their direct-space calculations.

The method of calculating the formation volumes in the direct-space approach differs from that outlined in the present paper, so that one cannot, in this case, construe the differences in the activation-volume results as being due to the shortcomings of the direct-space technique pointed out earlier.[3,4] However, Hardy[5] has pointed out that current elasticity-theory methods of obtaining the volume changes induced by a defect are generally unreliable. The discrepancies in the activation volume found here, along with the corresponding differences in migration energies found in Ref. 6, cast a certain amount of doubt on the parameters of the carbon-iron interaction developed in Ref. 8 by direct-space technique.

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Lattice Thermal Conductivity of Solids

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Reformulation of the lattice thermal conductivity of solids has been given, using the fact that the three-phonon umklapp processes can be divided into different classes depending on the reciprocal-lattice vectors of the crystal concerned, and that they tend towards displaced distribution functions characteristic of their own. The expression obtained differs from that of Callaway by terms which are expected to be of minor importance in real systems.

I. INTRODUCTION

In the past, most of the calculations of the lattice thermal conductivity of crystals have been made by using the Boltzmann transport equation for phonons.[1-3] In its linearized form, this equation can be written as

$$\vec{v}\cdot\vec{\nabla}T\,\frac{dN}{dT}=\left(\frac{\partial N}{\partial t}\right)_{\text{scatt}}, \qquad (1)$$

where $N=N(\vec{q}j)$ is the phonon occupation number corresponding to state $\vec{q}j$ in the crystal under study and $\vec{v}=\vec{v}(\vec{q}j)$ is the phonon group velocity, $\vec{q}$ and j being the phonon wave vector in the reduced-zone scheme and the polarization index, respectively. The term $\vec{\nabla}T$ is the steady-state thermal gradient.

To calculate the lattice thermal conductivity, one has to solve Eq. (1) for N. Usually, it is assumed that N differs only slightly from the corresponding Planck distribution N^0, characteristic of the temperature of the system. This assumption can be taken to be valid at least for vanishingly small thermal gradient. One can therefore replace N by N^0 on the left-hand side of Eq. (1), obtaining

$$\frac{dN}{dT}=\frac{x}{T}\,\frac{e^x}{(e^x-1)^2}, \qquad (2)$$

where $x=\omega\hbar/kT$, $\omega=\omega(\vec{q}j)$ being the phonon frequency and k being the Boltzmann constant.

The term $(\partial N/\partial t)_{\text{scatt}}$ on the right-hand side of Eq. (1) describes the rate of increase of N as a result of the various scattering processes taking place in the crystal. If the scattering events do not interfere, then it is possible to write this term equal to the sum of the individual contributions $(\partial N/\partial t)_i$ of the different types of scattering processes, where i specifies the type of process. (By interference we mean that there exists no scattering event which belongs to two different types of scattering processes.) Since $(\partial N/\partial t)_i$ has a very complicated form even for highly simplified systems, the relaxation-time approach is often used. The relaxation time gives a statistical description of how the scattering processes of a given type tend to modify the phonon occupation number. Formally, the relaxation time τ_i is defined by

$$\left(\frac{\partial N}{\partial t}\right)_i = \frac{N_i - N}{\tau_i}, \tag{3}$$

where N_i is a function towards which the i-type processes tend.

The structure of N_i is decided by the conservation laws the scattering processes obey. For example, since scattering by point defects, etc., does not place any conservation condition on the phonon wave vector, these processes are expected to tend towards the Planck distribution. Recently, the present authors have shown in a paper[4] (hereafter referred to as I) that the three-phonon umklapp processes can be divided into different classes characterized by the reciprocal-lattice vectors of the crystal. The three-phonon umklapp processes which involve the reciprocal-lattice vector $\vec{g}$ tend toward $N(\vec{g})$, given by

$$N(\vec{g}) = \{\exp[\omega\hbar/kT + \vec{\lambda}(\vec{g})\cdot(\vec{q}-\vec{g})] - 1\}^{-1}, \tag{4}$$

$\vec{\lambda}(\vec{g})$ being a constant vector to be determined by the applied thermal gradient. These processes will be called $u(\vec{g})$ processes. In I, it has been established that since none of the three-phonon scattering events corresponds to two different reciprocal-lattice vectors, such a classification is always possible. In the above type of description, the normal processes are those for which $\vec{g}$ equals a null vector. In the following, we calculate the lattice thermal conductivity when the contribution to $(\partial N/\partial t)_{\text{scatt}}$ of different $u(\vec{g})$ processes are separately considered.

