# Electron Localization in Quasicrystals

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The question of whether scattering by the almost-periodic lattice potentials of recently discovered metallic quasicrystals is able to explain the recently observed short mean free paths (about 1 Å) in these materials is discussed. It is shown that scattering by a three-dimensional, almost-periodic potential cannot account for such resistivities, but a model which includes structural defects in the three-dimensional Penrose tiling and large scattering of electrons due to $s$-$d$ resonant scattering can account for the experimental observations.

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Recently, rapidly cooled alloys of aluminum and manganese have been found which exhibit an electron diffraction pattern consistent with icosahedral point-group symmetry.[1] As such point-group symmetry is not permitted in conventional crystallography, these compounds are believed to be "quasicrystals," which are almost periodic rather than periodic.[2] Almost-periodic substances are predicted to be able to exhibit exotic band structure, with gaps appearing in the neighborhood of every energy.[3]

Although electron and x-ray diffraction-peak widths show that quasicrystals are coherent over distances of the order of hundreds of angstroms,[1,4] the measured resistivities for quasicrystals are of the order of 150 $\mu\Omega$-cm, implying a mean free path of only a few angstroms.[5] These results would on the surface appear to imply that the almost-periodic nature of the arrangement of the ions might be responsible for the observed short mean free paths. The present Letter will explore whether scattering of electrons by the three-dimensional almost-periodic lattice potential in a quasicrystal is able to explain the observed high resistivities.

It is shown in this article that, surprisingly, the scattering of electrons by the potential due to the almost-periodic lattice proposed for the quasicrystals does not contribute any resistivity *to any order in time-dependent perturbation theory,* but that the observed resistivity can be accounted for by defects in the perfect Penrose tiling. Althouth there have recently been studies of the electronic structure of certain models for the quasicrystals,[6] these treatments do not address themselves to the question of the effects of almost-periodicity on experimentally observed transport properties, which is addressed here.

Since aluminum and manganese are both relatively good metals at low temperatures, it might be reasonable to assume that weak pseudopotential theory and the Ziman method[7] can be used. For the quasicrystals, the scattering rate is given by the standard formula[8]

$$T^{-1}=(2\pi/\hbar)\sum_{\mathbf{G}}|v(\mathbf{G})|^2|S(\mathbf{G})|^2\sin^2[(\hbar/2m)(k^2-|\mathbf{k}-\mathbf{G}|^2)t]/t[(\hbar^2/2m)(k^2-|\mathbf{k}-\mathbf{G}|^2)]^2, \quad (1)$$

where $T$ is the scattering time, $\mathbf{k}$ is the electron wave vector, and $\mathbf{G}$ are the quasicrystal reciprocal lattice vectors,[4,9] which are linear combinations with integer coefficients of the six vectors given by $\mathbf{G}_j=(2\pi/a)(1+\tau^2)^{-1/2}\mathbf{g}_j$, where $\{\mathbf{g}_j\}$ is $\{(\tau,0,1),(1,-\tau,0),(\tau,0,-1)(1,\tau,0),(0,1,\tau),(0,-1,\tau)\}$, where $a$ is the length of a rhombohedral tile edge, and $\tau$ is the "golden mean" [i.e., $\tau=(\sqrt{5}+1)/2$]. Here, $v(\mathbf{G})$ is the Fourier transform of the atomic potential and $S(\mathbf{G})$ is the structure factor of the quasicrystal.[8] I have omitted the factor $1-\cos\theta$ in Ziman's formula[7] (where $\theta$ is the angle between $\mathbf{k}-\mathbf{G}$ and $\mathbf{k}$) for simplicity. The time $t$ is taken to infinity after the summation over $\mathbf{G}$ is performed. We will see that $T^{-1}$ approaches zero for the almost-periodic structure as $t$ approaches infinity.

Elser calculated the structure factor for the quasicrystal by representing it as a projection of a simple hypercubic lattice in six dimensions into the physical three-dimensional hyperplane.[9] He finds that $S(\mathbf{G})$ is proportional to sums of products $S_jS_lS_m$ with unequal values of $i,j,l$ where $S_j=\sin z_j/z_j$, $z_j=\frac{1}{2}\mathbf{G}_\perp\cdot\mathbf{a}_j^\perp$, where $a_j^\perp$ represents a projection of a simple hypercubic primitive lattice vector into the hyperplane perpendicular to the physical hyperplane and $\mathbf{G}^\perp$ is the projection of its reciprocal lattice vector in the hyperplane perpendicular to the physical one. The projection into the physical hyperplane gives $\mathbf{G}$ [in Eq. (1)]. Then, if

