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Correlation of temperature factors with physical properties in cubic elements

N. M. BUTT, J. BASHIR, M. NASIR KHAN
Pakistan Institute of Nuclear Science and Technology, P.O. Nilore, Islamabad, Pakistan

The recommended value of the Debye–Waller thermal parameter, *B*, for 22 cubic elements, based on experimental measurements using X-ray, neutron, and γ-ray diffraction as well as high-voltage electron diffraction, has recently been published. Using these data, interesting correlations can be made of the parameter *B* with thermal, mechanical and defect properties of these cubic elements. These results show an evident relationship between the microscopic and bulk properties.

1. Introduction

The temperature dependence of the intensity of radiation (X-rays, neutrons, γ-rays, and electrons) diffracted from a crystal has been dealt with extensively using the Debye–Waller theory [1, 2]. The effect of the temperature is to reduce this intensity by an exponential factor known as the Debye–Waller factor, $\exp(-2B\sin^2\theta/\lambda^2)$, where θ is the Bragg angle at which the diffracted intensity has been measured and λ is the wavelength of the radiation. The quantity B is usually referred as the Debye–Waller thermal parameter or the temperature factor, and is related to the Debye temperature, Θ, of the solid through the relation

$$B = (6h^2/mk)(T/\Theta^2)[\phi(x) + x/4] \qquad (1)$$

where $x = \Theta/T$ and the remaining symbols have their usual meanings as described in [1]. For a monatomic cubic crystal for which the vibrations are isotropic, the mean square amplitude of atomic vibrations perpendicular to the diffracting plane, $\langle u_s^2\rangle$, is related to B via the relation

$$\mathrm{B} = 8\pi^2\langle u_s^2\rangle \qquad (2)$$

The quantity B is a fundamental parameter of a solid at a given temperature. Apart from the fact that its temperature dependence leads to useful information on the atomic behaviour of solid materials [3], a knowledge of its value at room temperature is important, for example, in the design of the moderators of nuclear reactors.

Interrelation between different properties of materials are useful for the understanding of physical properties of the materials, as well as for the prediction of unknown parameters where no experimental data are available. A large number of papers has been published where quantities such as melting point, thermal expansion coefficient, Debye temperature, moduli of elasticity, defect formation and migration energies, cohesive energy, etc., have been interrelated [4–12].

In the present investigations using recently published data of temperature factors B of the cubic elements [13], we have found interesting correlations of this microscopic parameter with several macroscopic or bulk properties such as melting point, coefficient of thermal expansion, mechanical properties, and crystal defect energies. Correlations with other quantities, such as cohesive energy, heat of fusion and density, etc., have also been investigated.

2. Results and discussion

2.1. General properties

2.1.1. Cohesive energy

The cohesive energy, U_c, is defined as the energy per atom required to decompose a solid into free atoms. In Fig. 1 the parameter B is plotted against the cohesive energy U_c. The least square fit to the plot yielded a relation

$$B = 7.3/U_c^{1.76} \qquad (3)$$

with a linear correlation coefficient of 0.97. However, when B is plotted against a^2/U_c where a is the lattice parameter (Fig. 2), we get two different straight lines depending upon the type of the crystal structure of the element. These straight lines can be described by the following relations

$$B = 0.15\,a^2/U_c \quad \text{for fcc metals} \qquad (4a)$$

$$B = 0.27\,a^2/U_c \quad \text{for bcc metals} \qquad (4b)$$

Similar relations hold between the temperature factors and the heat of fusion which is the energy per atom required to melt the solid (Figs 3 and 4). Both the cohesive energy and heat of fusion data is from Gschneidner [14].

2.1.2. Density

The plot of B versus density, ρ, is shown in Fig. 5. The density data are taken from Barrett and Massalski [15]. The temperature factor, B, decreases with increasing density. This is to be expected as higher density means tighter interatomic bonding and hence lower values of the temperature factors. The two alkali metals, potassium and sodium, and lead show some

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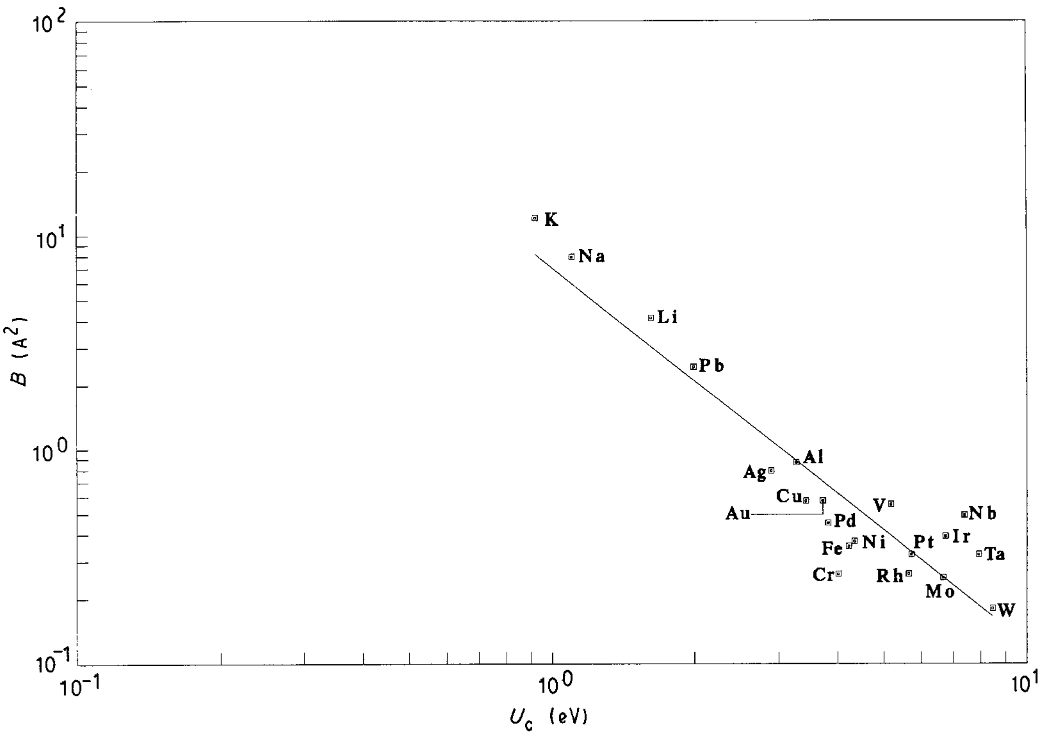

Figure 1 Temperature factor, B, versus cohesive energy, U_c. (⊡) Observed, (——) calculated.

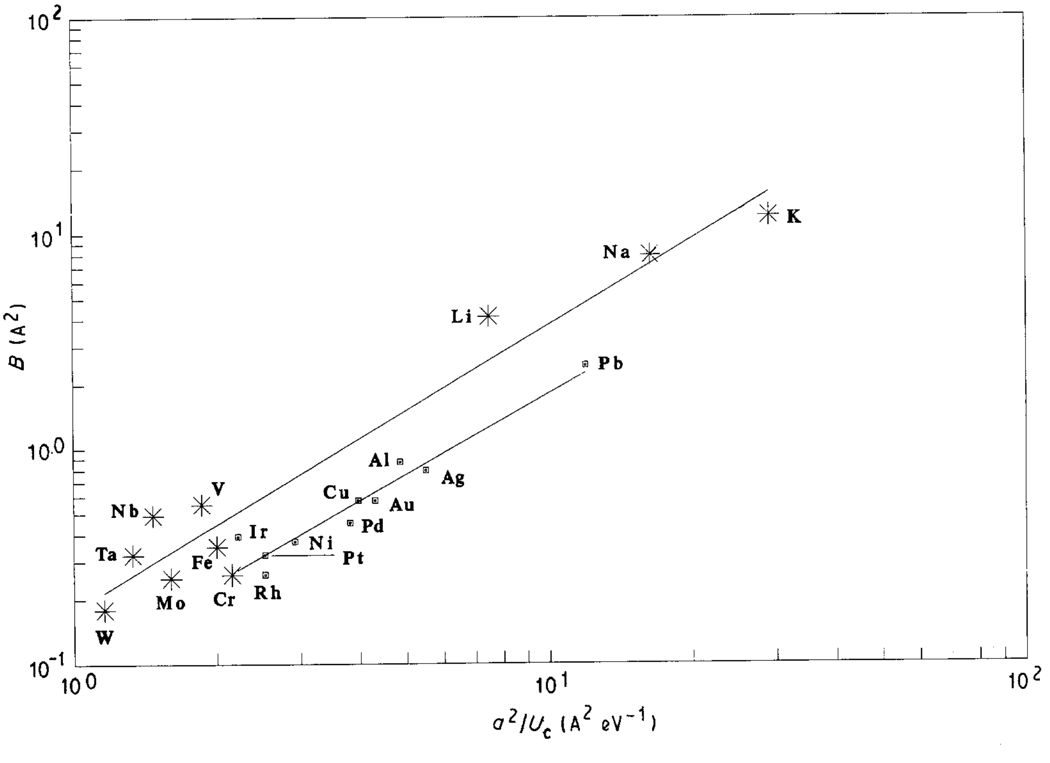

Figure 2 B versus a^2/U_c, where a is the lattice constant. (⊡) fcc, (*) bcc, (——) calculated.

deviations from the normal straight-line behaviour which is best described by the relation

$$B = 3.2\rho^{0.83} \quad (5)$$

2.2. Thermal properties

2.2.1. Melting temperature

Melting point is an important but not too well-understood property of materials. Several attempts have been made to correlate the melting point with other physical properties of the materials. In 1879, Carnelley [16] pointed out that the melting point increases with increase in the bond strength of the element. Since then, numerous attempts have been made to deduce simple rules relating melting point and other physical properties of solids [4, 10, 17–26].

