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Local and Quasilocal Relaxation Processes in Crystals with Impurities

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Diffusional relaxation of impurity atoms in a crystal containing a fixed local perturbation center is investigated. It is shown that diffusional relaxation in such a system can be described by a set of orthogonal relaxation modes, each of which is characterized by a single relaxation time. Depending on the form of the perturbation the relaxation modes may either describe local or quasilocal relaxation processes. The distribution function of the inverse relaxation times is obtained; it is the imaginary part of the Green's function of the relaxation equation. The Green's function is derived from the Dyson equation, which yields an exact solution in the case of local perturbations. The analogy with local and quasilocal oscillations of a crystal lattice containing separate impurity centers is noted. The presence of a local perturbation in relaxing systems leads to the appearance of local peaks in the inverse-relaxation-time density distribution outside the spectral region of the unperturbed crystal and of quasilocal peaks within the region. A maximum of internal friction may correspond to each such peak.

1. I. M. Lifshitz[1] was the first to investigate the frequency spectrum of the natural oscillations of a harmonic crystal lattice with isotropic impurity, and to find the local normal oscillations whose frequencies lie beyond the limit of the frequency spectrum of the oscillations of an ideal lattice. Yu. M. Kagan and Ya. A. Iosilevskiĭ [2] investigated the so-called quasilocal oscillations connected with the presence of an isotopic impurity; these oscillations correspond to frequency-spectrum peaks lying in the region of allowed frequencies of the unperturbed lattice. An important role is played here by the form of the quasicontinuous frequency spectrum of the ideal lattice, which depends on the dimensionality of the problem.

Local and quasilocal oscillations, bound and resonant states of electrons in a crystal with impurity, etc., are by far not the only possible cases of realization of local and quasilocal states. There is one more case of practical importance when local and quasilocal states can exist in a crystal. We have in mind diffusion relaxation processes of atom redistribution occurring in a crystal lattice in the field of local perturbations. The relaxation-time spectrum of these processes can be measured by the internal-friction method, which has recently been extensively used to investigate metals and alloys.

The inhomogeneous distribution of the atoms of the components of a binary solid solution of the substitution (interstitial) type is described by the set of probabilities of occupying the sites (interstices) of the crystal lattice by atoms of one of the components. Since the atoms become redistributed over the sites (interstices) of the lattice in order to attain equilibrium, these probabilities depend on the time. Whereas in the description of the crystal-lattice vibrations each lattice site can be set in correspondence with three displacement amplitudes, in the description of the diffusion redistribution of the atoms each site can be set in correspondence with its own relaxing quantity, namely the probability of occupying the site by an atom of one of the components. Neither the displacement amplitudes nor the occupation probabilities pertaining to different sites are independent. The former are connected by the equations of crystal-lattice dynamics, and the latter by the random-walk diffusion equations. In either case, the presence of local perturbations can lead to the appearance of local or quasilocal states. In spite of the different nature of these processes, the analogy can be quite far reaching.

In diffusion relaxation in the field of local perturbations, the local states are relaxation modes with a single relaxation time corresponding to a δ-like peak of the distribution function of the reciprocal relaxation times; this peak lies outside the region of the quasicontinuous spectrum of the reciprocal relaxation times of the unperturbed system. The quasilocal states represent relaxation processes that do not have equal relaxation times. They break up into a group of relaxation processes with close relaxation times. Corresponding to these times is a peak of finite width in the relaxation-time spectrum. This peak is located in the region of the relaxation-time spectrum of the unperturbed system.

2. Let us consider the diffusion relaxation of a binary interstitial solution. The analysis is equally applicable to a binary substitutional solution.