II. FORMULATION

Let us define $\tau(\vec{g})$ to be the phonon relaxation time corresponding to the $u(\vec{g})$ processes, so that the contribution $(\partial N/\partial t)_{\vec{g}}$ to $(\partial N/\partial t)_{\text{scatt}}$ of these processes can be given by

$$\left(\frac{\partial N}{\partial t}\right)_{\vec{g}} = \frac{N(\vec{g}) - N}{\tau(\vec{g})}. \tag{5}$$

[$\tau(\vec{g})$ is, of course, a function of the phonon state.] Accordingly, Eq. (1) can be written as

$$\vec{v}\cdot\vec{\nabla}T\,\frac{x}{T}\,\frac{e^x}{(e^x-1)^2} = \frac{N^0 - N}{\tau_u} + \sum_{\vec{g}} \frac{N(\vec{g}) - N}{\tau(\vec{g})}, \tag{6}$$

where the first term on the right-hand side takes account of the contributions of all those processes which tend towards the Planck distribution. (We include in this class the scattering by all types of defects and by the crystal boundary.) The contribution of each of these processes to the right-hand side of Eq. (6) is given by $(N^0 - N)$ divided by the corresponding relaxation time. The total contribution of all these processes is, therefore, given by $(N^0 - N)$ divided by τ_u, where τ_u^{-1} is defined as the sum of the individual inverse relaxation times. Here $\vec{g}$ runs over all permissible values of the reciprocal-lattice vectors, including the null vector (normal processes); remember that since $\vec{q}$ is confined to the first Brillouin zone, $\vec{g}$ takes only a limited number of values. All the τ's in Eq. (6) are functions of $\vec{q}j$.

To zeroth order in the thermal gradient $\vec{\nabla}T$, the constant vector $\vec{\lambda}(\vec{g})$ should vanish. In first-order approximation, however, $\vec{\lambda}(\vec{g})$ is not necessarily along $\vec{\nabla}T$. Therefore, the constant relating these two terms should be a tensor $\alpha_{ss'}(\vec{g})$, which we define by the relation

$$T\lambda_s(\vec{g}) = \sum_{s'} \alpha_{ss'}(\vec{g})\,\nabla T_{s'}, \tag{7}$$

where the index s specifies the sth component of a vector in the coordinate space. We now write

$$N(\vec{g}) = N^0 - \vec{\lambda}(\vec{g})\cdot(\vec{q}-\vec{g})\,e^x/(e^x-1)^2. \tag{8}$$

Here we have assumed that this approximate expansion for $N(\vec{g})$ [retaining the term linear in $\vec{\lambda}(\vec{g})$] holds for all phonons.[5] This may, perhaps, appear to be not justified, particularly for very small values of the phonon frequency. Although we can satisfy ourselves by assuming that Eq. (8) holds for all phonons that contribute significantly to the heat transport, it would still be desirable to justify this in a convincing way.

By substituting Eq. (6) in Eq. (5), we can easily obtain

$$n = -\frac{\tau v}{T}\,\frac{xe^x}{(e^x-1)^2}\left(\hat{q}\cdot\vec{\nabla}T + \sum_{\vec{g}} \frac{T\vec{\lambda}(\vec{g})\cdot(\vec{q}-\vec{g})}{xv\tau(\vec{g})}\right), \tag{9}$$

where

$$n = N - N^0,$$

$$\tau^{-1} = \tau_u^{-1} + \textstyle\sum_{\vec{g}} \tau^{-1}(\vec{g}),$$

and $\vec{v}$ is assumed to be along $\hat{q}$—a unit vector along $\vec{q}$. Using Eq. (6), Eq. (7) can also be written as

$$n = -\frac{\tau v}{T}\,\frac{xe^x}{(e^x-1)^2} \times \sum_s \left[\hat{q}_s + \sum_{s'}\sum_{\vec{g}} \frac{(q_{s'} - g_{s'})\,\alpha_{s's}(\vec{g})}{xv\tau(\vec{g})}\right] \nabla T_s. \tag{10}$$