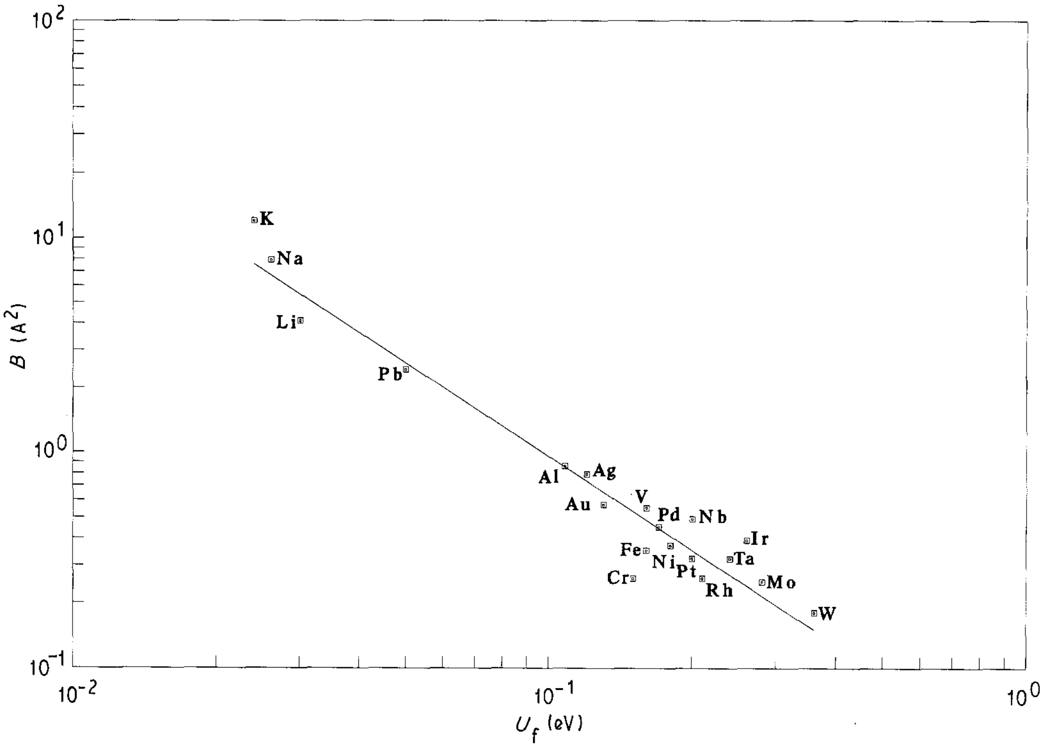

Figure 3 Temperature factor versus heat of fusion, U_f. (⊡) Observed, (——) calculated.

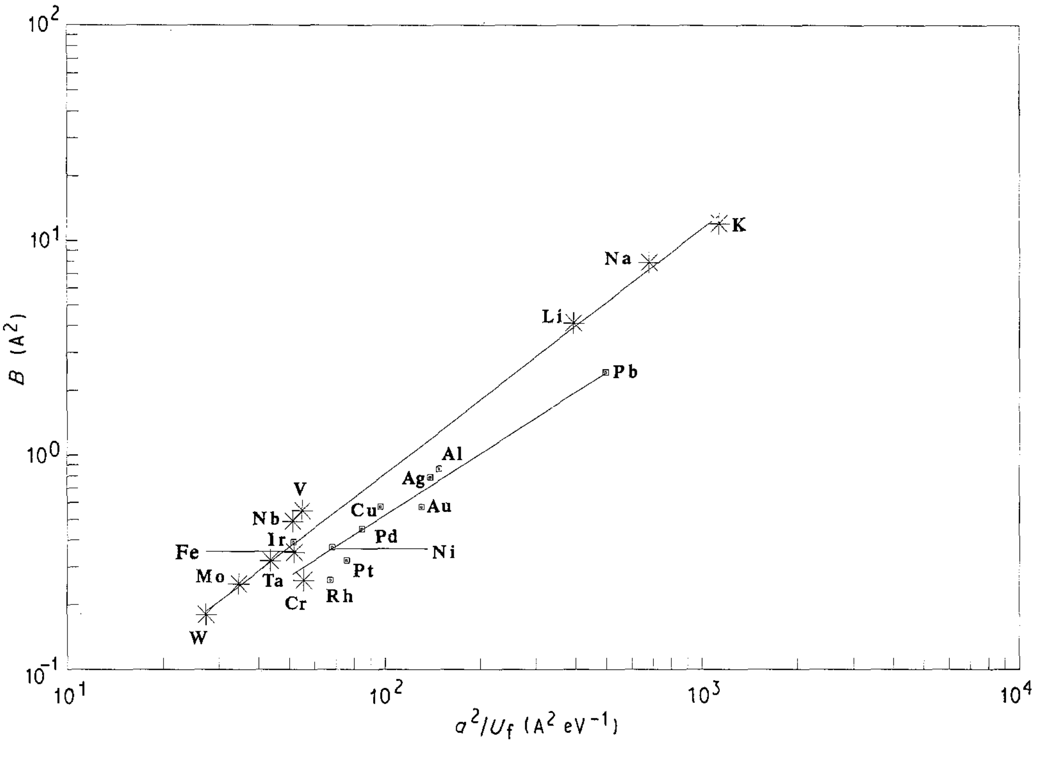

Figure 4 B versus a^2/U_f. (⊡) fcc, (∗) bcc, (——) calculated.

Fig. 6 illustrates the inverse relationship between B and the melting point, T_m. The values of the lattice constants and the melting point data are from Barrett and Massalski [15] and Ashcroft and Mermin [27]. This behaviour is expected, because the melting point is a function of cohesive energy and hence the bond strength which reflects the magnitude of the forces between the atoms. The relation between B and T_m, as obtained from the least square fit, is

$$B = 59036/T_m^{1.56} \qquad (6)$$

If B is plotted against a^2/T_m (Fig. 7), once again we observe a similar trend to that observed in the case of cohesive energy and heat of fusion, i.e. two different straight lines are obtained. These lines correspond to metals crystallizing in fcc and bcc structures. The

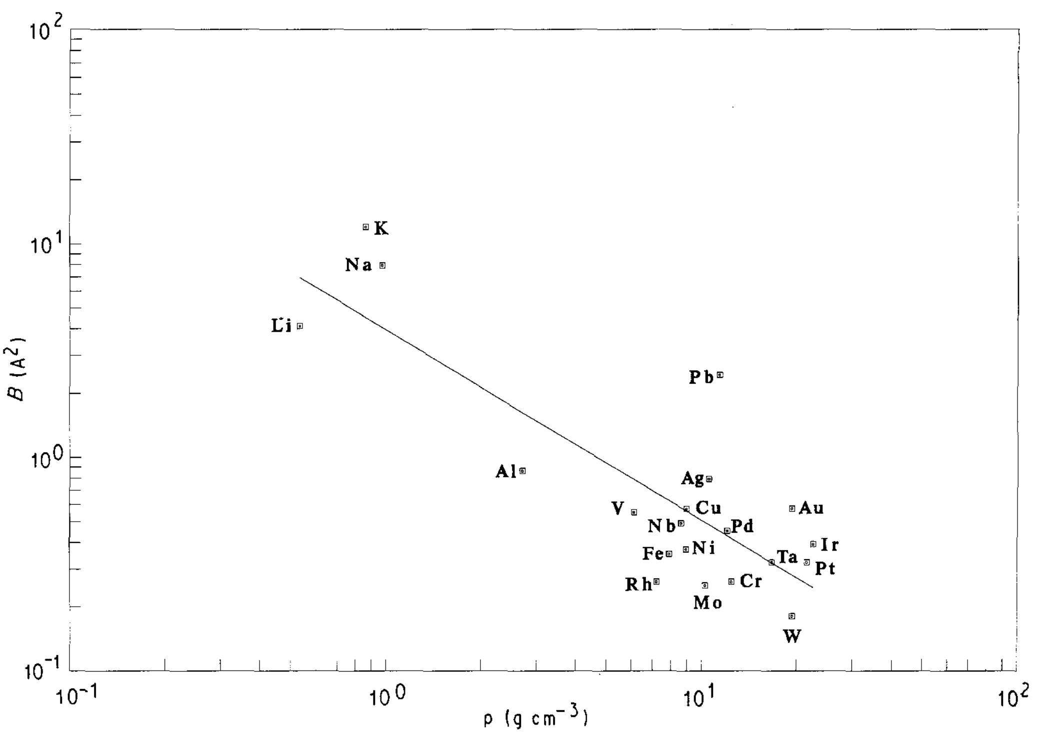

Figure 5 Temperature factor versus density, ρ. (□) Observed, (——) calculated.

