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# Calculation of the β-Factors for bcc Metals

A. V. Bochkarev

Moscow Timiryazev Agriculture Academy, Timiryazevskaya ul. 47, Moscow, 127550 Russia
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Abstract—To evaluate the attainable accuracy of determination of the equilibrium isotopic effect for solids, the values of the β-factors were calculated for bcc metals (alkaline metals, V, Nb, Ta, Cr, α-Fe, Mo, W). The calculation was conducted by the direct integration over the first Brillouin band with the use of the force constants of the Born–van Karman model. The results are compared to those obtained previously by the simple cluster technique and by a method based on the thermal capacity of a crystal. The calculation results for lnβ by the two methods are in agreement despite the fact that the cluster method cannot reproduce the phonon spectrum of the crystal. Based on these facts it was concluded that the isotopic effect in metal crystals is localized, as in molecules, and cannot be used to study the phonon spectrum of the crystal and related characteristics. On the other hand, it was demonstrated, that the cluster approach can be successfully used in calculations on the equilibrium isotopic effect, particularly for crystals with defects, amorphous solids, and surfaces. The relative attainable accuracy of calculation of lnβ for metal crystals was determined to be 10–15%. Comparison of the lnβ values for the crystals and corresponding diatomic molecules made it possible to find a correlation between these values only within classes of compounds of similar chemical nature.

According to the theory of isotope equilibrium, for the reaction of isotope exchange between substances AX and BX
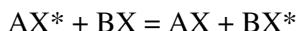
$$AX^* + BX = AX + BX^*$$

(X* designates the heavy isotope of the element X) the factor of the isotope separation $\alpha_{X^*/X}$ is calculated by

$$\ln\alpha_{X^*/X} = \ln\beta_{AX^*/AX} - \ln\beta_{BX^*/BX}, \quad (1)$$

where $\beta_{AX^*/AX}$ is the so-called β-factor, which is usually calculated in harmonic approximation by the Urey formula [1, 2]:

$$\ln\beta = \frac{1}{l}\sum_{i=1}^{N} \ln\{[\sinh(u_i/2)/u_i]/[\sinh(u_i^*/2)/u_i^*]\}. \quad (2)$$

Here, l is the number of isotopically substituted equivalent atoms, N is the number of vibrational degrees of freedom of substance AX, $u_i = hc\nu_i/kT$ are dimensionless normalized frequencies, h is the Plank constant, k is the Boltzmann constant, c is the speed of light, T is the absolute temperature, and ν_i is the frequency (cm^{-1}) of the ith vibration. The sign X* designates the quantities corresponding to the heavy isotope. The factor β is a thermodynamic value and equals to the equilibrium constant of the exchange reaction between substance AX and hypothetical monoatomic ideal gas consisting of isotope X*.

In contrast to ionic crystals, for which the β-factor is calculated with consideration for only close neighbors [3], the interatomic interaction in metal crystals is essentially noncentral and long-range. Therefore, the models of force field treating only the interactions near-est-neighbor and next-to-nearest-neighbor are assumed to be totally inapplicable to metals. At first glance, this opinion seems to contradict to the well-established fact for molecules that the equilibrium isotopic effect (the value of the β-factor) depends only on nearest-neighbor interaction and (to a lesser extent) on next-to-nearest neighbor interactions of substituted atoms [4]. The purpose of this paper is to elucidate whether isotope substitution in metals is a localized perturbation (as in all molecules) or metal crystals constitute a special case from this viewpoint. Earlier [5], we calculated the lnβ values for metals with the bcc lattice using the simplest cluster approach. Here, we calculated lnβ for these metals by direct integration over the first Brillouin band with the use of the most accurate force fields. The comparison of the results obtained by these two methods and also by a new method of calculation of lnβ, introduced by Polyakov [6], makes it possible to evaluate the accuracy of the modern calculation techniques.

Note, that the calculation of the β-factor for metal crystals is of interest in its own right—these values are necessary to predict attainable separation factors for a optimally chosen chemiexchange systems for the separation of the isotopes of a given element [7].

CALCULATION OF β FACTORS OF METAL CRYSTALS

Calculation of lnβ for metals can be generally performed by the following methods: (i) the cluster technique described in [5]; (ii) direct integration of $\ln\beta(\theta_1, \theta_2, \theta_3)$ over the first Brillouin band; (iii) indirect methods, primarily the Polyakov technique mentioned above.

Cluster method. The essence of the method is to calculate the vibrational frequencies for the clusters constituting the lattice. The well-known method of *GF* matrices, which was developed to calculate the parameters of molecular vibrations [8], was used. The cluster method is based on the notion of local character of the isotopic effect, as discussed above. Although interactions in metal crystals are characterized by a long range, we must bear in mind that we implicitly take into account these interactions by assuming that the force field and geometry of a cluster is identical to those of the indefinite crystal and that the purpose of this work is to determine the value of isotopic effect, and not the precise phonon spectrum. Note that the cluster method does not use the symmetry and, therefore, can be used to calculate the properties of imperfect crystals.