Now it is possible to write down an expression for the heat flux per unit area $\vec{Q}$ in the crystal:

$$\vec{Q} = \textstyle\sum_j (2\pi)^{-3} \int d\vec{q}\, n\omega\hbar\vec{v}, \tag{11}$$

where integration over the first Brillouin zone is implied. [In Eq. (11), we have not written explicitly the dependence of the integrand on j.] Equation (11) can also be written in the component form as

$$Q_s = -\sum_j \frac{k}{(2\pi)^3} \int d\vec{q}\,\hat{q}_s v^2 \tau\, \frac{x^2 e^x}{(e^x-1)^2}$$

$$\times \sum_{s'} \left(\hat{q}_{s'} + \sum_{s'} \sum_{\vec{\mathrm{g}}} \frac{(q_{s''} - g_{s''})\, \alpha_{s''s'}(\vec{\mathrm{g}})}{x v \tau(\vec{\mathrm{g}})} \right) \nabla T_{s'} . \quad (12)$$

Obviously, the conductivity tensor $K_{ss'}$ is given by

$$K_{ss'} = \sum_{j} \left[\frac{k}{(2\pi)^3} \int d\vec{\mathrm{q}}\, \hat{q}_s \hat{q}_{s'}\, v^2 \tau \, \frac{x^2 e^x}{(e^x - 1)^2} + \sum_{s''} \sum_{\vec{\mathrm{g}}} \frac{k \alpha_{s''s'}(\vec{\mathrm{g}})}{(2\pi)^3} \int d\vec{\mathrm{q}}\, \hat{q}_s (q_{s''} - g_{s''}) \times \frac{v\tau}{\tau(\vec{\mathrm{g}})} \frac{x e^x}{(e^x - 1)^2} \right] . \quad (13)$$

It has been shown in I that the $u(\vec{\mathrm{g}})$ processes conserve the quantity $\sum_{\vec{\mathrm{q}}\, j} (\vec{\mathrm{q}} - \vec{\mathrm{g}})$ just as the three-phonon normal processes conserve the total wave vector of the system. We have, therefore, the following condition which determines $\alpha(\vec{\mathrm{g}})$:

$$\sum_{j} \int d\vec{\mathrm{q}}\, (\vec{\mathrm{q}} - \vec{\mathrm{g}}) \left(\frac{\partial N}{\partial t} \right)_{\vec{\mathrm{g}}} = \vec{0} . \quad (14)$$

Using Eq. (8) and keeping in mind that $N = N^0 + n$, we can write

$$N - N(\vec{\mathrm{g}}) = n + \frac{1}{T} \frac{e^x}{(e^x - 1)^2} \sum_{ss'} (q_s - g_s)\, \alpha_{ss'}(\vec{\mathrm{g}})\, \nabla T_{s'} . \quad (15)$$

Equations (5), (10), and (15) can now be used to reduce Eq. (14) to the form

$$A_{ss'}(\vec{\mathrm{g}}) + \sum_{ss'} \sum_{\vec{\mathrm{g}}'} B_{ss''}(\vec{\mathrm{g}}, \vec{\mathrm{g}}')\, \alpha_{s''s'}(\vec{\mathrm{g}}') = 0, \quad (16)$$

where we have defined

$$A_{ss'}(g) = \sum_{j} \int d\vec{\mathrm{q}}\, (q_s - g_s)\, \hat{q}_{s'} \frac{\tau v}{\tau(\vec{\mathrm{g}})} \frac{x e^x}{(e^x - 1)^2} , \quad (17)$$