If we denote by $c(\mathbf{r}, t)$ the probability that the interstitial atom will occupy the position $\mathbf{r}$, then the random-walk equation characterizing the diffusion redistribution of the interstitial atoms over the interstices takes the form

$$\frac{dc(\mathbf{r},t)}{dt}=\sum_{\mathbf{r}'}L(\mathbf{r},\mathbf{r}')c(\mathbf{r}',t), \tag{1}$$

where $L(\mathbf{r}, \mathbf{r}')$ is the probability that the interstitial atom will jump from the interstice $\mathbf{r}'$ into the interstice $\mathbf{r}$ in a unit time. The sum is taken over all the interstices. $-L(\mathbf{r}, \mathbf{r})$ is the probability that the interstitial atom will go away from the interstice $\mathbf{r}$ in a unit time. From the particle-number conservation law it follows that

$$\sum_{\mathbf{r}}L(\mathbf{r},\mathbf{r}')=0. \tag{2}$$

In the presence of a local perturbation (which may be, for example, a vacancy or an atom of a third component), the quantities $L(\mathbf{r}, \mathbf{r}')$ can be represented in the form

$$L(\mathbf{r}, \mathbf{r}') = L_0(\mathbf{r}-\mathbf{r}') + \Delta L(\mathbf{r}, \mathbf{r}'), \tag{3}$$

where $L_0(\mathbf{r}-\mathbf{r}')$ are the transition probabilities in the ideal lattice. The dependence of $L_0(\mathbf{r}-\mathbf{r}')$ on the coordinate difference is connected with the translation invariance of the ideal Bravais lattice considered here. From the condition that the number of particles be constant in the absence of a perturbation we have in analogy with (2)

$$\sum_{\mathbf{r}} L_0(\mathbf{r}-\mathbf{r}') = 0. \tag{4}$$

Using (3), we can rewrite Eq. (1) in operator form

$$\frac{dc}{dt} = (\hat{L}_0 + \Delta\hat{L})c. \tag{5}$$

We seek the non-equilibrium part of $c(\mathbf{r}, t)$ in the form $\exp(-\nu t)\tilde{c}(\mathbf{r})$, where ν is the reciprocal relaxation time.

Then

$$(-\hat{L}_0 - \Delta\hat{L})\tilde{c}(\mathbf{r}) = \nu\tilde{c}(\mathbf{r}). \tag{6}$$

The eigenvalues $\nu = \nu_i$ of Eq. (6) describe the spectrum of the reciprocal relaxation times. The distribution function of the reciprocal relaxation time $g(\nu)$ can be represented in the form

$$g(\nu) = \frac{1}{N}\sum_i \delta(\nu-\nu_i) = \frac{1}{N\pi}\operatorname{Im}\sum_i \frac{1}{\nu-\nu_i-i\varepsilon}$$

$$= \frac{1}{N\pi}\operatorname{Sp}\frac{1}{\nu\hat{1}+\hat{L}-i\varepsilon\hat{1}},$$

where N is the number of interstices in the lattice; $\epsilon > 0$, $\epsilon \to 0$ or

$$g(\nu) = \frac{1}{N\pi}\operatorname{Im}\operatorname{Sp}\hat{G}(\nu-i\varepsilon), \tag{7}$$

where $\hat{G}(\nu)$ is a Green's function satisfying the equation

$$(\nu\hat{1} + \hat{L}_0 + \Delta L)\hat{G} = 1. \tag{8}$$

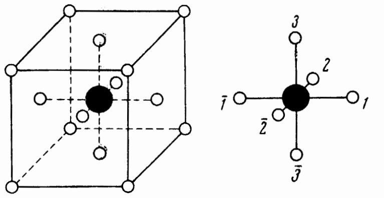
Putting $\nu\hat{1} + \hat{L}_0 = (\hat{G}^0)^{-1}$, where $\hat{G}^0$ is the Green's function of the relaxing system in the absence of local perturbations ($(\hat{G}^0)^{-1}\hat{G}^0 = 1$), we can write for $\hat{G}$ the Dyson equation

$$\hat{G} = \hat{G}^0 - \hat{G}^0\Delta\hat{L}\hat{G}. \tag{9}$$

Thus, the problem of finding the distribution function of the reciprocal relaxation times in a system with perturbations reduces to a determination of the Green's function from the Dyson equation (9).