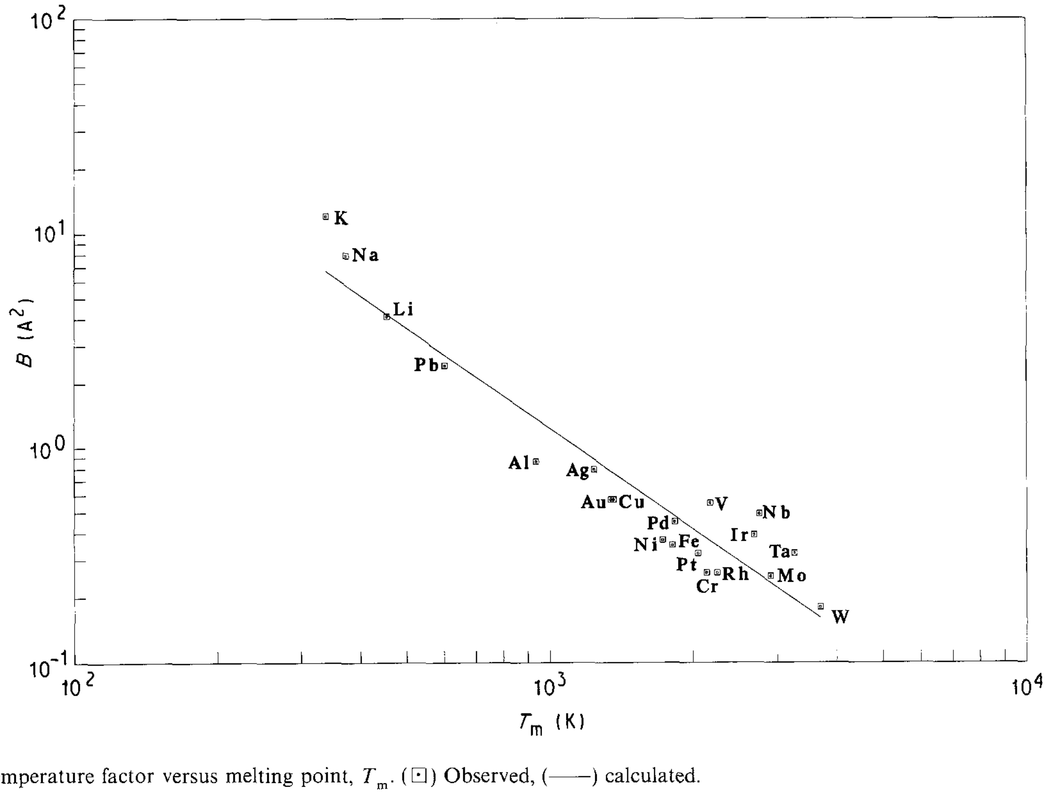

Figure 6 Temperature factor versus melting point, T_m. (□) Observed, (——) calculated.

relationship between B, the lattice constant, a, and the melting point, T_m, is

$$B = \delta_i a^2/T_m \quad (7)$$

where δ_i are constants and $i = 1, 2$ represents fcc and bcc metals. The constants and the corresponding standard deviations as computed numerically with least square fit are 67(2) and 283(1) for fcc and bcc metals, respectively.

2.2.2. Coefficient of thermal expansion

The coefficient of thermal expansion of solids is an important fundamental parameter particularly in metals and is crucial in designing a variety of useful devices which are subjected to severe variations of temperature. It is, therefore, interesting to explore the properties which appear to be correlated with the coefficient of thermal expansion. Several useful relations exist relating α to various other physical properties. Hanneman and Gatos [28] showed that a linear

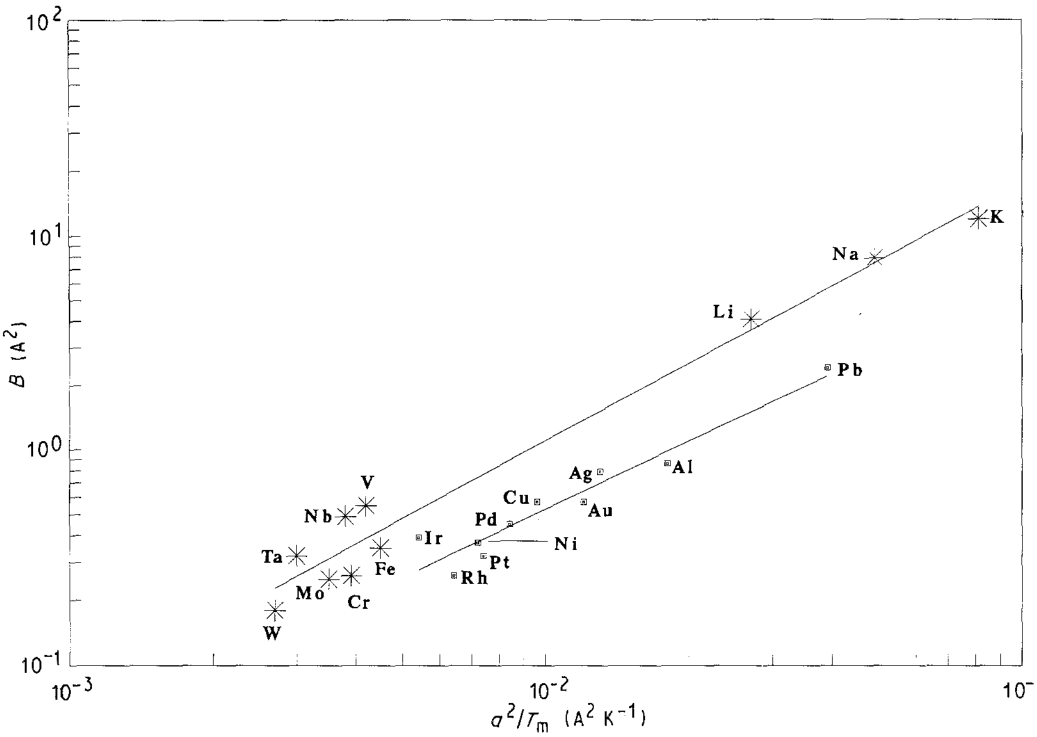

Figure 7 B versus a^2/T_m. (⊡) f c c, (∗) b c c, (——) calculated.

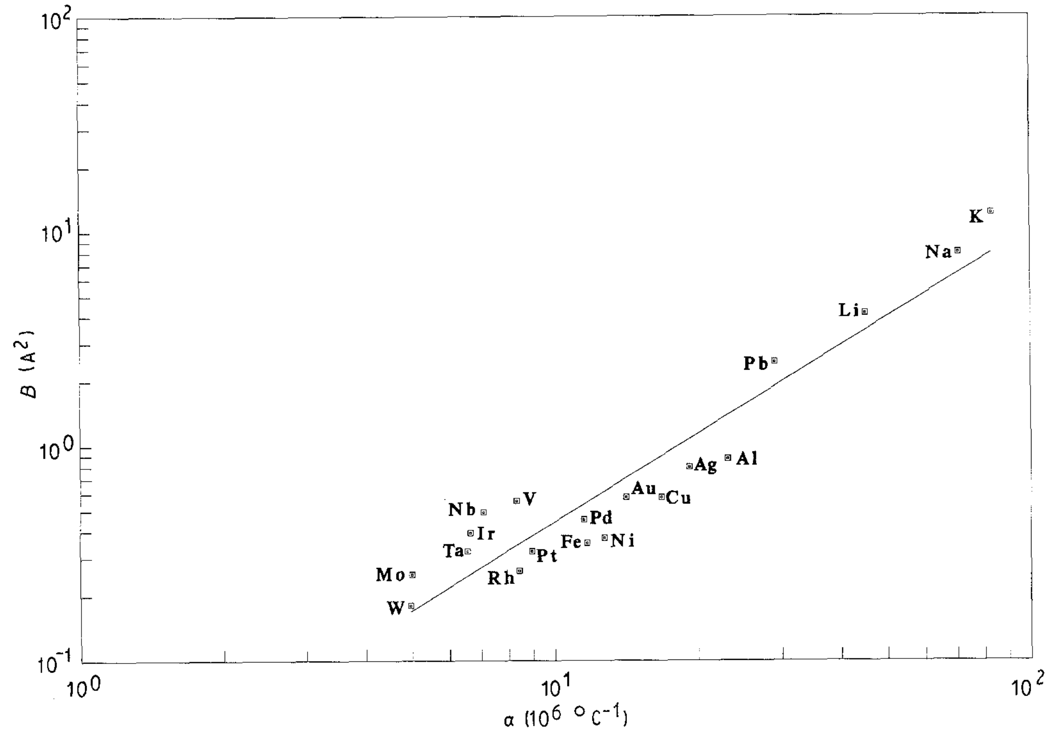

Figure 8 Temperature factor versus coefficient of thermal expansion, α. (⊡) Observed, (——) calculated.