$$B^{(1)}_{ss'}(\vec{\mathrm{g}}, \vec{\mathrm{g}}') = \sum_{j} \int d\vec{\mathrm{q}}\, (q_s - g_s)(q_{s'} - g'_{s'}) \times \frac{\tau}{\tau(\vec{\mathrm{g}})\, \tau(\vec{\mathrm{g}}')} \frac{e^x}{(e^x - 1)^2} , \quad (18)$$

$$B^{(2)}_{ss'}(\vec{\mathrm{g}}, \vec{\mathrm{g}}') = \sum_{j} \delta_{\vec{\mathrm{g}}\vec{\mathrm{g}}'} \int d\vec{\mathrm{q}}\, (q_s - g_s)(q_{s'} - g_{s'}) \times \frac{1}{\tau(\vec{\mathrm{g}})} \frac{e^x}{(e^x - 1)^2} , \quad (19)$$

$$B_{ss'}(\vec{\mathrm{g}}, \vec{\mathrm{g}}') = B^{(1)}_{ss'}(\vec{\mathrm{g}}, \vec{\mathrm{g}}') - B^{(2)}_{ss'}(\vec{\mathrm{g}}, \vec{\mathrm{g}}'), \quad (20)$$

where $\delta_{\vec{\mathrm{g}}\vec{\mathrm{g}}'}$ is the Kronecker δ function. Equations of the form of Eq. (14), whose number is equal to nine times the number of the allowed values of the reciprocal-lattice vector (determined by the lattice structure of the crystal), can be solved in principle to obtain the tensor $\overleftrightarrow{\alpha}(\vec{\mathrm{g}})$. Substituting the value of $\alpha_{ss'}(\vec{\mathrm{g}})$ in Eq. (13), we get an expression for the conductivity-tensor element $K_{ss'}$.

III. DISCUSSION

We have calculated the lattice thermal conductivity in the tensor form. Equation (13) gives an expression for the tensor component $K_{ss'}$, which consists of two types of terms: Let us, for the time being, name the first term the "normal term" and the rest "special terms." It is interesting to compare the normal term with the thermal-conductivity expression for a classical (monoatomic) gas, which in its tensor form can be given by

$$K_{ss'} = \delta_{ss'} \tfrac{4}{3}\pi \int_0^\infty dv\, E \tau v^4 \frac{dn}{dT} , \quad (21)$$

where v is the velocity of the gas atoms, and E is the corresponding (translational) energy (equal to $\frac{1}{2}mv^2$). The term τ denotes the relaxation time, which is possibly a function of v, for the random collision of the atoms with one another. n represents the number of atoms per unit volume of the configuration and velocity spaces and can be given by

$$n = N (m / 2\pi k T)^{3/2}\, e^{-E/kT} , \quad (22)$$

m and N being the mass per atom and the number density of the atoms in the ordinary space, respectively. It is clearly seen that the normal term in Eq. (13) is essentially of the same form[6] as Eq. (21). [Equation (21) can be easily translated into an integral over the energy variable.] There are no terms in Eq. (21) analogous to the special terms in Eq. (13). This result can be interpreted to mean that the various scattering processes behave like random processes so far as the normal term is concerned. The special terms in Eq. (13), on the other hand, reflect the characteristic nature of the processes that they are not, in fact, random, but take place in accordance with certain conservation laws.

