temperature $T \sim T_c$, T_1 becomes shorter than that in a normal state, and (ii) for temperatures $T \ll T_c(0)$, T_1 becomes longer compared with that in a normal state. Our experimental result can be understood qualitatively on the basis of the theory of gapless superconductivity.

We have greatly benefited from discussions with M. Cyrot, P. G. de Gennes, and K. Maki, and from correspondence with V. Ambegaokar.

[1]K. Asayama and Y. Masuda, J. Phys. Soc. Japan 20, 1290 (1965).

[2]W. Fite, II, and A. G. Redfield, Phys. Rev. Letters 17, 381 (1966), and Phys. Rev. 162, 358 (1967).

[3]B. G. Silbernagel, M. Weger, W. G. Clark, and J. E. Wernick, Phys. Rev. Letters 17, 384 (1966).

[4]B. G. Silbernagel, M. Weger, W. G. Clark, and J. E. Wernick, Phys. Rev. 153, 535 (1967).

[5]K. Asayama and Y. Masuda, in Proceedings of the International Conference on Magnetic Resonance and Relaxation, Fourteeth Colloque Ampere, Ljubljana, Yugoslavia, September, 1966, edited by R. Blinc (North-Holland Publishing Company, Amsterdam, The Netherlands, 1968), p. 439.

[6]S. Komjathy, J. Less-Common Metals 3, 486 (1961).

[7]M. Cyrot, C. Froidevaux, and D. Rossier, Phys. Rev. Letters 19, 647 (1967).

[8]L. C. Hebel and C. P. Slichter, Phys. Rev. 113, 1504 (1959); Y. Masuda and A. G. Redfield, Phys. Rev. 125, 159 (1962).

[9]B. G. Silbernagel and V. Jaccarino, J. Phys. Soc. Japan 23, 472 (1967).

[10]A. Griffin and V. Ambegaokar, in Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus, Ohio, 1964, edited by J. G. Daunt, D. O. Edwards, F. J. Milford, and M. Yaqub (Plenum Press, New York, 1965), p. 524.

[11]M. Cyrot, J. Phys. (Paris) 27, 283 (1966).

[12]Groupe de Superconductivité d'Orsay, Physik Kondensierten Materie 5, 141 (1966).

[13]D. Eppel, W. Pesch, and L. Tewordt, Z. Physik 197, 46 (1966).

STARK LADDER IN SOLIDS?

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It is shown that the Stark ladder for conduction electrons in a constant electric field does not follow from the existing theory. The former proofs of the ladder are shown to be based on inconsistent assumptions. A discussion is given of a tight-binding model which leads to a ladder when overlap is completely neglected.

Since the Stark ladder for a Bloch electron in a constant electric field was first predicted,[1] a number of attempts have been made to find experimental evidence for its existence.[2] All these attempts were unsuccessful, and different reasons were given for the failure to detect effects connected with the Stark ladder.[3] It is shown that the previous derivations of the Stark ladder[1,4,5] are based on inconsistent assumptions. This statement is counter to the prevailing opinion in the literature.[1,3-8] It was already pointed out[9] that some previous calculations of the Franz-Keldysh effect and Zener tunneling contain a contradiction which reflects the inconsistency in the Stark ladder. In order to obtain a qualitative picture of the problem, the tight-binding approximation for a Bloch electron in an electric field is discussed. It is shown that a Stark ladder follows from the periodicity of the lattice if there is no overlap between electronic functions on different sites.

In order to show where the inconsistencies in the previous derivations lie, we consider for simplicity the one-dimensional case. Schrödinger's equation for an electron in a periodic potential $V(x)$ and a constant electric field E is ($\hbar = 1$)

$$\left[\frac{1}{2m}\left(-i\frac{\partial}{\partial x}\right)^2 + V(x) + eEx\right]\psi(x) = \epsilon\psi(x). \tag{1}$$

The first indication of a Stark ladder[1] came from the translational features of the Hamiltonian (1). It is easily seen that if ϵ is an eigenvalue for the state $\psi(x)$, then

$$\epsilon + maeE \tag{2}$$

is an eigenvalue for the state $\psi(x-ma)$, where a is the lattice constant and m is any integer. The term $maeE$ leads to what is called the Stark ladder.[1] From Eq. (1) it is clear that since there are no restrictions on ϵ that one started with, there is no reason to conclude that the only pos-

sible values of the energy are $maeE$ and that the energy spectrum is quantized. One way to obtain quantized levels is to limit the possible values of ϵ by using a one-band model.[1,5,8] One starts with the Schrödinger equation in the nk representation,[5,8]

$$\left[\epsilon_n(k)+eEi\frac{\partial}{\partial k}+eEX_{nn}(k)\right]B_n(k)+\sum_{m\neq n}eEX_{nm}(k)B_m(k)=\epsilon B_n(k), \quad (3)$$

where

$$X_{nm}(k)=\int u_{nk}^*(x)i\frac{\partial}{\partial k}u_{mk}(x)dx \quad (4)$$

with $u_{nk}(x)$ being the periodic part of the Bloch function. The function $B_n(k)$ is assumed to be periodic because it appears as expansion coefficients in a series of Bloch functions $\psi_{nk}(x)$ for the solution of Eq. (1):

$$\psi(x)=\sum_{nk}B_n(k)\psi_{nk}(x). \quad (5)$$

A one-band model is obtained by neglecting the interband terms in Eq. (3), which then becomes

$$\left[\epsilon_n(k)+eEi\frac{\partial}{\partial k}+eEX_{nn}(k)\right]B_n(k)=\epsilon B_n(k). \quad (6)$$