relation exists between the thermal expansion coefficient, α, and compressibility of the materials. Plendl [29] showed that α is inversely proportional to the atomic coordination valence and directly proportional to atomic coordination number of the metallic elements, whereas Van Uitert [20] pointed out that for metals crystallizing in f c c, b c c or hexagonal close-packed metals, the product αT_m is constant.

Konyaeva [12] has pointed out that the thermal expansion coefficient decreases as the binding or cohesive energy of the element increases. As the temperature factor is also inversely proportional to the cohesive energy, B and α are therefore directly related, as shown in Fig. 8. The least square fit to the data yields the following relation between B and α

$$B = 196 \times 10^{-3} \alpha^{1.25} \tag{8}$$

with a linear correlation factor of 0.93. At this point it is important to point out that experimentally determined α values show considerable fluctuations. This may partly be due to different impurity contents of the various samples and partly due to different methods of determining the data.

As Van Uitert pointed out that

$$T_m = \text{constant}/\alpha \tag{9}$$

using Equations 8 and 10 we get

$$B = \text{constant}\, a^2\alpha \tag{10}$$

where the value of the constant depends upon the structure of the element. The plot of B versus $a^2\alpha$ once again shows two different straight lines (Fig. 9). The values of the constants obtained by linear regressions are 3.85×10^{-3} and 6.25×10^{-3} for the fcc and bcc metals, respectively.

2.3. Mechanical properties

The elastic properties of interest are the elastic constants, C_{11}, C_{12}, C_{44}, Young's modulus Y, bulk modulus K and its reciprocal compressibility, $\varkappa$, shear modulus, G, Poisson's ratio, ν, and the hardness, H of the material.

As the three moduli of elasticity and the Poisson's ratio are related through the relations

$$Y = 2G(1 + \nu) \tag{11}$$

and

$$K = Y/3(1 - 2\nu) \tag{12}$$

for an isotropic material which is free from texture, there are only two independent parameters, i.e. Young's and bulk modulus. As the compressibility is the reciprocal of the bulk modulus, we will consider only the Young's modulus, Y, and the compressibility, $\varkappa$.

2.3.1. Compressibility

The volume compressibility, $\varkappa$, and its reciprocal the bulk modulus, K, provide a convenient measure of the decrease in volume with pressure. Compressibility has been related to many physical properties of solids, such as melting point [30], energy of repulsion [31], atomic volume [32] and coefficient of thermal expansion [28], etc. Materials with large interatomic distances are generally more compressible than the more tightly bound materials; hence the compressibility decreases with increasing atomic radius [33]. Bulk modulus also depends on the valency of the metal again because of the stronger binding. The materials with higher densities have higher bulk modulus because the short-range forces make it increasingly difficult to compress the solid as the atoms move together. As the elements in which the atoms are tightly bonded have smaller B values, the temperature factor, B, and the compressibility, $\varkappa$, are directly related (Fig. 10).

2.3.2. Young's modulus

The Young's modulus, Y, has been related to the Debye temperature and monovacancy formation energy [9, 34]. The dependence of the Young's modulus on the specific heat of the solid was studied by Buch [35]. In Fig. 11, we have plotted Y versus the temperature factor B. The Young's modulus and the compressibility data are from the compilation of Gschneidner [14]. The agreement between the theoretical estimates and the experimentally observed values is seen to be very good.

2.3.3. Hardness

The hardness of a material is not a simple property

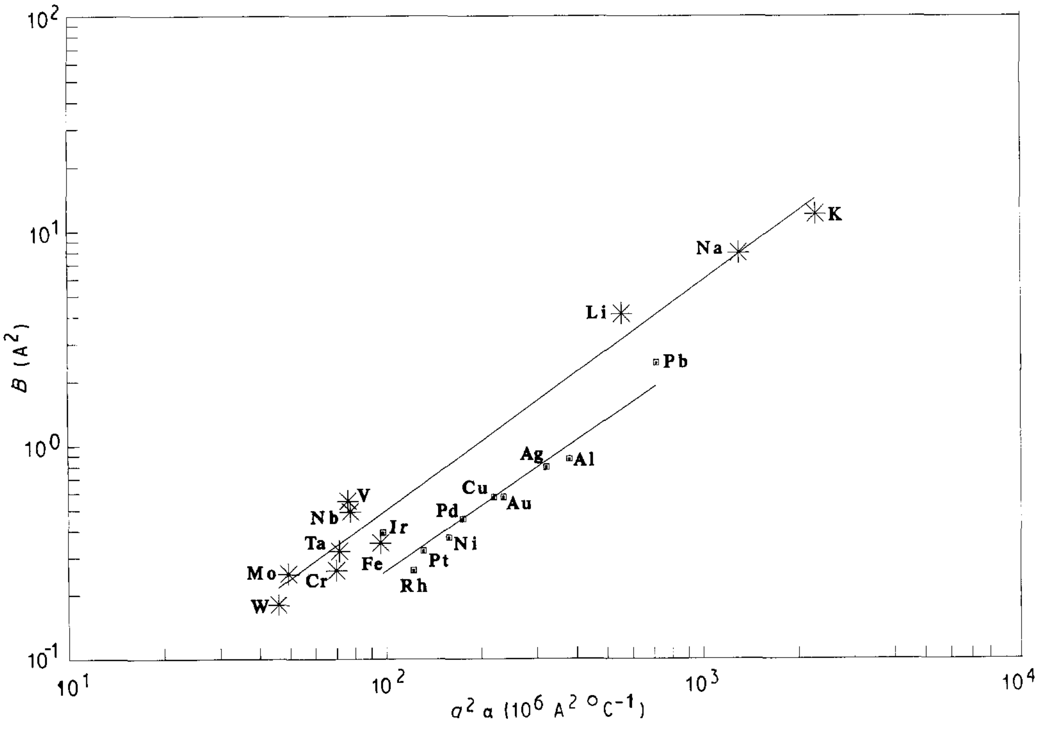

Figure 9 B versus $a^2\alpha$. (□) fcc, (∗) bcc, (——) calculated.

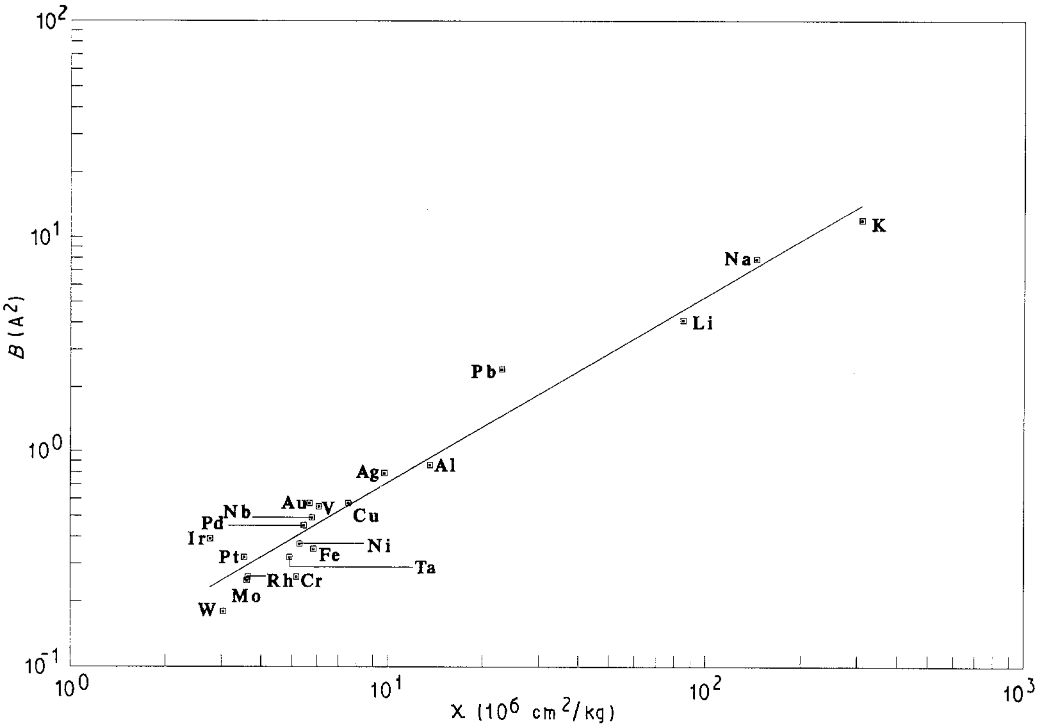

Figure 10 Temperature factor versus compressibility, $\varkappa$. (⊡) Observed, (——) calculated.