The above derivation is, in fact, a generalization of Callaway's formalism.[2] Callaway has taken account of the fact that the three-phonon normal processes behave differently from those processes which destroy the phonon wave vector.[4,7] (He has included the so-called three-phonon umklapp processes in the category of wave-vector destroying processes.) This distinction automatically and fruitfully results in an expression for the lattice thermal conductivity that consists of two terms, one of which is normal in the same sense as discussed above. The significance of the other term has been discussed by him and is well known: This term signifies the fact that the thermal conductivity becomes infinitely large when there are only normal processes.[8-10] This result can easily be obtained in the present case. Consider a system in which there are no processes other than the normal one, that is, τ_u and $\tau(\vec{\mathrm{g}})$ are infinitely large and $\tau(\vec{0})$ is finite. In this case, Eq. (14) is identically satisfied for all nonzero values of $\vec{g}$. Consequently, only those equations of the type of Eq. (16), for which $\vec{g}=\vec{g}'=\vec{0}$, survive. As can be easily seen from Eqs. (17)–(20), in this particular case the constants $A_{ss'}(\vec{0})$ are, in general, finite, whereas the constants $B_{ss'}(\vec{0})$ become zero, with the result that $\alpha_{ss'}(\vec{0})$ rises to infinitely large values, giving in its turn infinitely large values for the thermal conductivity through the special terms in Eq. (13).[2]

Alternatively, one can infer the above result directly from Eq. (6), which in the presence of only normal processes reads

$$\vec{v}\cdot\vec{\nabla}T\,\frac{x}{T}\,\frac{e^{x}}{(e^{x}-1)^{2}}=\frac{N(\vec{0})-N}{\tau(\vec{0})}\quad . \tag{23}$$

This equation permits a solution $N(\vec{0})$ of the form given by Eq. (4) for N, when $\vec{\nabla}T=\vec{0}$, since a distribution $N(\vec{0})$ can exist freely[11] in the presence of normal processes. This distribution, being anisotropic, corresponds to a heat flux. Thus, it is possible to conceive of a heat flux in the presence of normal processes when there is no thermal gradient. In fact, the normal processes can only redistribute phonons into different phonon states, but cannot destroy the anisotropy in the phonon distribution. Remember that the absence of the thermal gradient does not necessarily mean an isotropic phonon distribution; it merely implies that the distribution function has no spatial variation.[12]

In the present case, we start with the concept that the $u(\vec{g})$ processes behave more like the normal processes, rather than like other processes, in the sense that they also satisfy a definite type of wave-vector conditon. In fact, as discussed in I, the wave-vector condition in the case of $u(\vec{g})$ processes states that the total wave vector measured with respect to some appropriate origin (decided by the reciprocal-lattice vector $\vec{g}$) in the wave-vector space is conserved. Like the normal one, these processes are also expected to lead to certain special terms, besides the normal term, in the expression for the lattice thermal conductivity. The significance of these special terms is expected to be more or less similar in nature to what it is in the case of normal processes. In fact, if one considers a case in which there are no processes other than the $u(\vec{g})$ processes, then one can obtain an infinitely large thermal conductivity. This can be done in the same way as was used in the case of normal processes. For example, one can use Eqs. (16)–(20) for this purpose, putting τ_u and $\tau(\vec{g}')$ equal to infinity and $\tau(\vec{g})$ [corresponding to the $u(\vec{g})$ processes in question] finite. Alternatively, it is better to start directly with Eq. (6). In this particular case, N is determined by an equation that differs from Eq. (23), having $\vec{g}$ instead of $\vec{0}$. As has been shown in I, this equation permits a solution $N(\vec{g})$ for N of the form given by Eq. (4) in the absence of $\vec{\nabla}T$; a heat flux in the system is associated with $N(\vec{g})$. In fact, it is not possible for the $u(\vec{g})$ processes alone to bring a disturbed phonon system to an isotropic distribution. Instead, the system relaxes to a distribution of the form given by Eq. (4), which can exist freely[11] in the presence of the processes in question. The $u(\vec{g})$ processes, therefore, do not necessarily lead to a thermal resistance when they are the sole scattering processes. A situation of this type, however, is purely hypothetical, since it is impossible to conceive of a system in which only one given type of umklapp processes takes place. This is because all types of three-phonon umklapp processes (including the normal processes) are due to the same anharmonicity in the crystal. If the temperature of the system is sufficiently low, then it is possible for only three-phonon normal processes to be taking place significantly. However, if the temperature is so large that a given type of umklapp processes occurs, then there are no reasons for the absence of other types.