As a concrete simple example, from which we can easily see how local states are produced in a relaxing system, let us consider the diffusion relaxation of an interstitial impurity over octahedral interstices in an fcc solvent lattice.

Let the center of the local perturbations be an impurity atom occupying a solvent lattice site and having an intrinsic mobility that can be neglected compared with the mobility of the interstitial atom. The octahedral interstices in the fcc lattice also form an fcc lattice without a basis. We can thus consider the distribution of the interstitial atoms over the points of an interstice fcc lattice in the field of a stationary impurity center located outside this lattice (see the left-hand figure). Let the probability of a transition of the migrating interstitial atom between the neighboring[1)] octahedral interstices in the absence of a local perturbation be $L_0 \exp(-Q/T)$, where L_0 is a frequency factor, Q the migration energy, and T the temperature. Using cyclic boundary conditions and changing over to k-space in (6) at $\Delta\hat{L} = 0$, we obtain the proper reciprocal relaxation times of the unperturbed system



Distributions of interstitial atoms over the points of an fcc interstice lattice. The light circles denote the fcc interstice lattice over which the interstitial atoms can become redistributed. The black circle denotes the position of the impurity atom—the center of the local perturbations. On the right are indicated the impurity center and those nearest interstitial positions, the transitions between which can be influenced by this center.

$$\nu = \nu_{\mathbf{k}} = L_0 \exp(-Q/T)\sum_l (1-\exp(i\mathbf{k}\mathbf{b}_l)), \tag{10}$$

where $\mathbf{b}_l$ are the vectors connecting the fcc lattice point with its nearest neighbors ($l = 1, 2, \ldots, 12$).

We now consider the relaxation in the presence of a perturbation. Let the potential of the local center have such a short range, that its influence changes the transition probability only between the positions of the first coordination sphere around the local center (see the right-hand figure). If the transition probabilities are equal to $L_0 \exp[-(Q-V)/T]$, then the matrix element of the perturbation operator takes the form

$$\Delta L(\mathbf{r}, \mathbf{r}') = a\sum_{ij}\delta(\mathbf{r}-\mathbf{a})\delta(\mathbf{r}'-\mathbf{a}_j)t_{jj}$$

$$-4\alpha\delta(\mathbf{r}'-\mathbf{r})\sum_i \delta(\mathbf{r}-\mathbf{a}), \tag{11}$$

where $\alpha = L_0 \exp(-Q/T)[\exp(V/T)-1]$; $\mathbf{a}_i$ are the radius vectors of the octahedral interstices of the first coordination sphere, drawn from the position of the local center ($i = 1, 2, \ldots, 6$);

$$t_{ij} = \begin{cases} 1 & \text{if} \quad \mathbf{a}_j - \mathbf{a}_i = \mathbf{b}_l \\ 0 & \text{if} \quad \mathbf{a}_j - \mathbf{a}_i \neq \mathbf{b}_l \end{cases},$$

where $\mathbf{b}_l$ is any of the 12 translations of the fcc lattice. It is easy to see that the perturbation operator (11) satisfies the condition $\sum_{\mathbf{r}} \Delta L(\mathbf{r}, \mathbf{r}') = 0$, which follows from (2) and (4). Substituting (11) in (9), we obtain

$$G(\mathbf{r}, \mathbf{r}') = G^0(\mathbf{r}-\mathbf{r}') + \alpha\sum_j G^0(\mathbf{r}-\mathbf{a}_j)G(\mathbf{a}_j, \mathbf{r}'), \tag{12}$$

[1)] Throughout the discussion that follows, only the transition probabilities between the nearest neighboring interstices are assumed to be different from zero.