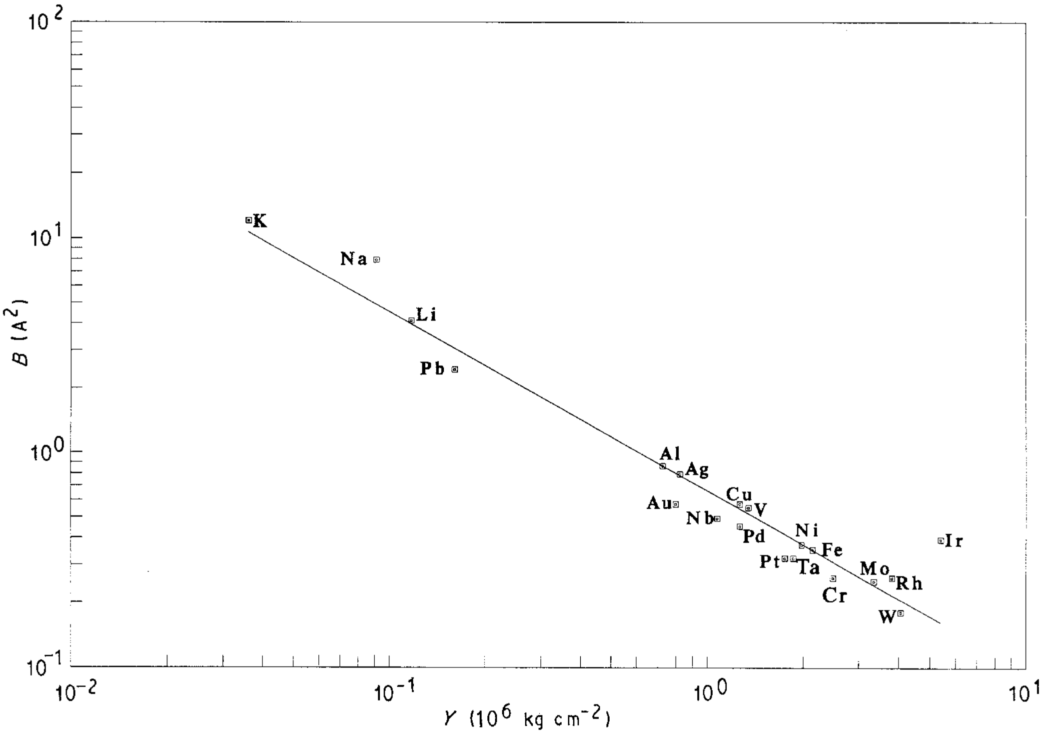

Figure 11 B versus Young's modulus, Y. (⊡) Observed, (——) calculated.

and complex stresses are involved during its testing. The hardness of cubic elements under discussion seems to be well correlated with B (Fig. 12). The elements having larger mean square amplitude of atomic vibrations have low hardness, while the elements with smaller values of B have high hardness values. Once again this is the consequence of the strong interatomic forces between the atoms.

2.3.4. Elastic constants

The elastic constants C_{11}, C_{12} and C_{44} are the stress components which in a specific direction determine the strain produced in that direction. The elastic constants C_{11}, C_{12} and C_{44} show good correlation when plotted against B (Figs 13, 14 and 15). Elastic constants data were taken from Brandes [36]. The values of the constants and the slopes as obtained by linear

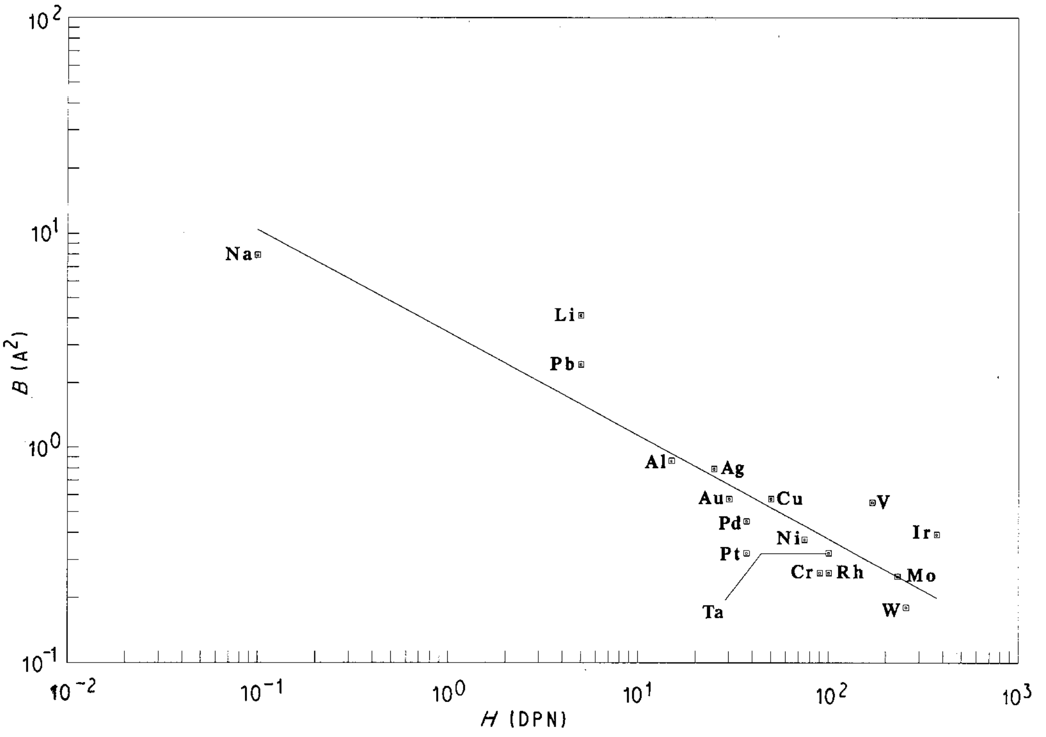

Figure 12 Temperature factor versus hardness, *H*. (⊡) Observed, (——) calculated.

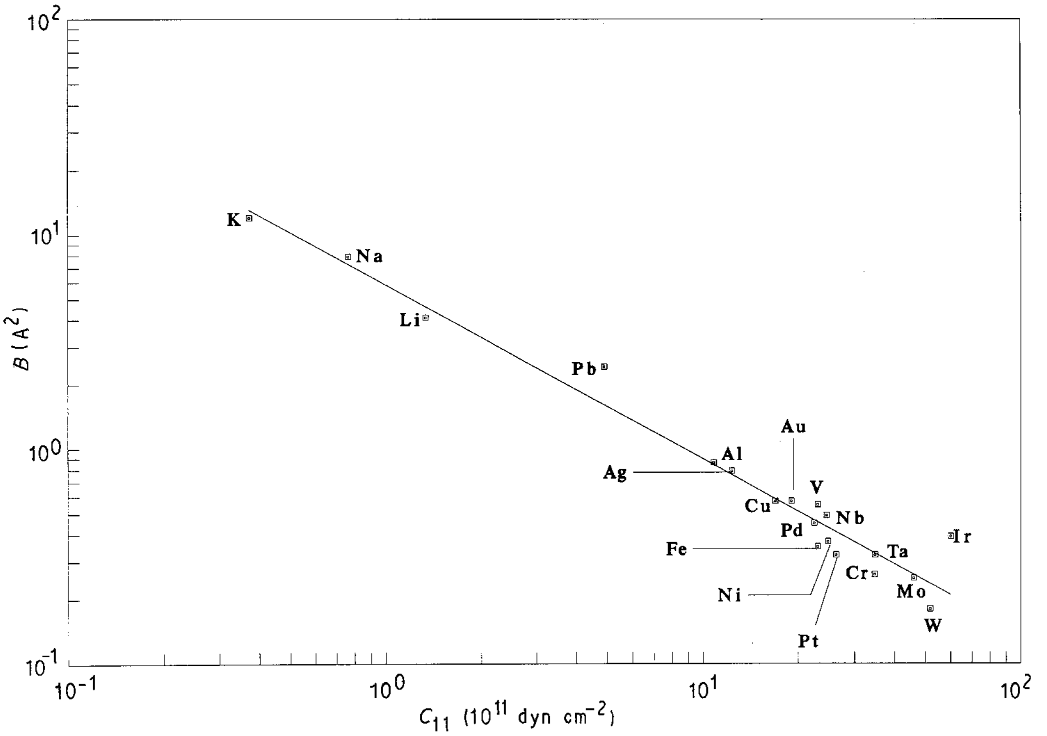

Figure 13 *B* versus C_{11}. (⊡) Observed, (——) calculated.

regression for the Young's modulus, compressibility, hardness and the three elastic constants, are summarized in Table I.