$$\mathbf{G}=\sum_j n_j\mathbf{G}_j,$$

we have

$$z_l=\tfrac{1}{2}\mathbf{G}_\perp\cdot\mathbf{a}_j^\perp=\tfrac{1}{2}\sum_j n_j\mathbf{G}_\perp^l\cdot\mathbf{a}_j^\perp=\tfrac{1}{2}\sum_j n_jP_{jl}^\perp, \quad (2)$$

where $P_{jl}^\perp$ is the projection operator onto the hyper-

plane perpendicular to the physical one, discussed by Elser.[8] As the limit of large $t$ is considered, only values of $\mathbf{G}$ in a small range around a value of $\mathbf{G}$ for which $|\mathbf{k}-\mathbf{G}|$ is very nearly equal to $|\mathbf{k}|$ can contribute. Then the values of $\mathbf{G}$ which contribute most strongly to Eq. (1) are the projections of points in a narrow strip perpendicular to the physical hyperplane, whose width corresponds to this region, in the reciprocal lattice of the six-dimensional simple hypercubic lattice.[9] This is illustrated by a simple one-dimensional example in Fig. 1.[9] We can see that although there exists a continuum of $\mathbf{G}$ values which contribute to Eq. (1), most correspond to very large values of $\mathbf{G}_\perp$ (i.e., they are far from the physical hyperplane) in the limit as the strip width approaches zero (i.e., as $t\rightarrow\infty$). Since Elser's structure factor becomes small when $\mathbf{G}_\perp$ becomes large, the structure factor for most of these points will be negligibly small, and hence, as we shall see, will make a contribution to Eq. (1) which approaches zero as $t$ approaches infinity. This is the reason that $T^{-1}$ is zero for the almost-periodic lattice. In more detail, if we could find a value of $\mathbf{G}$, call it $\mathbf{G}_0$, which is a combination of the six vectors $\{\mathbf{G}_j\}$ with small integer coefficients, such that $|\mathbf{k}-\mathbf{G}_0|$ is arbitrarily close to $|\mathbf{k}|$, the $\mathbf{G}$ values which dominate Eq. (1) would be those with $\mathbf{G}=\mathbf{G}_0+\Delta\mathbf{G}$, where $\Delta\mathbf{G}=(2\pi/a)[\tau^2+1]^{-1/2}$ times $(F_{l_1}\tau-F_{l_1+1},0,0)$, $(0,F_{l_2}\tau-F_{l_2+1},0)$, or $(0,0,F_{l_3}\tau-F_{l_3+1})$, where $\{F_l\}$ are the Fibonacci numbers, given by $F_l=F_{l-1}+F_{l-2}$, $F_1=1$, $F_2=2$. For large $l$, $F_l\tau-F_{l+1}$ is approximately proportional to $(F_l^{-1})$, a small number (this is actually true for $\tau$ any irrational number and $F_{l+1}$ and $F_l$ any two integers such that $F_{l+1}/F_l$ is a rational approximation to $\tau$). The vector $\Delta\mathbf{G}$ is easily shown to be a reciprocal lattice vector for the quasicrystal. These values of $\Delta G$ give the largest contribution to $S(\mathbf{G})$ since they give terms in $S$ which fall off only as $F_l^{-1}$, whereas other small values of $\Delta\mathbf{G}$ would make $S$ fall off faster. For very small values of $\Delta\mathbf{G}$, it is easily shown by use of Elser's results[9] that the dominant part of $S(\mathbf{G})$ is proportional to $F_l^{-1}$ for the large $l$ values, which occur when we have a small value $\Delta\mathbf{G}$ (remember that small $\Delta\mathbf{G}$ corresponds to large values of $\mathbf{G}_\perp$). This is easily shown by use of Elser's expressions for the projection operator and the structure factor, along with Eq. (2). [Again, this behavior of $S(\mathbf{G})$ is true for any projection angle of the physical hyperspace and hence any value of $\tau$, as stated above.] This is true for all values of $\mathbf{G}_0$ [most $\mathbf{G}_0$'s make $S(\mathbf{G})$ very small to start with]. Then, $1/T$ in Eq. (1) is proportional to

$$F_{l_{\min}}\sum_{l=l_{\min}}^{\infty}F_l^{-2},$$

where $l_{\min}$ is the minimum value of $l$ for which the energy difference in the argument of the sine is less than $\hbar/t$. [The factor $F_{l_{\min}}$ comes from the fact that the average value of the factor $\sin^2[\ ]t/t[\ ]^2$ in Eq. (1) in the range of $\mathbf{G}$ values for which it is reasonably large is proportional to $t$, which is proportional to $F_{l_{\min}}$ since $|\Delta\mathbf{G}|$ is proportional to $F_{l_{\min}}^{-1}$.] Thus, since the energy difference is nearly proportional to $F_l^{-1}$, as stated earlier, $l_{\min}$ approaches infinity as $t$ approaches infinity and hence $T^{-1}$ given by Eq. (1) approaches zero, i.e., the almost-periodic potential leads to no damping of the states, and hence, according to Ziman's work, will result in no resistivity. [Each term in Eq. (1) falls off at least that quickly; most fall off more rapidly as $t\rightarrow\infty$.] Although for some special almost-periodic potentials in one dimension, the spectrum will be completely fragmented by gaps[10] (making it highly likely that the Fermi level falls in a gap), in three dimensions there must be some bands which lie at the Fermi level. Including the difference between aluminum and manganese pseudopotentials would not change the results qualitatively.