where the kernel is

$$\tilde{G}^0(\mathbf{r}-\mathbf{a}_j)=\sum_i G^0(\mathbf{r}-\mathbf{a}_i)(4\delta_{ij}-t_{ij}).$$

It follows from (12) that

$$\sum_j \{\delta_{ij}-\alpha\tilde{G}^0(\mathbf{a}_i-\mathbf{a}_j)\}G(\mathbf{a}_j,\mathbf{r}')=G^0(\mathbf{a}_i-\mathbf{r}'). \tag{13}$$

Introducing the matrix

$$\Lambda_{ij}=\delta_{ij}-\alpha\tilde{G}^0(\mathbf{a}_i-\mathbf{a}_j), \tag{14}$$

we obtain

$$G(\mathbf{a}_i,\mathbf{r}')=\sum_j \Lambda_{ij}^{-1}G^0(\mathbf{a}_j-\mathbf{r}') \quad \text{и}$$

$$G(\mathbf{r},\mathbf{r}')=G^0(\mathbf{r}-\mathbf{r}')+\alpha\sum_{ij}\tilde{G}^0(\mathbf{r}-\mathbf{a}_i)\Lambda_{ij}^{-1}G^0(\mathbf{a}_j-\mathbf{r}'). \tag{15}$$

Putting $\mathbf{r}'=\mathbf{r}$ and summing over $\mathbf{r}$, we get

$$\operatorname{Sp}\hat{G}=\operatorname{Sp}\hat{G}^0-\alpha\sum_{ij}\Lambda_{ij}^{-1}\frac{d}{d\nu}\tilde{G}^0(\mathbf{a}_j-\mathbf{a}_i). \tag{16}$$

We have used the identity

$$\sum_{\mathbf{r}} G^0(\mathbf{r}-\mathbf{a}_l)G^0(\mathbf{a}_j-\mathbf{r})=-\frac{d}{d\nu}G^0(\mathbf{a}_j-\mathbf{a}_l).$$

Let $\tilde{\mathbf{v}}_s$ be orthonormal eigenvectors and λ_s the corresponding eigenvalues (which can be degenerate) of the matrix $G_{ij}^0 \equiv G^0(\mathbf{a}_i-\mathbf{a}_j)$; $s=1, 2, \ldots, 6$. Then

$$\tilde{G}_{ij}^0=\sum_{p=1}^{6}\lambda_p v_p^i v_p^j,$$

$$\Lambda_{ij}^{-1}=\sum_{s=1}^{6} v_s^i v_s^j/(1-\alpha\lambda_s). \tag{17}$$

Substituting (17) in (16) we obtain

$$\operatorname{Sp}\hat{G}=\operatorname{Sp}\hat{G}^0+\alpha\sum_{s=1}^{6}\frac{d\lambda_s/d\nu}{\alpha\lambda_s-1}, \tag{18}$$

$$g(\nu)=g_0(\nu)+\frac{1}{N\pi}\operatorname{Im}\sum_{s=1}^{6}\frac{\alpha d\lambda_s/d\nu}{\alpha\lambda_s-1}, \tag{19}$$

where $g_0(\nu)$ is the distribution function of the reciprocal relaxation times in the unperturbed system. In the sum of (19), which gives the increment to the density of the reciprocal relaxation times of the unperturbed system, each term can be expressed in the region of its maximum, where