The main features of a cluster calculation of $\ln\beta$ performed in [5] are as follows. Fragments of the lattice formed by 1, 9, 15, 27, and 51 atom were considered (the "cluster" formed by one atom is a three-dimensional harmonic oscillator, with the force constants being the same as in other clusters). The simplest force field is described by three parameters: the interaction constant for nearest neighbors f_R, the interaction constant for next-to-nearest neighbors, and the nondiagonal constant f_{RR}. These values, in turn, were determined from the crystal elasticity constants C_{11}, C_{12}, and C_{44} without invoking any additional information. For initial clusters and clusters in which the central atom is substituted by the isotope, the *GF* matrices were constructed and the corresponding vibrational frequencies determined; then the value of $\ln\beta$ was calculated by the Urey formula (2).

For most metals considered in [5], the use of the simplest cluster (three-dimensional harmonic oscillator, $n = 1$) gives a result coinciding with the results obtained for clusters of larger size. This does not mean that interatomic forces in metal crystals have a short range: the force constants calculated in the normal-mode coordinates (used in our calculations) effectively incorporate long-range interactions as in calculations of molecular vibrations. This feature is a general property of force constants calculated in the normal-mode coordinates. Note that force constants calculated in the Cartesian coordinates, as in the Born–van Karman model, exhibit no such property.

Calculation by direct integration. Each elementary cell of a bcc lattice contains one atom. Thus, every atom can be determined by its elementary cell, i.e., the radius vector $\mathbf{r}_n = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$, where n_1, n_2, and n_3 are integer numbers, and $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are the fundamental translation vectors.

Calculation of $\ln\beta$ was performed by the formula

$$\ln\beta = -\iiint\limits_V \sum_{i=1}^{3} \ln\left\{ \frac{\sinh[u_i^*(\mathbf{k})/2]}{\sinh[u_i(\mathbf{k})/2]} \left[\frac{u_i(\mathbf{k})}{u_i^*(\mathbf{k})}\right] \right\} dV, \quad (3)$$

where V is the first Brillouin band. Here, $u_i(\mathbf{k}) = hc\nu_i(\mathbf{k})/kT$ are normalized frequencies and $\nu_i(\mathbf{k})$ are the vibrational frequencies (cm^{-1}) corresponding to the wavevector $\mathbf{k}$.

The literature data on the force constants of the Born–van Karman model [9] were used. For a given wavevector $\mathbf{k}$, the vibrational frequencies are eigenvalues of the symmetrical a 3×3 matrix; the formulas for the matrix elements as functions of the wavevector components are given in [10]. The triple integral (3) was computed by the recursive call of the integration procedure described in [11]. The results of the calculations together with results of the cluster calculations [5] and the values of $\ln\beta$ for the corresponding diatomic molecule are listed in the table. The force constants for Li are given in the literature at 98 and 293 K; we calculated $\ln\beta$ at all temperatures using both sets of constants and then evaluated $\ln\beta$ by a linear interpolation of the results obtained. A similar procedure was applied to Rb (the force constants are available in the literature for 12, 85, 120, and 205 K). For other metals, the sets of the force constants are available in the literature only for single temperature

Me	Na	K	V, Nb, Ta	Cr	Mo	W	Fe
T, K	90	9	296	300	296	298	295

For V, Nb, and Mo, two sets of the force constants determined at the same temperature are given; the average $\ln\beta$ values calculated with both sets are given in the table. For Cs and Ba, the literature data are absent. The listed values of the force constants and $\ln\beta$ for the diatomic molecules were calculated in harmonic approximation by the Urey formula with the use of experimental frequencies ν; these frequencies, in turn, were calculated from ω_e, $\omega_e x_e$ and higher-order constants of anharmonicity given in [12].

The Polyakov procedure. This procedure is described in details in [6, 13]. It is used to calculate the β-factors of minerals at moderate and high temperature in geochemical studies and normally yields excellent results for diamond and graphite. In this method, $\ln\beta$ is expressed through the difference of the vibrational energies of the crystal in terms of thermodynamic perturbation theory. The subsequent differentiation with respect to the temperature with the use of analytical expansions makes it possible to represent $\ln\beta$ as a function of the thermal capacity; therefore, the temperature dependence of $\ln\beta$ can be determined from the experimental data on the temperature dependence of the thermal capacity of the crystal. The coefficients of the thermal dependence of $\ln\beta$ are determined by solving an overdetermined system of linear equations, for example, by the least-squares method with a singular transformation of the mapping matrix [11], a procedure that makes it possible to evaluate the accuracy of the result obtained. To evaluate the effectiveness of this method, we calculated $\ln\beta$ for the metals listed in table using the data on the thermal capacity from [14].