These results can be generalized to arbitrary order in time-dependent perturbation theory by replacing $v(\mathbf{G})S(\mathbf{G})$ by the $T$ matrix for the quasicrystal, which can be expressed as a perturbation-theory expansion in $v$. Since $\Delta\mathbf{G}=\sum_i n_i\mathbf{G}_i$, if the $n_i$'s are divided among the matrix elements in a given order in perturbation theory (i.e., each term is proportional to $\langle\mathbf{k}|v|\mathbf{k}+\mathbf{G}_1\rangle\langle\mathbf{k}+\mathbf{G}_2|v|\mathbf{k}+\mathbf{G}_3\rangle\ldots$), the $T$ matrix is proportional to $\prod_j m_j^{-1}$ or smaller where $\{m_j\}$ are integers such that $\sum_j m_j=F_l$, since each $S(\mathbf{G})$ associat-

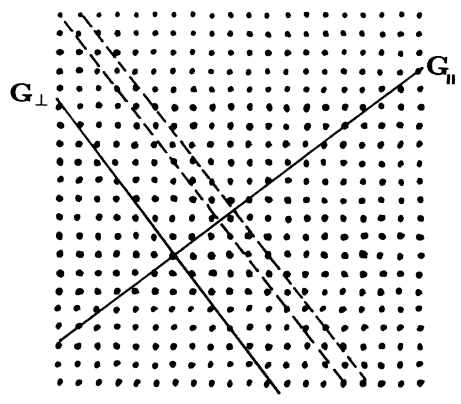


FIG. 1. The calculation of the electron scattering rate for electrons in a one-dimensional almost-periodic lattice projected from a two-dimensional simple square lattice. The reciprocal lattice is calculated by projecting from the square-lattice reciprocal lattice shown onto the $G_\parallel$ axis. The strip between the dotted lines illustrates the range of $\mathbf{G}$ values which contribute to Eq. (1) for a finite value of $t$. The projection of each reciprocal lattice point that falls inside this strip onto the $G_\parallel$ axis gives the allowed values of $\mathbf{G}$ which contribute to Eq. (1).

ed with each matrix element is proportional to the reciprocal of one of these integers or smaller. Thus, each order in perturbation theory will approach zero faster than the zeroth-order term as $l$ approaches infinity. Hence, the often used procedure of replacing the pseudopotential in the Ziman formula by a $T$ matrix[11] cannot account for the observed resistivity.

The manganese atoms, however, could be strong scatterers, for which perturbation theory is not valid, for electrons at the Fermi surface because of resonant scattering by the $3d$ states, as occurs in liquid metals.[11] Consider, as a model for this, electrons propagating through an almost-periodic array of hard spheres (representing the manganese atoms). Certainly for electron wavelengths long compared to the sphere radius, the method of Lax may be applied.[12] The resulting decay distance for the wave is the reciprocal of the product of the total scattering cross section and the number of scatterers per unit volume. Lax's arguments for a periodic crystal can be taken over for the almost-periodic case, if for the structure factor occurring in the expression for the total scattering cross section we use the one found by Elser.[9] Whereas for the periodic case the cross section is zero for all wave vectors except those which satisfy the Bragg condition, for the almost-periodic case there is almost a continuum of $\mathbf{k}$ values satisfying the Bragg condition. The discussion after Eq. (2), however, shows that the structure factor is negligibly small for most elastic-scattering processes. This implies that the wave function will not decay in the present three-dimensional almost-periodic potential, despite the fact that the potential is strong. Thus, the occurrence of high resistivity can only be accounted for by including defects in the almost-periodic quasicrystal structure. For example, Elser proposed the existence of structural defects, which introduce a Debye-Waller–type factor but do not preclude the occurrence of a well-defined diffraction pattern.[13] Henley suggested that these defects might be responsible for the observed resistivity.[14]

