Clustering of mobile defects and quantum diffusion in metals

A. I. Morozov and A. S. Sigov

Moscow Institute of Radio Engineering, Electronics, and Automation

(Submitted 17 March 1988)
Zh. Eksp. Teor. Fiz. **95**, 170–177 (January 1989)

Clustering of mobile defects by interaction with one another in a crystal matrix is considered. It is shown that the form of the resultant clusters can depend strongly on the competition between the short- and long-range parts of the interaction. The temperature dependence of the diffusion of quantum defects, with account taken of their clustering, is obtained.

INTRODUCTION

A number of interstitial impurities can diffuse in a metal from one interstice to another. Examples are hydrogen isotopes and positive muons. The diffusion can be either classical or by quantum tunneling.

The interaction of hydrogen atoms in a metal matrix is the subject of many works (see, e.g., Ref. 1). All of them take into account only one type, elastic, of long-range interaction between the impurities, meaning indirect interaction via acoustic phonons. The energy of this interaction is[1]

$$W_{\text{elast}}(\mathbf{R}) = W(\mathbf{n})\Omega/R^3, \tag{1}$$

where $\mathbf{R}$ is the distance between the impurities, Ω is the unit-cell volume, and $\mathbf{n} = \mathbf{R}/R$. Depending on the orientation of the vector $\mathbf{n}$ relative to the crystal-lattice axes, $W(\mathbf{n})$ can be either positive or negative.

One of us[2] has pointed out the substantial role of another long-range interaction, indirect interaction via Friedel oscillations of the electron density. Let $V_1(\mathbf{q})$ be the Fourier component of the potential of the interaction of an electron with a point defect (we confine ourselves hereafter to the Born approximation). The energy of interaction via the conduction electrons is then given, in analogy with the RKKY interaction, by

$$W_{\text{el}}^{(0)}(\mathbf{q}) = |V_1(\mathbf{q})|^2\Pi(\mathbf{q},0), \tag{2}$$

where $\Pi(\mathbf{q},0)$ is the static polarizability of the electron gas. Allowance for screening in the random-phase approximation leads to the appearance of a dielectric constant

$$\varepsilon(\mathbf{q},0) = 1 - 4\pi e^2\Pi(\mathbf{q},0)/q^2 \tag{3}$$

in the denominator of (2):

$$W_{\text{el}}(\mathbf{q}) = W_{\text{el}}^{(0)}(\mathbf{q})/\varepsilon(\mathbf{q},0).$$

If the point defect has a charge Ze, we have

$$V_1(\mathbf{q}) \xrightarrow[\mathbf{q}\to 0]{} -4\pi Ze^2q^{-2}, \text{and } W_{\text{el}}(\mathbf{q}) \xrightarrow[\mathbf{q}\to 0]{} -4\pi Z^2e^2q^{-2}$$

and compensates fully for the Fourier component, which diverges for small $\mathbf{q}$, of the direct interaction between the impurities:

$$W_{\text{imp}}(\mathbf{q}) \xrightarrow[\mathbf{q}\to 0]{} 4\pi Z^2e^2q^{-2}.$$

The direct interaction is thus screened at atomic distances, and the long-range part of W_{el}, which is due to Kohn singularities of $\Pi(\mathbf{q},0)$, is given in the case of a spherical Fermi surface (FS) by[3]

$$\widetilde{W}_{\text{el}}(\mathbf{R}) = \frac{\Omega N(0)|V_1(2k_F)|^2}{2\pi\varepsilon^2(2k_F,0)}\frac{\cos 2k_F R}{R^3}, \tag{4}$$

where k_F is the Fermi momentum of the electrons and $N(0)$ is their density of states on the FS. For interaction between impurities of different species, $|V_1(2k_F)|^2$ must be replaced by

$$[V_1(2k_F)V_2^*(2k_F) + \text{c.c.}]/2,$$

where the subscripts 1 and 2 pertain to the different impurity species. Owing to the temperatures smearing of the $\Pi(\mathbf{q},0)$ singularity, the interaction $\widetilde{W}_{\text{el}}(\mathbf{R})$ is exponentially damped over distances $R_0 = a\varepsilon_F/T$, where a is the interatomic distance and ε_F is the Fermi energy.[4] This effect is immaterial in the considered low-temperature region. A static disorder does not lead to exponential damping of $W_{\text{el}}(R)$.[5,6]

The resultant long-range interaction between the impurities is given by

$$W(\mathbf{R}) = W_{\text{elast}}(\mathbf{R}) + \widetilde{W}_{\text{el}}(\mathbf{R}). \tag{5}$$

The value of $W(n)$ ranges from 1 eV for heavy interstitial impurities to 10^{-2} eV in the case of hydrogen in a metal.[7] The quantity $N(0)|V_1(2k_F)|^2/2\Pi\varepsilon^2\times(2k_F,0)$ with parameters typical of metals ranges from 10^{-2} to 1 eV, i.e., $\widetilde{W}_{\text{el}}(\mathbf{R})$ is of the same order as $W_{\text{elast}}(\mathbf{R})$. Indirect interaction via the electrons may turn out to be predominant in the case of substitutional impurities.