Values of lnβ for bcc metals and for corresponding diatomic molecules (a is the lattice constant, F is the force constant of the diatomic molecule, mdyne/Å)

T, K	I	II	III	I	II	III
	^{6}Li/^{7}Li, $a = 3.51$ Å, $F(\text{Li}_2) = 0.247$			^{23}Na/^{24}Na, $a = 4.2906$ Å, $F(\text{Na}_2) = 0.168357$		
50	0.45242	0.48014	0.1479	0.03305	0.03086	0.013779
100	0.14783	0.16265	0.0576	0.00877	0.00842	0.004136
150	0.06917	0.07816	0.03	0.00382	0.00381	0.001918
200	0.03884	0.04487	0.0181	0.00207	0.00216	0.001096
250	0.02459	0.02871	0.012	0.0013	0.00139	0.000706
300	0.01677	0.01976	0.0085	0.00086	0.00096	0.000493
350		0.01432	0.0063	0.0006	0.00071	0.000363
400		0.01079	0.0049	0.00043	0.00054	0.000278
	^{39}K/^{41}K, $a = 5.32$ Å, $F(\text{K}_2) = 0.097$			^{85}Rb/^{87}Rb, $a = 5.7$ Å, $F(\text{Rb}_2) = 0.082$		
50	0.01442	0.01452	0.006408	0.00273	0.00272	0.0054
100	0.00362	0.00377	0.001729	0.00065	0.00067	0.0014
150	0.00155	0.00169	0.00078	0.00027	0.00029	0.0006
200	0.00083	0.00095	0.000441	0.00014	0.00015	0.0004
250	0.00051	0.00061	0.000283		9.20E-05	0.0002
300	0.00034	0.00042	0.000197		6.00E-05	0.0002
350	0.00023	0.00031	0.000145		4.10E-05	0.0001
400		0.00024	0.000111		2.90E-05	9E-05
	^{50}V/^{51}V, $a = 3.024$ Å, $F(\text{V}_2) = 1.585072$			^{93}Nb/^{95}Nb, $a = 3.2986$ Å		
50	0.05929	0.04939	0.0183	0.04293	0.0376	–
100	0.01971	0.01583	0.0069	0.01321	0.0114	–
150	0.00946	0.00751	0.0035	0.00615	0.00531	–
200	0.00547	0.00433	0.0021	0.00351	0.00304	–
250	0.00354	0.00281	0.0014	0.00226	0.00196	–
300	0.00246	0.00196	0.001	0.00158	0.00137	–
350		0.00145	0.0007	0.00116	0.00101	–
400		0.00111	0.0006	0.00088	0.00077	–
	^{180}Ta/^{181}Ta, $a = 3.3029$ Å			^{52}Cr/^{53}Cr, $a = 2.885$ Å, $F(\text{Cr}_2) = 2.448$		
50	0.0084	0.00703	–	0.07322	0.07092	0.022229
100	0.00247	0.00202	–	0.02557	0.02461	0.008834
150	0.00114	0.00093	–	0.01253	0.01205	0.004662
200	0.00065	0.00053	–	0.00732	0.00705	0.002833
250	0.00041	0.00034	–	0.00466	0.0046	0.001887
300	0.00029	0.00024	–	0.00309	0.00323	0.001341
350	0.00021	0.00017	–	0.00237	0.00239	0.001
400	0.00016	0.00013	–		0.00184	0.000773
	^{92}Mo/^{98}Mo, $a = 3.147$ Å			^{184}W/^{186}W, $a = 3.1652$ Å		
50	0.19879	0.17753	–	0.02453	0.02236	–
100	0.06673	0.05804	–	0.00771	0.00689	–
150	0.03222	0.02774	–	0.00363	0.00323	–
200	0.01869	0.01605	–	0.00208	0.00185	–
250	0.01211	0.01042	–	0.00134	0.0012	–
300	0.00845	0.00729	–	0.00093	0.00083	–
350	0.00622	0.00538	–	0.00069	0.00061	–
400	0.00476	0.00413	–	0.00053	0.00047	–
	α-^{54}Fe/^{56}Fe, $a = 2.8662$ Å, $F(\text{Fe}_2) = 1.013387$					
50	0.12385	0.12015	0.023735			
100	0.04253	0.04097	0.008198			
150	0.02072	0.01994	0.003995			
200	0.01206	0.01164	0.002331			
250	0.00782	0.00758	0.001519			
300	0.00555	0.00532	0.001065			
350	0.00407	0.00393	0.000787			
400	0.00309	0.00302	0.000605			

Note: I is the cluster model calculation, II is the result direct integration, III is the value for the diatomic molecule.