In order to determine the damping of the electron wave function using Lax's formula we must calculate the total cross section for incoherent scattering produced by the defects, which requires a knowledge of the average of the square of the structure factor over all defect configurations. This may be found by use of the method of Zia and Dallas,[15] which shows that the structure factor of quasicrystal is given by

$$\int d^3p\, R(-\mathbf{p})\, U(\mathbf{k},\mathbf{p}). \tag{3}$$

Here $U(\mathbf{k},\mathbf{p})$ is the spatial Fourier transform of the function $U(\boldsymbol{\xi},\boldsymbol{\eta})$ defined by

$$U(\mathbf{r}^6) = U(\boldsymbol{\xi},\boldsymbol{\eta}) = \textstyle\sum_j \delta^6(\mathbf{r}^6 - \mathbf{R}_j^6), \tag{4}$$

where $\mathbf{r}^6$ is the six-dimensional position vector and $\{\mathbf{R}_j^6\}$ are the location of the lattice points in a six-dimensional simple hypercubic lattice and $\boldsymbol{\xi}$ and $\boldsymbol{\eta}$ are the three-vectors labeling points in the physical three-dimensional hyperplane and the hyperplane perpendicular to it, respectively. $R(\mathbf{p})$ is the Fourier transform of the function $R(\boldsymbol{\eta})$ which is unity if $\boldsymbol{\eta}$ falls within the triacontrahedron cell containing the coordinates in the hyperplane perpendicular to the physical hyperplane of those points in the six-dimensional lattice which when projected into the physical hyperplane give the quasicrystal lattice, and zero otherwise. To account for the structural defects, we add a small six-dimensional random variable $\mathbf{u}_j^6$ to $\mathbf{R}_j^6$, which has components only in the hyperplane perpendicular to the physical one. The average of the square of Eq. (3) is easily shown to be proportional to

$$\int d^3p\, d^3p' \textstyle\sum_{jj'} \exp[i\mathbf{k}^6\cdot(\mathbf{R}_j^6 - \mathbf{R}_{j'}^6)]\, R(-\mathbf{p})\, R(-\mathbf{p}')\, \langle e^{i\mathbf{p}\cdot\mathbf{u}}\rangle \langle e^{-i\mathbf{p}'\cdot\mathbf{u}}\rangle + \int d^3p\, |R(-\mathbf{p})|^2 [1 - |\langle e^{i\mathbf{p}\cdot\mathbf{u}}\rangle|^2], \tag{5}$$

where $\mathbf{k}^6$ is the six-dimensional wave vector corresponding to the three-dimensional vectors $\mathbf{k}$ and $\mathbf{p}$ in Eq. (3), respectively, and the angular brackets denote an average over the $u$'s, with distribution function $P(\mathbf{u})$. The first term on the right-hand side of Eq. (5) gives the Bragg scattering, reduced by an effective Debye-Waller factor $\langle e^{i\mathbf{p}\cdot\mathbf{u}}\rangle$ and the second term gives the incoherent scattering. For example, if $P(\mathbf{u})$ is a Gaussian function $(\alpha^3/\pi^{3/2})\exp(-\alpha|\mathbf{u}|^2)$, where $\alpha$ is a parameter, the second term in Eq. (9) is easily found to be proportional to

$$1 - [\alpha^3/(2\pi)^{3/2}]\,\Omega_t^{-1} \int_{\Omega_t} d^3r \int d^3r' \exp(\tfrac{1}{2}\alpha^2|\mathbf{r}'-\mathbf{r}|^2), \tag{6}$$

where $\Omega_t$ is the volume of the triacontrahedron and the subscript $\Omega_t$ on the integral signifies an integral over this volume. If $\alpha^{-1}$ is small compared to a mean radius of the triacontrahedron, Eq. (6) gives zero except for $r^{-1}$ in a shell of thickness $\alpha^{-1}$ around the boundary of the triacontrahedron. Thus, Eq. (6) gives a result $3(1-\gamma)\langle u^2\rangle^{1/2}/R$, where $\gamma$ is a number of order unity and $R$ is the mean radius of the triacontrahedron. The factor $\langle u^2\rangle^{1/2}/R$ is of the order of the density of defects (i.e., number per lattice site). This is easily seen in the one-dimensional example.[9] Then, if $\langle u^2\rangle^{1/2}$ is equal to $\frac{1}{5}$ of the mean triacontrahedron radius, the incoherent part of the mean square structure factor is $\approx 0.6$ but the low-order Bragg peaks are only reduced by about 50% by the effective Debye-Waller factor.

Thus, we see that the contribution to the mean-

square structure factor for incoherent scattering can be of the order of the Bragg-scattering part. Since the total-scattering cross section for a single hard sphere is $4\pi$ times the square of the sphere radius,[8] we must conclude on the basis of Lax's argument that the incoherent scattering could lead to a total-scattering cross section for the quasicrystal comparable to the square of this radius, and hence to a decay distance of the wave function not much larger than the radius of a manganese atomic core. This could explain the fact that the quasicrystals seem to have mean free paths of the order of an angstrom, like transition-metal metallic glasses and liquid metals. It would also imply that if quasicrystals could be made which had fewer defects or which did not have *d* states at or near the Fermi level, their resistivities should be much smaller, and perhaps interesting electrical properties due to almost-periodicity could be observed in such substances.[3]

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