2.4. Crystal defect properties

Vacancies play an important role for diffusion of atoms in crystalline solids. In metals, as in the other solids, vacancies are created by the thermal excitation, because as the atoms vibrate around their equilibrium positions, some acquire enough energy to leave the site completely. Thus the formation energy, Q_v, is the energy required to produce a single vacancy.

The vacancy formation energy and activation energy for self diffusion are all dependent on the bonding strength of the constituent atoms. Gorecki [37] has collected considerable experimental data and has shown that $Q_v = U_o/3$, where U_o is the bonding energy per atom. Sherby and Simnad [38] pointed out

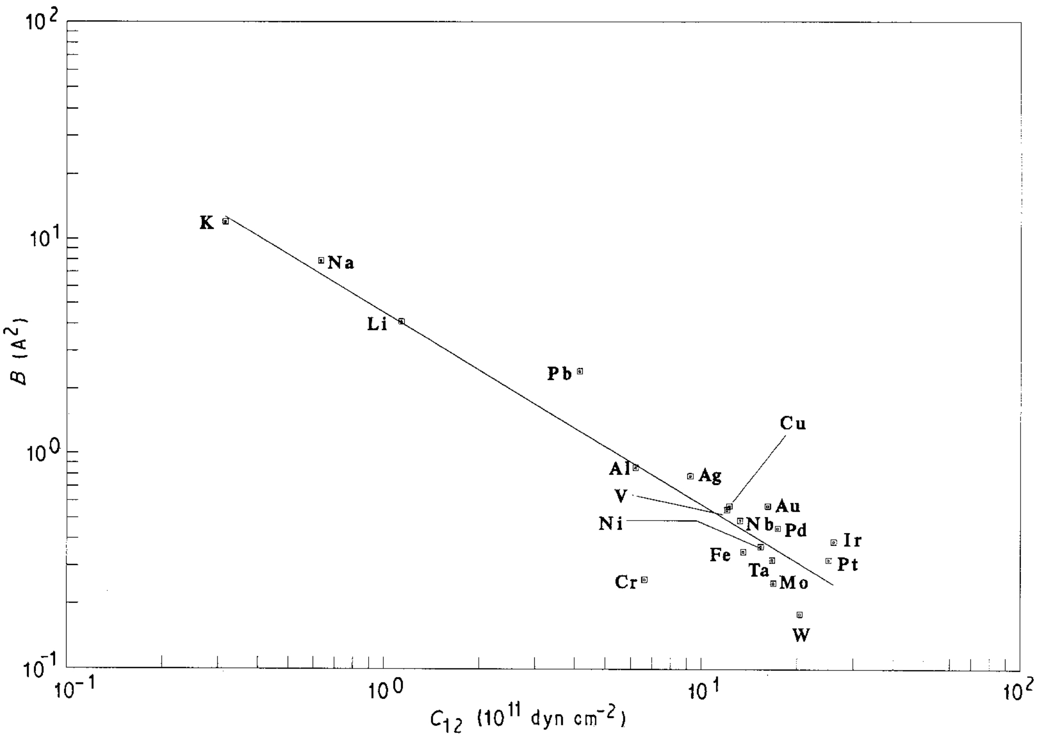

Figure 14 B versus C_{12}. (⊡) Observed, (——) calculated.

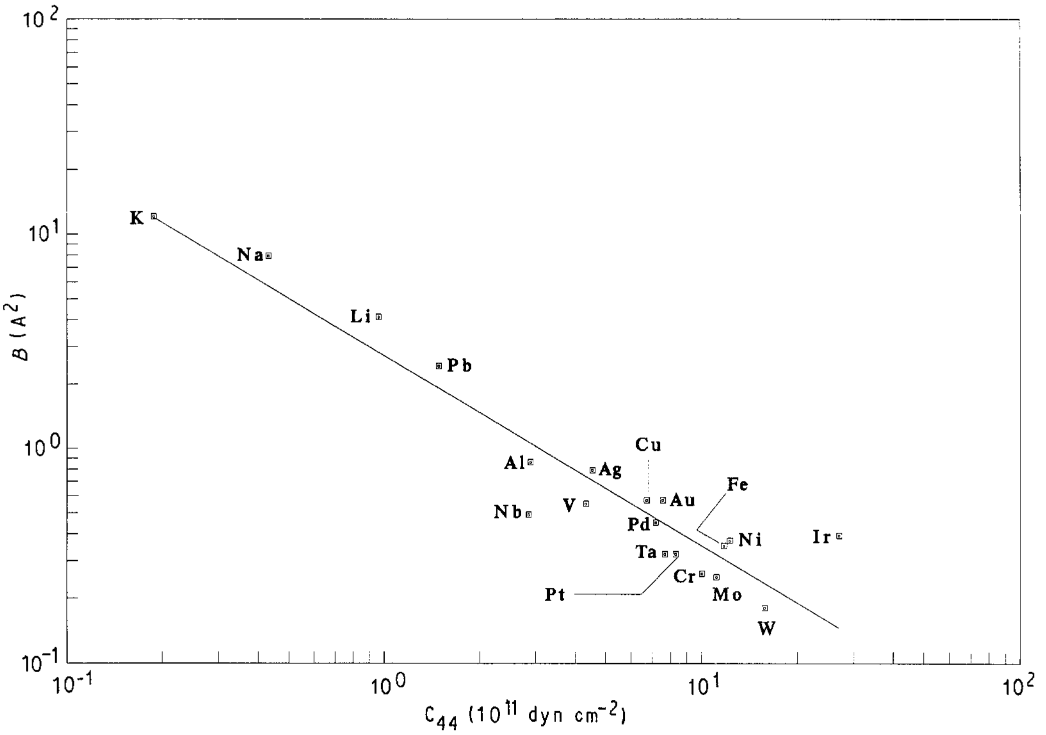

Figure 15 B versus C_{44}. (⊡) Observed, (——) calculated.

that the activation energy for self diffusion is the function of the valency of the element. Tiwari and Patil [39] have shown that vacancy parameters are linear functions of valence bond strength (cohesive energy/most prominent valency of the element). A number of empirical relations have been suggested between the vacancy parameters and various physical properties such as melting point, coefficient of thermal expansion, Young's modulus, bulk modulus, Fermi energy, nearest neighbour interactions, and the Debye temperature [6, 7, 19, 25, 40–44].

Plots of vacancy formation energy, Q_v, and activation energy for self diffusion, Q_d, versus B are shown in Figs 16 and 17. Values of vacancy formation energy as well as the activation energy for self diffusion are from Siegel [45], Nihoul [46], Koehler [47] and Kraftmakher and Strelkov [48]. Once again no structure dependence was observed in these plots. However, plots of temperature factor versus a^2/Q_v and a^2/Q_d (Figs 18 and 19) show similar structure dependence, as was observed in the case of other properties. The structure dependence of these relations is due to the