In addition to impurity interactions with one another, there exist interactions with the crystal matrix; these have minima in the interstices (for interstitial impurities). We assume these minima to be abrupt enough and the matrix potential to be substantially stronger than $W(\mathbf{R})$. This allows us to neglect the displacements, due to $W(\mathbf{R})$, of of the equilibrium positions in the interstices, and examine the distribution of a small number of impurities among the interstices, with allowance for their pair interaction. In the case of small $R\sim a$, of course, account must be taken also of the short-range part of this interaction. The clustering of the defects will be dealt with in the first part of the paper, while in the second we shall study the temperature dependence of the impurity diffusion coefficient with account taken of their clustering.

CLUSTERING OF DEFECTS

Since $W(\mathbf{n})$ and $\widetilde{W}_{\text{el}}(\mathbf{R})$ can have either sign, there exists a set of interstices with $W(\mathbf{R}) < 0$, and the state with the lowest energy W_{gr} at $k_F a \sim 1$ corresponds to $R \sim a$. Therefore all the mobile point defects in a metal and neutral mobile impurities in a dielectric form clusters. With further lowering of the temperature, a transition takes place from the state of a lattice gas to one in which lattice-gas and lattice-liquid phases coexist, meaning an ordered solid solution. At low defect density x, the clustering temperature is much higher than the temperature $T_s = x(1-x)|W_{\rm gr}|$ of stratification into phases.[7,8]

The cluster forms and the structure of the highly-concentrated phase depend on the ratio of the short- and long-range parts of the pair-interaction potential. If the short-range part of the potential predominates the clusters take the form of isotropic or almost-isotropic aggregates of defects. In the opposite case they are strongly anisotropic. Depending on the form of $W(\mathbf{R})$, the number of particles in a cluster can increase as the temperature is lowered, or remain bounded. Examples of clusters of the first type are those of mobile defects in dielectrics (where $W_{\rm el} = 0$). Since $W(\mathbf{n})$ is minimal along definite crystallographic directions, the impurity atoms will form chains along these directions. In cubic crystals we have in the case of weak anisotropy

$$W(\mathbf{n})=\alpha\left[\frac{3}{5}-\left(\frac{X}{R}\right)^4-\left(\frac{Y}{R}\right)^4-\left(\frac{Z}{R}\right)^4\right], \tag{6}$$

where X, Y, and Z are the components of the vector $\mathbf{R}$ along the cubic-lattice axes and the sign of α depends on the combination of the elastic moduli.[9] If $c_{11}-c_{12}-2c_{44}<0$ we have $\alpha>0$ and defect chains will be produced along the [100], [010], and [001] directions. Interstitial silicon atoms were gathered into such chains in silicon crystals after prolonged annealing.[10] In this case the interstitial atoms are identical with the matrix atoms, so that subsequent annealing produced dislocations and stacking faults.

The foregoing defect arrangement in a cluster may be difficult in metals because $\widetilde{W}_{\rm el}(\mathbf{R})$ oscillates as a function of distance. The following clustering picture is then possible. Clusters of several particles (quasimolecules) are formed at a certain characteristic temperature T_{K1}, followed by clustering of the quasimolecules at a lower temperature T_{k2}. The characteristic distance between the quasimolecules in the resultant cluster is much larger than the distance between the defects in the quasimolecule. If the number of quasimolecules in the second-generation cluster is limited, the next stage of the clustering process sets in at a lower temperature T_{k3}, and so on.

Stratification into phases with low and high quasimolecule densities takes place at the temperature T_s.

Formation of quasimolecules consisting of two hydrogen atoms were observed by neutron diffraction in the compounds LuD_x (Ref. 11) and YH_x (Ref. 12). The deuterium atoms were located in tetrahedral pores of an fcc matrix. When a pair is produced, the second deuterium atom occupies the next nearest tetrahedral pore along the hexagonal axis. The phase diagram of hydrides of yttrium and of a number of rare-earth elements has the form shown in Fig. 1 (Refs. 13 and 14). The value of $x_{\rm cr}$ varies in the range 0.03–0.25, depending on the metal. The fraction of quasimolecules at 400 K is quite large, and it is the pair production which hinders a stratification into low- and high-density phases in the region of small x. A plot of the hydride resistance vs temperature revealed in the interval 160–200 K an anomaly[11,12] attesting to pair clustering.

