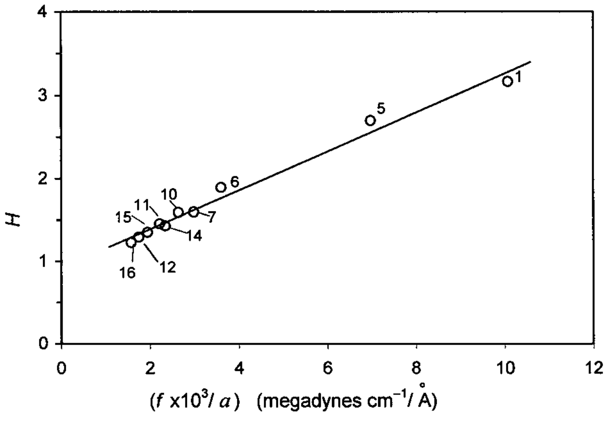

Figure 5 H versus (f/a).

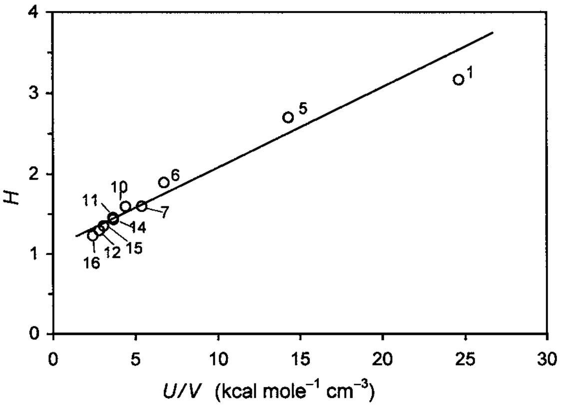

Figure 6 H versus (U/V).

where K_8 is a structural constant and z the valency. Combining Equations 22 and 23 and noting that for the alkali halides $z = 1$, we get

$$H - K_7 = (K_8/K_6)(f/a) \tag{24}$$

This is the same as Equation 21 with

$$C_6 = K_7 \tag{25}$$

and

$$C_7 = (K_8/K_6) \tag{26}$$

3.3. Relation between f and T_m

After trying different combinations, we observe a linear relation between f and (T_m/a^2). This is shown in Fig. 7. The relation may be expressed as

$$f = C_8(T_m/a^2) \tag{27}$$

where C_8 is a constant. The physical interpretation of this relation is straight-forward. We reproduce Equation 5 for the Debye temperature

$$\theta = K_1(T_m/mV^{2/3})^{1/2} \tag{5}$$

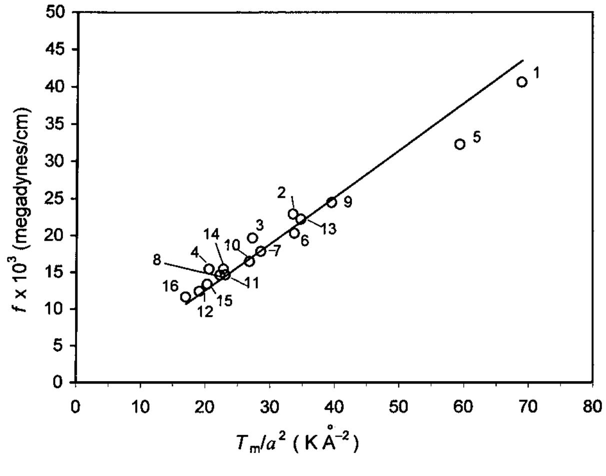

Figure 7 f versus (T_m/a^2).

The Debye temperature may be expressed in terms of the Debye frequency ν_D as

$$\theta = (h\nu_D/K_B) \tag{28}$$

Since the Debye frequency is a characteristic vibration frequency of the lattice, it may be written as

$$\nu_D = (1/2\pi)(f/m)^{1/2} \tag{29}$$

Combining Equations 5, 6, 28 and 29, we get

$$f = \left(4\pi^2 K_1^2 k_B^2 / h^2 K_2^{2/3}\right)(T_m/a^2) \tag{30}$$

which is the same as Equation 27 with

$$C_8 = \left(4\pi^2 K_1^2 k_B^2 / h^2 K_2^{2/3}\right) \tag{31}$$

3.4. Relation between *f* and *B*

A plot of f and $1/B$ is shown in Fig. 8. It is a linear plot which is represented by

$$f = C_9(1/B) \tag{32}$$

where C_9 is a constant.