To elaborate on the above point, let us consider the physical basis of the particular behavior of the normal processes.[8] Since these processes conserve the total wave vector of the phonon system, they cannot obstruct a constant heat flow which corresponds to a surplus total wave vector in its direction. Now consider, for example, a hypothetical case in which there exist only $u(\vec{g})$ processes, where $\vec{g}$ is perpendicular to the thermal gradient. Since the corresponding wave-vector condition states that the total wave vector changes by an amount equal to $\vec{g}$ whenever two phonons combine to give one, or vice versa, they do not destroy the total wave-vector component in the direction of the thermal gradient. They cannot, therefore, obstruct the heat flow. This supplies the justification of the results we get mathematically.

It is also interesting to consider one more hypothetical system. Consider the simultaneous occurrence of the $u(\vec{g})$ and $u(-\vec{g})$ processes. In this case, when $\vec{\nabla}T=\vec{0}$, neither $N(\vec{g})$ nor $N(-\vec{g})$ gives a solution for N in Eq. (6) [with only $\tau(\vec{g})$ and $\tau(-\vec{g})$ finite], unless both of them happen to be the same, which is possible if they are such that

$$\vec{\lambda}(\vec{g})\cdot\vec{g}=\vec{\lambda}(-\vec{g})\cdot\vec{g}=0;$$

that is, a distribution of the form

$$(e^{\hbar\omega+\vec{\lambda}\cdot\vec{q}}-1)^{-1},$$

where $\vec{\lambda}$ is such that $\vec{\lambda}\cdot\vec{g}=0$ can still exist in the system in the absence of the thermal gradient. This distribution corresponds to a heat flux perpendicular to $\vec{g}$. [This result can also be arrived at by using Eqs. (16)–(20).] In fact, this result is an outcome of the same wave-vector conservation conditions we have been talking about so far. Since either of the two types of processes considered above changes the phonon wave vectors in terms of $\vec{g}$, neither of them can destroy the phonon wave-vector components perpendicular to $\vec{g}$. Thus, these processes are not expected to obstruct a heat flux in the direction perpendicular to $\vec{g}$.

The above result is, in fact, more general. If there is more than one type of scattering process taking place in a system such that they all permit a particular anisotropic distribution as a solution for N, when $\vec{\nabla} T = 0$, then they can be said not to obstruct the heat flow corresponding to this distribution. In general, this is not possible; for example, when there are $u(\vec{g})$ processes corresponding to three values of $\vec{g}$ linearly independent of one another, no such distribution can exist. The simultaneous existence of these processes then does not permit a steady flow of heat in any direction in the absence of the thermal gradient, that is, they result in a finite thermal resistance to the heat flow in any direction. Stated more generally, it is because of the simultaneous existence of the different scattering processes that a system has a finite thermal gradient.

The expression for $K_{ss'}$ clearly shows that the anisotropic nature of the lattice thermal conductivity, if any, is due not only to the possible anisotropy in the phonon spectrum and in the structure of the relaxation times, but also to the specific lattice structure of the crystal, which manifests itself through the special terms in Eq. (13). Since experimental results, in general, do not show any appreciable anisotropy in the lattice thermal conductivity of most solids, we expect that the contribution of the special terms in Eq. (13) is in practical cases far less significant than the normal term. In fact, the lattice thermal conductivities of a number of solids have been satisfactorily explained[13-17] by the main term of Callaway's formalism,[2] which is the first (normal) term of Eq. (13). From this, it appears that it is very likely for the special terms in Eq. (13) to cancel the contributions of one another, so that their net contribution is small compared to that of the main term, at least when τ_u is sufficiently small.