In substances in which the density of immobile defects greatly exceeds that of the mobile ones, the clusters produced will consist of one immobile and several mobile impurities.

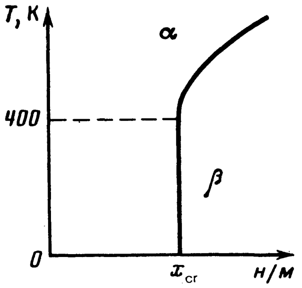

FIG. 1. Phase diagram of yttrium hydrides and of a number of rare-earth metals.

Formation of a cluster in the form of a chain of atoms is analogous to the polycondensation reaction $A_{m-1}+A \to A_m$ in a solution.[15,16] The fraction of single defects (monomers) is determined by the chemical-equilibrium constant, which depends on the temperature and on the difference of the binding-energies ε of clusters of m and $m-1$ particles. We assume for simplicity that ε is independent of m, as is always true of large m.

Let us find the clustering temperature T_k for two cases.

1. The temperature $T_k \gg \Delta$, where Δ is the characteristic bandwidth of the quantum impurity in a perfect crystal, with allowance for the polaron effect. In this case we can neglect the heat capacity of the lattice gas if we assume that all the impurities in the interstices are on the lower vibrational level (T_k is much lower than the local vibration frequency). We obtain then from the law of effective masses[17] for the equilibrium constant

$$K=\exp(\varepsilon/T), \tag{7}$$

and for the fraction of single defects

$$\varkappa=[2\beta+1-(4\beta+1)^{1/2}]/2\beta^2, \tag{8}$$

where $\beta = xK$ and

$$\varkappa=\begin{cases}1 & \text{if} \quad \beta\ll 1\\ \beta^{-1} & \text{if} \quad \beta\gg 1\end{cases}. \tag{9}$$

The characteristic clustering temperature is thus obtained from the condition $\beta = 1$ and is equal to

$$T_k=-\varepsilon/\ln x. \tag{10}$$

Equations (9) and (10) do not change when clusters of a different form are produced. Here ε is the specific binding energy of the cluster.

2. If, however, $T_k \ll \Delta$ but is much higher than the lattice-gas degeneracy temperature, the lattice gas can be regarded as ideal, monatomic, and Boltzmann-like. We neglect here and below the probability of tunneling of a cluster of two and more particles. In this case,

$$K=(\Delta/T)^3\exp(\varepsilon/T), \tag{11}$$

and the clustering temperature is determined from the condition $xK = 1$. It is easy to verify that in this case T_k is higher than when classical impurities are clustered.

We have considered so far clustering in analogy with a chemical reaction. However, as noted above, there exists a large number of interstices with $W(\mathbf{R}) < 0$. Recognizing that $W(\mathbf{R})$ decreases like R^{-3}, the value of $W(\mathbf{n})$ averaged over a unit sphere is zero, and that $\cos 2k_F R$ oscillates rapidly with a characteristic period of order a, we shall consider the following simplified model: one defect is at the origin and the other is at a distance R from it. In a spherical layer of radius R and thickness dR there are $4\pi R^2 dR/a^3$ states whose energy is distributed with equal probability in the interval from $-E_0a^3/R^3$ to $+E_0a^3/R^3_3$. The minimum distance between particles is $r_{\min} \sim a$ and the maximum is $r_{\max} \sim ax^{-1/3}$. The probability of finding a particle in a spherical layer of radius R and thickness dR is

$$dw(R) = \int_{-\infty}^{\infty} dEA \exp(-E/T)\theta\left(\frac{E_0a^3}{R^3} - |E|\right) \times \frac{2\pi R^5\, dR}{a^6E_0} = \frac{4\pi TAR^5\, dR}{E_0a^6} \operatorname{sh}\frac{E_0a^3}{R^3T}, \tag{12}$$

where A is obtained from the normalization condition.

This model allows for the presence of a large number of two-particle bound states, but ignores multiparticle effects. For the limiting case of one bound state of energy ε, however, it yields for T_k and for the limiting values of $\varkappa$ the same expressions as the preceding analysis [see Eqs. (9) and (10)].