$$\alpha\operatorname{Re}\lambda_s-1=0, \tag{20}$$

in the form

$$\frac{1}{N\pi}\frac{\Gamma_s}{(\nu-\nu_{s0})^2+\Gamma_s^2} \tag{21}$$

where $\Gamma_s=-\operatorname{Im}\lambda_s(\nu_{s0})/\operatorname{Re}\lambda_s'(\nu_{s0})$, and ν_{s0} is the solution of (20). (Only the terms linear in $\nu-\nu_{s0}$ have been retained in the expansion of $\lambda_s(\nu)$ about ν_{s0}.) The terms of the sum in (20) have a resonant form, and as $\Gamma_s \to 0$ the corresponding term of the sum tends to $N^{-1}\delta(\nu-\nu_{s0})$. Thus, the δ-like peak in the spectrum of the reciprocal relaxation times always takes place for ν_{s0} lying outside the spectra of the unperturbed problem, where $\Gamma_s=0$ (local relaxation process). If ν_{s0} is smaller than the maximum reciprocal relaxation time of the unperturbed system, then the distribution function of the reciprocal relaxation times has a pronounced maximum if the width Γ_s is sufficiently small (quasilocal relaxation process). Let us calculate the eigenvalues of the matrix $\tilde{G}_{ij}^0$, given by

$$(\tilde{G}_{ij}^0)=\begin{pmatrix} ABB & CBB \\ BAB & BCB \\ BBA & BBC \\ CBB & ABB \\ BCB & BAB \\ BBC & BBA \end{pmatrix}, \tag{22}$$

where

$$A=\tilde{G}_{11}^0=\frac{4}{N}\sum_{\mathbf{k}}\frac{1-\exp(i\mathbf{k}\mathbf{b}_l)}{\nu-\nu_{\mathbf{k}}},$$

$$B=\tilde{G}_{12}^0=\frac{1}{N}\sum_{\mathbf{k}}\frac{2\exp(i\mathbf{k}\mathbf{b}_l)-\exp(2i\mathbf{k}\mathbf{a}_i)-1}{\nu-\nu_{\mathbf{k}}},$$

$$C=\tilde{G}_{1\bar{1}}^0=\frac{4}{N}\sum_{\mathbf{k}}\frac{\exp(2i\mathbf{k}\mathbf{a}_i)-\exp(i\mathbf{k}\mathbf{b}_l)}{\nu-\nu_{\mathbf{k}}}; \qquad \begin{pmatrix} l=1,2,\ldots,12; \\ i=1,2,\ldots,6. \end{pmatrix}$$

The unit vectors of the basis in which the matrix (22) is written are numbered in the sequence 1, 2, 3, $\bar{1}$, $\bar{2}$, $\bar{3}$. The unit vectors correspond to the interstices shown in Fig. b.

The system of orthonormalized eigenfunctions and eigenvalues of the matrix G_{ij}^0 is such that

$$\lambda_1=A+C+4B\equiv 0,\ \hat{\mathbf{v}}_1=\frac{1}{\sqrt{6}}(111\,111);$$

$$\lambda_2=\lambda_3=A+C-2B,\ \hat{\mathbf{v}}_2=\frac{1}{2}(01\bar{1}01\bar{1}),\ \hat{\mathbf{v}}_3=\frac{1}{2\sqrt{3}}(\bar{2}11\bar{2}11);$$

$$\lambda_4=\lambda_5=\lambda_6=A-C,$$

$$\hat{\mathbf{v}}_4=\frac{1}{\sqrt{2}}(100\,\bar{1}00),\ \hat{\mathbf{v}}_5=\frac{1}{\sqrt{2}}(010\,0\bar{1}0),\ \hat{\mathbf{v}}_6=\frac{1}{\sqrt{2}}(001\,00\bar{1}). \tag{23}$$

Since an interstitial-atom redistribution corresponding to $\lambda_4=\lambda_5=\lambda_6$ does not lead to a change in the shape of the crystal, it is possible to excite the corresponding relaxation modes by applying external loads, as is done in the internal-friction method. For our purposes it is therefore necessary to consider only those terms in the sum of (19) which correspond to

$$\lambda_2=\lambda_3=\frac{6}{N}\sum_{\mathbf{k}}\frac{1+\exp(2i\mathbf{k}\mathbf{a}_i)-2\exp(i\mathbf{k}\mathbf{b}_l)}{\nu-\nu_{\mathbf{k}}}.$$