Its solution is[8]

$$B_n(k)=\text{const}\times\exp\left\{-\frac{i}{eE}\int_0^k[\epsilon-\epsilon_n(k)-eEX_{nn}(k)]dk\right\}. \quad (7)$$

The periodicity requirement on $B_n(k)$ leads to the Stark ladder[1,5,8]:

$$\epsilon=maeE+\frac{a}{2\pi}\int_0^{2\pi/a}[\epsilon_n(k)+eEX_{nn}(k)]dk. \quad (8)$$

As is seen, now the energy spectrum is discrete, the second term in (8) being a well-defined constant. The inconsistency in this proof of Stark's ladder is as follows. From Eq. (4) one has

$$i\frac{\partial}{\partial k}u_{nk}(x)=\sum_m X_{mn}(k)u_{mk}(x). \quad (9)$$

The assumption that interband terms can be neglected leads to

$$i\frac{\partial}{\partial k}u_{nk}(x)=X_{nn}(k)u_{nk}(x) \quad (10)$$

with the solution

$$u_{nk}(x)=\Phi(x)\exp\{-i\int X_{nn}(k)dk\}, \quad (11)$$

where $\Phi(x)$ is a function of x only. It is clear that the usual boundary conditions on $u_{nk}(x)$, namely

$$u_{nk+2\pi/a}(x)=\exp\{-i(2\pi/a)x\}u_{nk}(x),$$

are not satisfied by solution (11), and the assumption (10) which comes from neglecting interband terms for all values of k is therefore contradictory. Since Eq. (10) cannot hold for all values of k [otherwise we would get solution (11) with the contradictions mentioned before], the one-band model for the entire Brillouin zone is inconsistent. Now, the periodicity requirements on $B_n(k)$ are a consequence of the boundary conditions on $u_{nk}(x)$, and since we have shown that the one-band model does not hold for all k values, one cannot assume that solution (7) is correct for the entire Brillouin zone, and therefore the periodic boundary conditions on $B_n(k)$ that led to the Stark ladder have no justification.

It is to be pointed out that the assumption $B_n(k)\gg B_m(k)$ in expansion (5) would not be sufficient for obtaining Eq. (6). The reason is that it is not enough to assume that $\psi(x)$ is expandable in one-band Bloch functions. One has also to assume that $x\psi(x)$ can be expanded in one-band Bloch functions. The last requirement will necessarily lead to the assumption $X_{nn}(k)\gg X_{mn}(k)$ for $n\neq m$ and therefore to Eq. (10).

The most general proof of the Stark ladder, without any assumption of a one-band model, was given by Wannier.[4] In order to discuss this proof let us write down Schrödinger's equation for a Bloch electron in a constant electric field in the kq representation[10]:

$$\left[\frac{1}{2m}\left(-i\frac{\partial}{\partial q}\right)^2+V(q)+eE\left(i\frac{\partial}{\partial k}+q\right)\right]C(kq)=\epsilon C(kq). \quad (12)$$

Equation (12) is an exact Schrödinger equation for the problem. In Wannier's proof[4] an approximate equation is used,

$$\left[\frac{1}{2m}\left(-i\frac{\partial}{\partial q}\right)^2+V(q)+eE\left(i\frac{\partial}{\partial k}+q\right)\right]b_l(q;k)=W_l(k)b_l(q;k), \quad (13)$$

where $b_l(q;k)$ is a Bloch-type function, l being a band index, and $W_l(k)$ is in some way connected

with the real energy values of the system. It is then shown that the function

$$\psi(qt) = b_l(q; k-eEt) \times \exp\left[\frac{i}{eE}\int_k^{k-eEt} W_l(k)dk\right] \quad (14)$$

is an exact solution of the time-dependent Schrödinger equation

$$\left[\left(-i\frac{\partial}{\partial q}\right)^2 + V(q) + eEq\right]\psi(qt) = i\frac{\partial\psi(qt)}{\partial t}. \quad (15)$$

The Fourier analysis of the solution (14) gives then the possible energies of the system as

$$\int_0^{2\pi/a} W_l(k)dk + maeE. \quad (16)$$

This is the familiar ladder (8). For deriving the main result (16), Eq. (13) was used with the particular assumption that the quantity $W_l(k)$ depends on a band index l and on k. This assumption is very crucial in Wannier's proof of the ladder. It makes the first term in formula (16) a well-defined constant. As was already mentioned, it is this restriction that leads to a Stark ladder. If, however, in Wannier's proof one would start with the exact Eq. (12) and not with Eq. (13), then $W_l(k)$ in formula (16) would have to be replaced by the energy ϵ. The result would be

$$\epsilon + maeE. \quad (17)$$

This result was already obtained from translational symmetry and leads to no Stark ladder because ϵ, like in (2), is arbitrary. We see therefore that Wannier's argument when applied to the correct equation does not lead to the ladder. It is to be noticed that the derivation of Eq. (13) is based on a perturbation procedure[1,4] which for an an electric field is very difficult to justify.