The average distance between impurities is $\langle R\rangle \sim r_{\max}$ at high temperatures $T \gg T_k$ and $\langle R\rangle \sim r_{\min}$ at low temperatures ($T \ll T_k$). The characteristic value of T_k can be obtained by studying the temperature dependence of $\langle R\rangle$. We obtain for T_k expression (10) in which $-\varepsilon$ is replaced by the minimum defect-interaction energy $W_{\rm gr}$. It can be concluded thus that the principal role in the clustering of mobile defects in the case of a potential $W(\mathbf{R}) \sim R^{-3}$ is played by states with the lowest energy, and the presence of a large number of states with $W(\mathbf{R}) < 0$ is immaterial for the determination of T_k. The probability of states with binding energy $\varepsilon < T$ (absence of binding) is

$$\varkappa = \gamma\left[\gamma + x\left(\frac{T}{W_{\rm gr}}\right)^2 \exp\left(\frac{|W_{\rm gr}|}{T}\right)\right]^{-1}, \tag{13}$$

where $\gamma \sim 1$. It can be seen that the presence of a large number of interstices with $W(\mathbf{R}) < 0$ leads to the appearance of a pre-exponential factor in (13), but does not affect the exponential decrease of $\varkappa$ at $T < T_k$.

For substances with large density of immobile defects it is necessary to replace x in (10) and (13) by the density of the immobile effects.

QUANTUM DIFFUSION IN A SYSTEM OF MOBILE DEFECTS

Clustering influences substantially the coefficient of quantum diffusion of impurities; a theory of this diffusion was developed in Refs. 18–20. We consider a concentration x such that the following condition is met:

$$W(ax^{-1/3}) \ll \Delta. \tag{14}$$

In this case, down to the phase-stratification temperature $T_s \sim W(ax^{-1/3})$, in the greater part of the crystal no defect localization is caused by the static collapse of the levels in the different interstices.[20] Let us consider a hypothetical picture of diffusion in the absence of clustering.

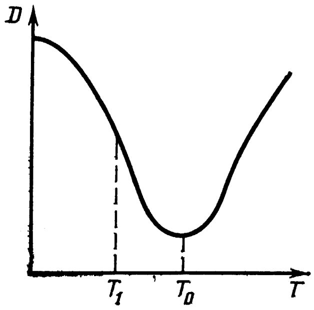

FIG. 2. Temperature dependence of the diffusion coefficient in the absence of clustering.

At high temperatures the main contribution to diffusion is due to a classical above-barrier activation mechanism, and the diffusion coefficient decreases as the temperature is lowered. Below a certain temperature T_0 the main contribution to the diffusion is made by tunneling processes, and D begins to increase as the temperature is lowered. A typical $D(T)$ plot is shown in Fig. 2 (Ref. 20). The diffusion consists first of individual below-barrier hops, and at temperature below T_1 the impurity motion acquires an itinerant character.[18–20] No consistent calculation of the diffusion coefficient in the region $T_1 < T < T_0$ has yet been made in view of difficulties similar to those encountered in localization theory. For a quantum-effect mean free path $l \lesssim a$ it is necessary to take into account all the corrections to the bare vertex of the defecton–phonon or defecton–electron interaction that causes the damping. All the calculations known to us for the diffusion coefficient in this region are based on replacing the total vertex by the bare one.

If $T < T_1$ we have $D \sim T^{-9}$ in dielectrics[18,19] and $D \sim T^{b-1}$ ($b < 1$) in metals,[2,21–24] while in semimetals $D(T)$ is a nonmonotonic function.[24]

Let us examine how $D(T)$ is changed by clustering. It was noted in Ref. 20 that for attraction between defects the diffusion at $T \ll |W_{\rm gr}|x^{2/3}$ has the usual activation character with an activation energy $E_a \approx |W_{\rm gr}|$. It will be shown below that at small x the clustering leads to a change of the diffusion coefficient in a substantially larger range of temperatures. The tunneling probability of a cluster consisting of two or more defects is vanishingly small. Therefore only single defects execute quantum tunneling and

$$D_{\rm qu}(T) = \varkappa(T)D_0(T), \tag{15}$$

where $D_0(T)$ is the quantum-diffusion coefficient in the absence of clustering, and $\varkappa$ is defined by Eq. (13). For $T \gg T_k$ we have $D_{\rm qu}(T) \approx D_0(T)$, and if $T \ll T_k$

$$D_{\rm qu}(T) = \gamma x^{-1}\left(\frac{W_{\rm gr}}{T}\right)^2 \exp\left(-\frac{|W_{\rm gr}|}{T}\right) \times\left[\frac{\min(T,\Delta)}{\Delta}\right]^3 D_0(T). \tag{16}$$