A practical application of the present theory is not possible at this stage. This is particularly so, since so far there have not been any calculations of $\tau(\vec{g})$—relaxation time corresponding to $u(\vec{g})$ processes. Also, the practical absence of the anisotropy in the thermal conductivity of solids cannot be successfully exploited to estimate the contributions of the special terms. The above calculation also requires the solution of a large number of coupled equations to get the components of the tensor $\overleftrightarrow{\alpha}(\vec{g})$. Since we do not have, in general, a first-hand knowledge of the various relaxation times, we often express them in terms of adjustable parameters, and this obviously poses a special difficulty in solving the aforesaid equations. Symmetry consideration may, however, reduce the number of equations to a significantly small value. For example, in his formalism, Callaway[2] has assumed $\vec{\lambda}(\vec{0})$ to be along $\vec{\nabla} T$, which simply means that $\alpha_{ss'}(\vec{0})$ has the form $\delta_{ss'} \times$ (constant).

In the present paper, we have attempted to draw a physical picture of how heat flow takes place in a lattice system. We have derived an analytic expression for the thermal conductivity, but we are not much interested in its quantitative implications. Our primary objective has been to get an insight into the way the three-phonon processes affect the lattice-energy transport, stressing the need to take into account the conservation conditions obeyed by the scattering processes. In view of the fact that the normal term we have named above satisfactorily explains most of the experimental results, particularly in semiconductors, we believe that the individuality of different processes is lost when there are different types of scattering processes, so that the contribution of the special terms is perhaps far less significant than that of the normal term. The above discussion essentially describes the "physics" underlying the nature of the present problem.

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number has no factor such as $T^{-3/2}$ in the expression for n. Futhermore, $\hbar\vec{q}$ plays the same role in the case of phonons as $\vec{p}$ ($=m\vec{v}$) in the case of gas atoms; both determine the phase space accessible to the respective systems.

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PHYSICAL REVIEW B VOLUME 4, NUMBER 12 15 DECEMBER 1971

Self-Diffusion in fcc γ- and bcc δ-Cerium

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The serial sectioning method was used to study self-diffusion in cerium metal. In the fcc γ phase, $D=0.6e^{-36\,600/RT}$ cm^2 sec^{-1}, and in the bcc δ phase, $D=1.2\times10^{-2}e^{-21\,500/RT}$ cm^2 sec^{-1}. The diffusion parameters in the fcc structure are compatible with a normal vacancy mechanism. The high diffusivities and low activation energy in the bcc phase are characteristic of diffusion behavior in anomalous bcc metals. Similarities with self-diffusion in bcc ϵ-plutonium are stressed.

INTRODUCTION

The diffusion behavior of the anomalous bcc metals has attracted considerable attention in the last several years. It is well established[1] that a number of bcc metals possess unusual properties with regard to self-diffusion and impurity diffusion. No single explanation[2-4] of the anomalous properties has yet completely been accepted.

β-titanium,[5] β-zirconium,[6] and γ-uranium[7] were originally considered as anomalous bcc metals. The bcc structure of these metals extends over a temperature range of several hundred degrees. It was therefore possible to detect a definite curvature of the Arrhenius plots for both, self- and solute diffusion. The activation energies for self-diffusion in the lower temperature range of the bcc phase had unusually low values, contrary to the usually obeyed semiempirical rules. Furthermore, the extremely low preexponential terms indicated negative entropies of activation.

More recently it has been shown that also β-hafnium,[8] ϵ-plutonium,[9] and β-praseodymium[10] have some of the characteristic features of the anomalous bcc metals. The bcc structure in this group extends only over a narrow range of temperatures, thus precluding the detection of curved Arrhenius plots. The activation energies, however, have anomalously low values. The preexponential terms, though low, are less anomalous than those of β-Zr and β-Ti.

bcc structures were found in seven other rare-earth metals in addition to praseodymium, either as the only existing solid allotropic form or as high-temperature structures. Information concerning the diffusion behavior of these metals is very scarce. This is due to the unavailability of metals of sufficient purity and to the difficulties involved in diffusion studies with highly reactive materials.

Self-diffusion in the high-temperature bcc phase of plutonium has been studied at normal[9] and at high pressures up to 12 kbar.[11] In contrast to most metals, the self-diffusion coefficients in plutonium increase with increasing pressure. This fact was related to the negative slope of the liquidus in the P-T diagram of plutonium.[12] In order to explain the negative volume of activation, a model was proposed[11] according to which the atom in the acti-