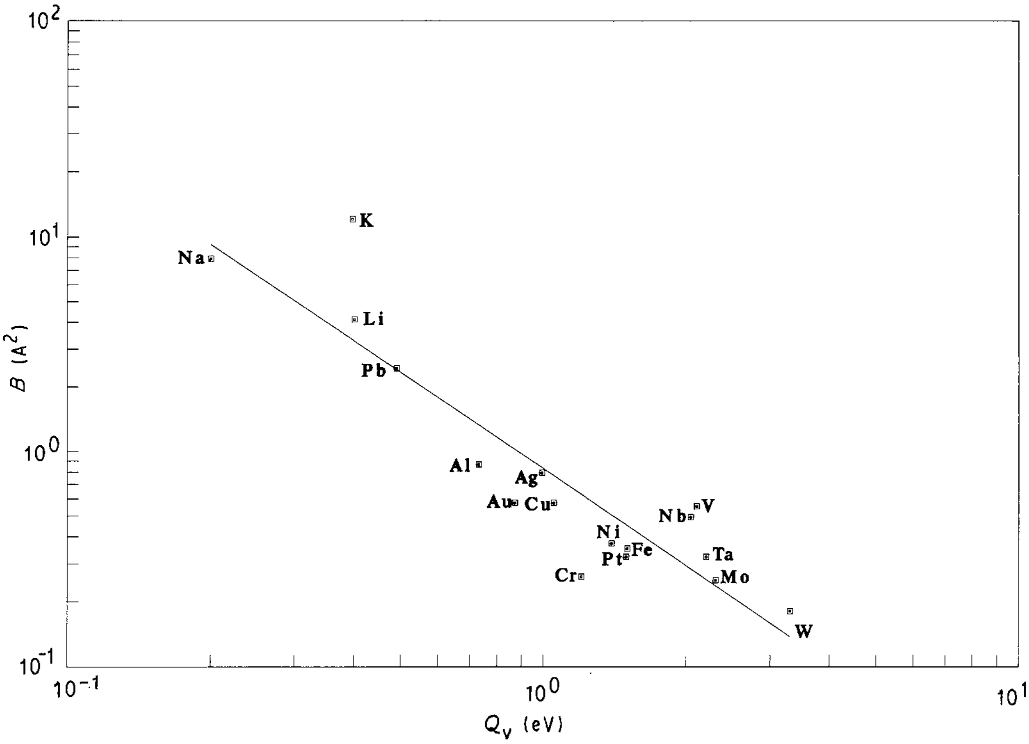

Figure 16 B versus monovacancy formation energy, Q_v. (——) Best fit described by the equation ln (B) = − 0.25–1.53 ln Q_v, (□) Observed.

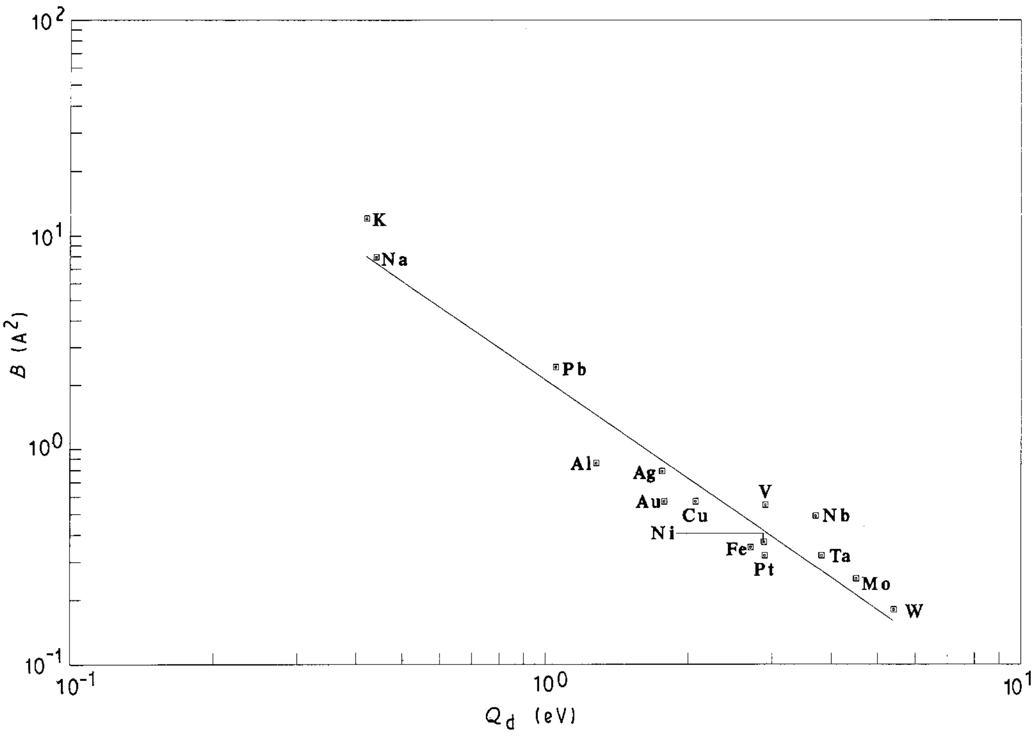

Figure 17 B versus activation energy for self diffusion, Q_d. (——) Best fit described by the equation ln B = 0.75–1.53 ln Q_d, (□) Observed.

fact that the number of bonds broken in the formation of a vacancy and the energy associated with their distortion at any point, are dependent on the crystal structure. Therefore, the nature of the bonding has a profound influence on the diffusion characteristics.

2.5. Correlation of B with the Periodic Table

The B factors of the cubic elements reveal some interesting trends when viewed in relation to the Periodic Table. The adjacent triads of vanadium, niobium and tantalum, chromium, molybdenum and tungsten, adopt the bcc type structure. The temperature factors decrease on descending the two groups, reflecting the increasing melting points and masses, but the origin of the reduction on passing from Group V to VI, e.g. vanadium to chromium is not clear. By contrast, the fcc triads of niobium, palladium and platinum, and copper, silver and gold, show a different, albeit internally consistent, trend which merits further scrutiny.

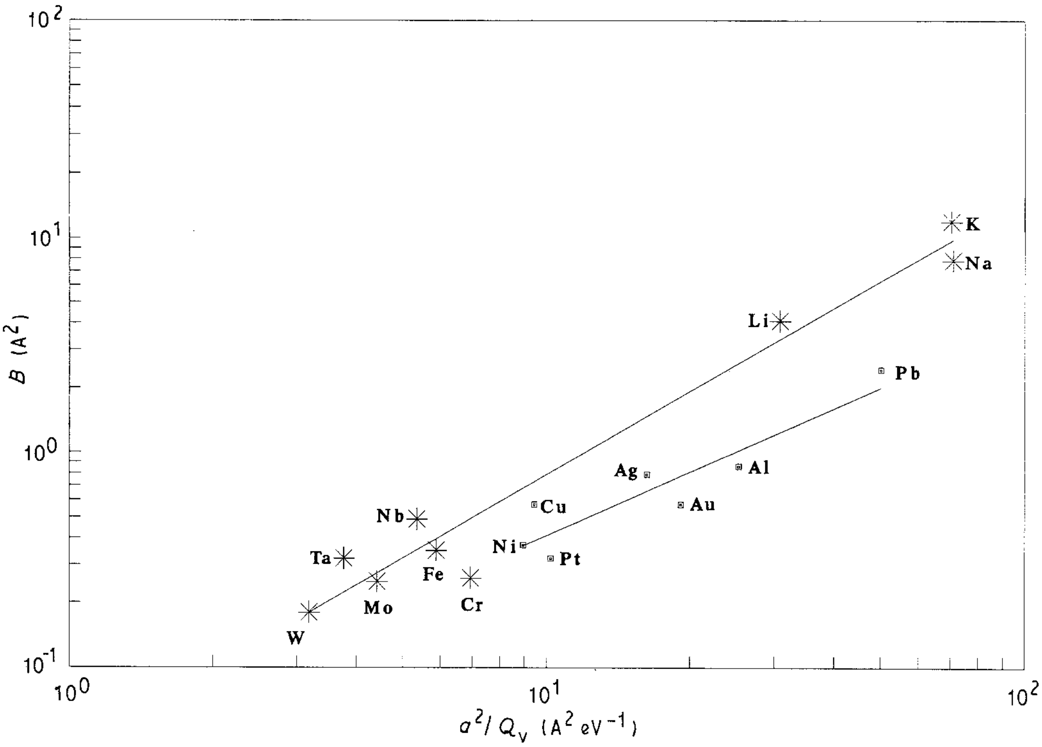

Figure 18 B versus a^2/Q_v. (——) Best fit to the experimental data which are described by the linear equation $B = C(a^2/Q_v)$. The values of the constants are − 3.15 and − 2.71 for (⊡) f c c and (∗) b c c metals, respectively.