DISCUSSION

As it can be seen from the table, there is generally good agreement between results obtained by the cluster method and direct integration. For alkaline metals, the error of calculation is commensurate with the experimental error in the separation factor for chemiexchange systems [15] (except for the paper [16], where the accuracy in determination of the separation coefficient for the lithium isotopes was about 3%); Note, however, that, for exchange in solids, the possibility of establishment of a real equilibrium with the internal phase of the crystal is problematie.

A good agreement is observed also for Cr, Mo, W, and α-Fe. Taking into account the long range of interatomic interactions in the crystals, this result can be regarded as evidence of the suitability of the cluster approach. It can be also regarded as supporting the assumption about the local character of isotopic effect in crystals, similar to molecular isotopic effect. This does not mean that the interatomic forces in crystals are of a short-range nature: it means only that the isotopic effect can be evaluated using the description of the total effect of long-range forces by a molecularlike effective local force field in the normal-mode coordinates.

It is necessary to note, that while giving reasonable lnβ values, the cluster approach cannot reproduce the total phonon spectrum and the corresponding thermodynamic properties, for example thermal capacity. This effect is related to an important feature of the β-factor: in contrast to the other thermodynamic quantities, the β-factor is primarily determined by the high-frequency part of the spectrum and is almost independent of the low-frequency part, which is effectively cancelled out in calculation of lnβ. It is evident that the equilibrium isotopic effect is an effective tool for studying local bonding in crystals: its value is determined only by the nearest neighbors of the isotope atoms in the lattice. The equilibrium isotope effect can not be applied to studying the total phonon spectrum of the crystal.

For the metals of subgroup Vb (V and Ta), the error of calculation is significantly higher. However, the agreement with experiment may also be regarded as satisfactory in view of considerable anomalities in their phonon spectrum [17]. As a result, to describe this spectra by the Born–van Karman model, it is necessary to introduce force constants of very high orders, a procedure that leads to a decrease in the accuracy of their determination [18]. Thus, the quality of the force field in the Born–van Karman model for these metals, especially vanadiun, is poor: in the original work [19], the agreement between the experimental and calculated curves of phonon dispersion is poor, with the highest discrepancy being observed at high frequencies, which primarily determine the isotopic effect value.

As to the accuracy of the calculated lnβ value in general, presently this accuracy is as high as 10–15%, a value that is commensurate with the experimental accuracy of the separation coefficient for solids.

The results of calculations by the Polyakov method exceed the results given in the table by more than an order of magnitude; therefore, we did not present them. It is evident, that this method is unsuitable for calculating or even estimating the β-factor for metals. This is not surprising, because the initial data in this method are the data on the thermal capacity which are not informative at high temperatures, because metal lattices are characterized by low vibrational frequencies; as a result, at the temperatures above 300 K, all these vibrations are already excited, and the molar thermal capacity of all metals is eventually constant. Quantum effects appear to affect the thermal capacity at low temperatures; here, however, the Polyakov method cannot be used for another reason—it is based on a rapid convergence of the expansion of thermodynamic perturbation theory, a condition that is violated in the low-temperature range. Meanwhile this method may be used to estimate the β-factors of hydrides and other simple salts characterized by high frequencies. We think that the main advantage of the Polyakov method is its capability of estimating the value of the β-factor without using the data on the frequencies of lattice vibrations; the question of its applicability can easily be solved based on the temperature behavior of the thermal capacity.

It is also interesting to examine the relationship between the values of lnβ for a crystal and the corresponding diatomic molecule. The table shows that generally there is no correlation. For all the alkaline metals, the values of lnβ for the crystal exceed those for the diatomic molecule by a factor of 2–3. For other metals listed in the table, which are *d* elements, it is impossible to establish any correlation, because these *d* elements correspond to different subgroups, with the number of valence electrons and their distribution over orbitals (bands) both for crystals and molecules being different.

CONCLUSIONS

The fact that the simplest cluster approach to calculation of lnβ gives values similar to those obtained by the Born–van Karman model suggests a local character of the isotopic effect for all systems, including solids, and allows us to recommend the local-field methods of calculation of the β-factor. It may be very useful for many real systems, because the cluster and similar approaches can be easily applied to calculation of the properties highly imperfect crystals, amorphous and other solids with out long-range ordering. In addition, this approach (in contrast to the Born–van Karman approach) may be used to calculate isotopic effects for surface exchange, which are very important in studying solid–solution equilibria in systems of practical interest.

It may be assumed, that, although the correlation between the β-factors for crystals and corresponding diatomic molecule is generally absent, it may be observed in the series of similar compounds, but this question needs further investigation.

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