Note that an exponential $D_{\rm qu}(T)$ dependence is observed not for $T \ll x^{2/3}|W_{\rm gr}|$ but for $T \ll |W_{\rm gr}/\ln x|$. Consider the following limiting cases:

(a) $T_k \gg T_0$. In this case there is no minimum of $D(T)$ at all. At the temperature T_0 for which

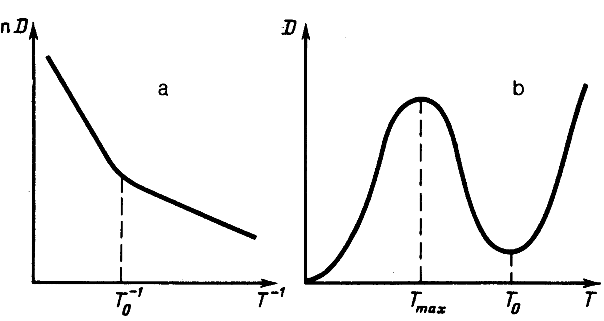

FIG. 3. Temperature dependence of the diffusion coefficient with allowance for clustering.

$$D_{\rm qu}(T_0) = D_{\rm ab}(T_0),$$

where $D_{\rm ab}(T) = \nu_0 \exp(-E_a/T)$ is the coefficient of above-barrier classical diffusion, and E_a is the activation energy, one exponential dependence replaces another, as shown in Fig. 3a. It must of course be noted that clustering changes also the value of E_a when $T < T_k$.

Note that notwithstanding the exponential character of the $D(T)$ dependence at low temperatures, the principal diffusion mechanism is tunneling.

(b) $T_k < T_0$. In this case $D(T)$ goes through a minimum at $T = T_0$, and then reaches a maximum at $T = T_{\rm max}$ and tends to zero as $T \to 0$ (Fig. 3b). For a power-law $D_0(T)$ dependence of the form $D_0 \sim T^{-n}$ with $n \sim 1$ we have $T_{\rm max} \sim T_k$.

Let us consider now specific quantum-defect systems.

Hydrogen in metals. According to the estimates above, at realistic hydrogen concentrations we have $T_k \sim 10$–10^3 K. Therefore the case $T_k > T_0$ is realized in such a system. It is indeed the clustering which can explain the decrease of activation energy of transition-metal hydrides[25] when the temperature is lowered.

μ^+ in metals. In this case it is meaningful to speak only of formation of a bound state of muonium with an immobile impurity. It must be remembered, however, that after thermalization the muons have no equilibrium distribution over the interstices. It can be assumed that after thermalization a muon can occupy, with equal probability, any equivalent interstice. At the same time, for an equilibrium distribution the probability of staying in a given interstice as a result of interaction with an immobile defect depends on $W(R)$. The equations we derived pertain only to an equilibrium distribution, so that the ratio of the relaxation time of the distribution function to the lifetime of the muon plays an important role. The value of T_k for μ^+ is the same as for hydrogen in a metal, and in general both $T_0 < T_k$ and $T > T_k$ are possible for μ^+.

Solid solution of He^3 in He^4. In this system the clustering is least substantial. He^3 in He^4 has $W(\mathbf{n}) \sim 10^{-2}$–$10^{-1}$ K (Refs. 19 and 20), so that$T_k \sim 10^{-3}$–10^{-2} K. The case $T_k \ll T_0$ is therefore certainly realized for solid solutions of the helium isotopes.

CONCLUSION

We have shown thus that all mobile defects in metals and neutral mobile defects in dielectrics become clustered when the temperature is lowered, and the form of the clusters can depend substantially on the character of long-range indirect interaction via acoustic phonons and conduction electrons. The characteristic clustering temperature T_k is determined by the concentration of the defects and by their binding energy, and also by the bandwidth of the quantum defects at low clustering temperatures.

Clustering alters substantially the temperature dependence of the diffusion coefficient D. It can, in particular, eliminate completely the low-temperature minimum of the diffusion coefficient and result in a monotonically increasing $D(T)$ dependence. In other cases, clustering can destroy the monotonic increase of D with decrease of temperature in the low-temperature region, leading thereby to a suppression of the maximum of $D(T)$ at a temperature $T \sim T_k$ and to an exponential decrease of D at $T < T_k$.

The authors are deeply grateful to A. F. Andreev for interest in the work and for valuable remarks.

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Translated by J. G. Adashko