If $V>0$ then, bearing in mind that $\exp(V/T)\gg 1$ (V and T are of the order of several tenths and several hundredths of an electron volt, respectively), we seek the solutions $\nu\gg\nu_{\mathbf{k}.\max}$. Neglecting $\gamma_{\mathbf{k}}$ in comparison with ν in the denominator under the summation sign, we obtain from (20) the local reciprocal relaxation time

$$\nu\sim L_0\exp\{-(Q-V)/T\}. \tag{24}$$

The other limiting case $\alpha\to-1$ (at $V<0$, $\exp(V/T)\ll 1$) does not correspond to a quasilocal peak with a reciprocal relaxation time that approaches zero asymptotically. The reason for this is that transitions between the positions of the first coordination sphere and the neighboring interstices are not forbidden in our model. However, if we let the probabilities of such transitions approach zero, so that the positions of the first coordination sphere form an "island" isolated from the remaining lattice, then the "resonant" reciprocal relaxation time tends to zero as $\alpha \to -1$.[2)] The calculation of the position and of the width of the peak in the density of the reciprocal relaxation times can be carried out in the general case only numerically.

3. The local reciprocal relaxation time (24) should correspond to an absorption peak observed in internal-friction experiments. Such a peak was observed in fcc crystals by Ke,[3] who was the first to advance the hypothesis that the peaks obtained by him are connected with the redistribution of point defects of one type in the field of point defects of another type.

As to the centers for which $V < 0$, relaxation processes having one relaxation time cannot be connected with them at all. This circumstance may explain the anomalously large width of the internal-friction peaks frequently observed in experiments. (For a review of the literature on internal friction connected with point defects see [4].) A sufficiently pronounced internal-friction peak can be observed in this case only at small values of Γ.

In contrast to the case of the local relaxation process ($V > 0$), the quasilocal relaxation process cannot be represented even approximately in the traditional manner as a reorientation of a dumbbell made up of an immobile local center and the interstitial atom.

The resonant maxima in the density of the reciprocal-relaxation-time distribution, which are connected with local and quasilocal relaxation processes, correspond to irreducible representation of the point group of the perturbation. The number of resonant maxima should coincide in the general case with the number of irreducible representations of this group. For local centers with a potential having a very short range, extending only over the first coordination spheres of the interstitial positions, not all the irreducible representations can be realized (as is the case in the example of the fcc crystal considered above). As the radius of action of the perturbation increases, new irreducible representations appear, together with their associated local and quasilocal relaxation times. It must be borne in mind here, however, that the internal friction method can reveal only those representations which correspond to relaxation modes (redistribution of atoms) that lead to a change in the exterior shape of the sample.

Since the maximum number of irreducible representations for each point group is specified, an increase of the radius of action of the local center, starting with a certain value, does not lead to an increase in the number of resonant peaks, but only increases the degeneracy multiplicity of each peak (the number of relaxation modes corresponding to a given relaxation time) and shifts their positions. The degeneracy can be lifted for example, by a time-independent homogeneous elastic deformation of the crystal, which lowers the symmetry of the lattice, which in turn should lead to a splitting of the peaks. Such experiments can be exceedingly useful in the identification of the internal-friction mechanism. A study of the peak positions would make possible a sounding of the interaction between the impurities and the local centers.

It should be noted that, in the interpretation of data on the internal friction, peaks that differ greatly in temperature or in frequency are sometimes ascribed to different relaxation mechanisms. The discussion presented above shows that a series of peaks may be produced by one relaxation mechanism.

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[2)] In the model problem considered by us, concerning the spectrum of reciprocal relaxation times in a primitive cubic lattice, in which the escape of the migrating particle from one site ("trap") is difficult, the quasilocal reciprocal relaxation time $\nu_0 \to 0$ as $\alpha \to -1$, and the width of the peak $\Gamma \to 0$, so that the peak becomes asymptotically truly local.

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269