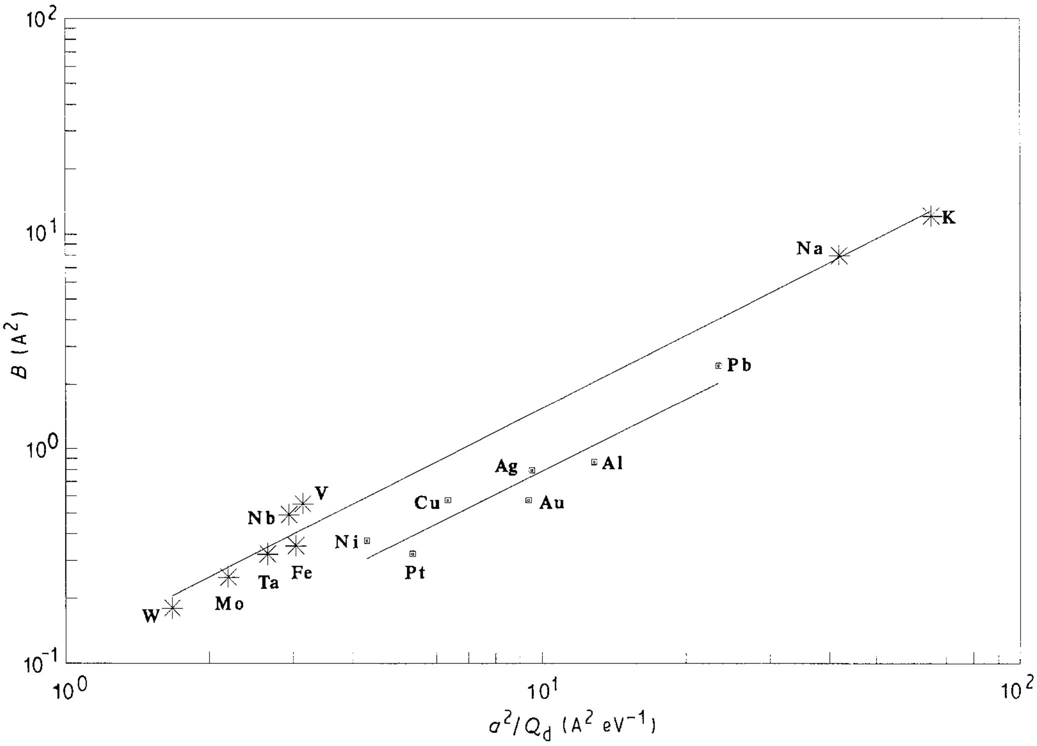

Figure 19 B versus a^2/Q_d. (——) Best fit to the experimental data. The values of the constants are − 2.81 and − 2.15 for the (⊡) f c c and (∗) b c c metals, respectively.

The B factor of iridium is notable, being larger than that of rhodium; this may stem from the fact that only one determination has been reported for each of these elements. The most striking anomaly in the list, however, is lead with a value that is substantially larger than that of any of the other elements in the fifth period. There can be little doubt that the value is incorrect, because all the determinations are in good accord and the Debye temperature (84 K) is in line with values obtained by other authors. One possibility is that the high value is related to the anomalously larger interatomic separation in metallic lead, but the

TABLE I Values of constants C, and slopes, S, as obtained from the least square fit to the plots of Debye–Waller parameter versus mechanical parameter. These plots are described by straight lines $\ln B = \ln C + S \ln P$, where P is the respective mechanical parameter

Mechanical parameter	Slope, S	Y intercept, $\ln C$	Linear correlation coefficient
Young's modulus, Y	– 0.84(4)	– 0.41(6)	– 0.97
Compressiblity, $\varkappa$	0.87(4)	– 2.34(11)	0.98
C_{11}	– 0.89(7)	1.77(11)	– 0.98
C_{12}	– 0.89(8)	1.51(19)	– 0.94
C_{44}	– 0.89(9)	0.99(14)	– 0.95
Hardness, H	– 0.48(6)	1.24(23)	– 0.91

question is open for investigation. It is not surprising, however, that lead appears to be out of line with some of the correlation plots.

3. Conclusion

The correlation of Debye–Waller parameter, B, with the physical properties of materials has been found to be systematic in the properties described above. These results reveal an important aspect, that the microscopic properties, such as the B factor, can furnish information on the macroscopic or bulk properties of these materials. This connection between the micro and macro aspects of materials sets new trends in the interpretation of behaviour of the materials.

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References

1. R. W. JAMES, in "Optical Principal of X-ray Diffraction" (Bell, London, 1967) p. 220.
2. B. E. WARREN, in "X-ray diffraction" (Addison Wesley, MA, 1969) p. 151.
3. B. T. M. WILLIS and A. PRYOR, in "Thermal Vibrations in Crystallography" (Cambridge University Press, 1975).
4. F. A. LINDEMANN, *Physik. Z.* **11** (1910) 609.
5. S. S. MITRA and P. K. JOSHI, *Physica* **26** (1960) 284.
6. K. MUKHERJEE, *Phil. Mag.* **12** (1965) 915.
7. H. R. GLYDE, *J. Phys. Chem. Solids* **28** (1967) 2061.
8. V. K. TEWARY, *J. Phys. F Metal Phys.* **3** (1973) 704.
9. G. GRIMVALL and S. SJODIN, *Phys. Scripta* **10** (1974) 340.
10. S. A. CHO and M. PUERTA, *High Temp. Sci.* **9** (1977) 223.
11. S. A. CHO, *Phys. Status Solidi.* **B94** (1979) K123.
12. A. G. KONYAEVA, *Russ. J. Phys. Chem.* **58** (1984) 1243.
13. N. M. BUTT, J. BASHIR, B. T. M. WILLIS and G. HEGER, *Acta Crystallogr.* **A44** (1988) 396.
14. K. A. GSCHNEIDNER, in "Solid State Physics", Vol. 16, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1964) p. 275.
15. C. S. BARRETT and T. B. MASSALSKI, in "Structure of Metals" (McGraw-Hill, New York, 1980) p. 275.
16. T. CARNELLEY, *Ber. Dtsch. Chem. Ges.* **12** (1879) 439.
17. Z. G. SZABO and B. LAKATOS, *Naturwiss.* **39** (1952) 486.
18. R. C. G. KILLEAN and E. J. LISHER, *J. Phys. C Sol. Stat. Phys.* **8** (1975) 3510.
19. S. I. BEN-ABRAHAM, A. RABINOVITCH and J. PELLEG, *Phys. Status. Solidi* **B84** (1977) 435.
20. L. G. VAN UITERT, *J. Appl. Phys.* **50** (1979) 8052.
21. *Idem, J. Amer. Ceram. Soc.* **64** (1981) 544.
22. *Idem, J. Appl. Phys.* **52** (1981a) 5553.
23. *Idem, ibid.* **52** (1981b) 3738.
24. S. A. CHO, *J. Phys. F Met. Phys.* **12** (1982) 1069.
25. R. I. M. H. RASHID and N. H. MARCH, *Phys. Chem. Liq.* **19** (1989) 41.
26. A. P. UBBELOHDE, in "Molten State of Matter" (Wiley, New York, 1978) p. 3.
27. N. W. ASHCROFT and N. D. MERMIN, in "Solid State Physics" (Holt, Rienhart and Winston, New York, 1976) p. 1.
28. R. E. HANNEMAN and H. C. GATOS, *J. Appl. Phys.* **36** (1965) 1794.
29. J. N. PLENDL, *Phys. Status Solidi* **B57** (1973) 187.
30. T. W. RICHARDS, *J. Amer. Chem. Soc.* **37** (1915) 1643.
31. J. C. SLATER, *Phys. Rev.* **23** (1924) 488.
32. C. P. KEMPTER, *Phys. Status Solidi* **8** (1965) 161.
33. R. E. NEWNHAM, in "Structure Property Relations" (Springer, Berlin 1975) p. 174.
34. K. MUKHERJEE, *Phys. Lett.* **8** (1964) 17.
35. A. BUCH, *J. Inst. Metals* **94** (1965) 424.
36. A. E. BRANDES, in "Smithell's Metal Reference Book, 6th Edn (Butterworths, London, 1983) pp. 5–15.
37. T. GORECKI, *Z. Metallkde* **65** (1974) 426.
38. O. D. SHERBY and T. M. SIMNAD, *Trans. ASM* **54** (1961) 227.
39. G. P. TIWARI and R. V. PATIL, *Trans. J. Inst. Metals* **17** (1976) 476.
40. J. ASKILL, *Phys. Status Solidi.* **11** (1965) K49.
41. C. L. REYNOLDS and P. R. COUCHMAN, *Phys. Lett.* **50A** (1974) 157.
42. C. L. REYNOLDS, *Phil. Mag.* **31** (1975) 1223.
43. P. R. COUCHMAN, *Phys. Lett.* **54A** (1975) 309.
44. M. DOYAMA and J. S. KOEHLER, *Acta Metall.* **24** (1976) 871.
45. R. W. SIEGEL, in "Point Defects and Defects Interactions in Metals", edited by Jin-khi Takamura (North-Holland, Amsterdam, 1982) p. 544.
46. J. NIHOUL, in "Vacancies and Interstitials in Metals", edited by A. Seeger (North-Holland, Amsterdam, 1970) p. 841.
47. J. S. KOEHLER, in "Vacancies and Interstitials in Metals", edited by A. Seeger, North-Holland, Amsterdam, 1970) p. 175.
48. Ya. A. KRAFTMAKHER and P. G. STRELKOV, *ibid.* p. 63.

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