From Equation 4, we have

$$B = (6h^2 T/mk_B\theta^2) \tag{4}$$

Combining Equation 4 with Equations 28 and 29, we get

$$f = (24\pi^2 Tk_B)(1/B) \tag{33}$$

which is the same as Equation 32 with

$$C_9 = (24\pi^2 Tk_B) \tag{34}$$

3.5. Kaleidoscopic relation

It is thus seen that the Debye-Waller factor, the melting temperature and the hardness, along with the lattice constant, are related to the force constant through Equations 21, 27 and 32; the force constant, in turn, is related to the compressibility. The inter-relationships represented by Equations 1, 9 and 15 are, in fact, a consequence of a kaleidoscopic relationship of these properties with the force constant, shown in Fig. 9. The combination of any two of the Equations 21, 27 and 32 results in one of the Equations 1, 9 or 15.

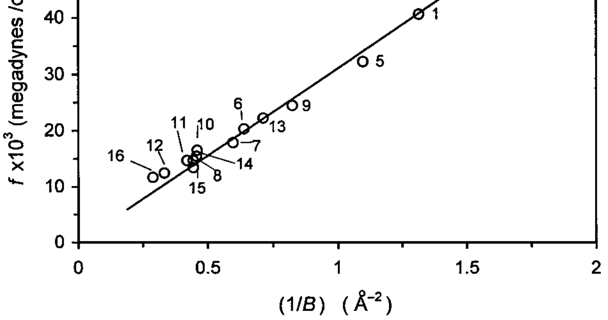

Figure 8 f versus $(1/B)$.

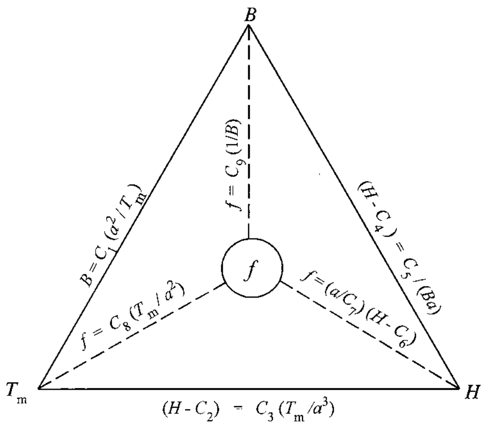

Figure 9 Kaleidoscopic relation between B, H, T_m and f.

4. Summary and conclusions

A number of correlations between some micro and macro properties of alkali halide crystals are examined. The Debye-Waller factor, the melting temperature and the hardness, along with the lattice constant, are shown to correlate with one another. Appropriate equations are proposed. Further, a kaleidoscopic relation is found to exist between these properties and the force constant calculated from the compressibility. The various relations are shown to have a physical basis. Most of them result from combinations of a few well-established relations like the Lindemann and Madelung formulae for the Debye temperature, Plendl *et al.*'s formulation for hardness and the concept of a force constant.

The relations developed in Section 2 have been used to predict properties for which experimental values are not available like the lithium halides and the fluorides of K and Rb. It may be of interest to try these relations on other materials like crystals with NaCl structure other than the alkali halides, the fluorite-type crystals and the zinc-blende-type crystals. Other properties like Debye temperatures, thermal expansion coefficient and defect formation energies could also be included in a broader kaleidoscopic framework.

An observation to be noted is that the Moh hardness fits into these relations rather than the Vickers hardness. In Figs 2–6, the plots do not pass through the origin but have intercepts on the y-axis. As a result, in Equations 9, 11, 15, 21 and 22, the hardness occurs reduced by a constant which has nearly the same value (1.0 ± 0.1). In an attempt to avoid this, we drew log-log plots. These plots passed through the origin but led to relations which could not be supported by a physical explanation and, further, were mutually inconsistent. Hence, the above-mentioned equations were retained. The significance of the reduced hardness occurring in these equations needs further examination.

Acknowledgements

Grateful thanks are due to the referee for a careful scrutiny of the manuscript and for valuable suggestions.

DBS acknowledges financial assistance from the University Grants Commission.

Appendix

TABLE II Values of constants occurring in equations proposed in this paper; the constants are without units when the quantities in the respective equations are taken with units given in Table I

Equation no.	Equation	Values of constants
1	$B = C_1(a^2/T_m)$	$C_1 = 52.83$
9	$H - C_2 = C_3(T_m/a^3)$	$C_2 = 0.99$
		$C_3 = 0.13$
11	$H - K_4 = K_5\psi^{-1}$	$K_4 = 0.93$
		$K_5 = 3.51$
15	$H - C_4 = C_5(1/Ba)$	$C_4 = 0.99$
		$C_5 = 6.88$
21	$H - C_6 = C_7(f/a)$	$C_6 = 0.92$
		$C_7 = 0.23$
22	$U/V = K_6(H - K_7)$	$K_6 = 10.02$
		$K_7 = 1.08$
27	$f = C_8(T_m/a^2)$	$C_8 = 0.63$
32	$f = C_9(1/B)$	$C_9 = 31.08$

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Received 15 March 2002
and accepted 4 February 2003