Let us now consider two limiting cases in the dynamics of conduction electrons in solids and demonstrate that a Stark ladder in the energy spectrum is very improbable. In the limit when the periodic potential of the crystal, $V(x)$ in Eq. (1), is very weak, one approaches the free-electron case for which the energy spectrum is known to be continuous.[11] It is therefore clear that one should not expect a Stark ladder to exist when the periodic potential of the crystal is very weak. This comment can be considered as another indication of inconsistency in Wannier's "general proof" because in the latter the strength of the periodic potential is not mentioned. The other limiting case is the tight-binding approximation. A Stark ladder is most favorably expected in solids where such an approximation is applicable.[3-8] We show that this view is unjustified for conduction electrons and that no ladder is obtained even in the most favorable case for its existence. In the tight-binding approximation the potential of the crystal is written as a sum of atomic potentials V_A:

$$V(x) = \sum_{n=1}^{N} V_A(x-na), \quad (18)$$

where we have assumed that the length of the linear chain is Na. Let $\psi_A(x)$ be a solution of Schrodinger's equation for an isolated atom corresponding to the energy ϵ_A. Consider first the most extreme limit when there is no overlap between different atomic functions and between an atomic function on one site and an atomic potential on any other site. For this case, in the absence of an electric field, any atomic function $\psi_A(x-ma)$ will be an eigenstate of Eq. (1) corresponding to the energy ϵ_A. The level ϵ_A is therefore N-fold degenerate. When considered as a perturbation, the electric field will split this level into N sublevels with energies

$$\epsilon_m = \epsilon_A + eEX + meEa, \quad (19)$$

where m assumes values from 1 to N. The quantity eEX gives the regular atomic Stark shift[11]:

$$eEX = eE\int x\,|\psi_A(x)|^2 dx. \quad (20)$$

The state that corresponds to ϵ_m in (19) is $\psi_A(x-ma)$. In order for the perturbation procedure to be valid the width of the split level, $NeEa$, has to be smaller than the energy interval to the next atomic level. The above result is therefore correct only for a limited finite crystal. It is important to notice that the ladder structure in the spectrum (19) follows merely from the periodic spacing of the isolated atoms and has nothing to do with any band structure in the spectrum of the solid. The ladder follows from the fact that the potential difference on adjacent sites in the crystal is originated by the electric field only, and equals eEa. In a real crystal, however, there is always some overlap between adjacent atomic functions, which is the origin of energy bands. The width of a band $\Delta\epsilon$ in the tight-binding approximation is given by the overlap integral and

is of the order[12]

$$\Delta\epsilon \sim \int \psi_A^*(x) V_A(x) \psi_A(x+a) dx. \quad (21)$$

Result (21) is obtained from Eq. (1) by considering the periodic potential as a perturbation on a set of isolated atoms in the case $E=0$. Under this crystal perturbation the N-fold degenerate atomic level splits into N levels that form a band of width $\Delta\epsilon$. The spacing between the levels in the band is of the order $\Delta\epsilon/N$. One arrives therefore at the following result: When there is no overlap in the crystal, Eq. (1) leads to a Stark ladder (19) with a spacing eEa, while, when $E=0$ and the overlap is taken into account, Eq. (1) gives a band of width $\Delta\epsilon$ [relation (21)] with levels of the order $\Delta\epsilon/N$ apart. It is clear that when both perturbations are switched on (a Bloch electron in an electric field), a Stark ladder (19) could be expected only when $\Delta\epsilon/N$ is much smaller than eEa. An exact Stark ladder (19) is obtained only in the limit of a vanishing band width, $\Delta\epsilon=0$. We come to the conclusion that the banding of an atomic level destroys the Stark ladder and that the latter should not be expected for conduction electrons in crystals. The ladder (19) that is predicted by the tight-binding approximation is connected with an array of isolated atoms and follows from the periodicity of the crystal only. Such a ladder could in principle be measured by exciting a nonconduction electron to jump from one site in a crystal to the next one.

The inconsistency in using Bloch functions for the one-band approximation[3-8] can now be seen from a different point of view. For constructing a Bloch function $\psi_{nk}(x)$ out of atomic functions $\psi_A(x)$ in the tight-binding approximation, the following expression is used[12]:

$$\psi_{nk}(x) = \sum_{m=1}^{N} \exp(ikma)\psi_A(x-ma). \quad (22)$$

It is easy to check that $\psi_{nk}(x)$ is a Bloch function when the summation in (22) extends from $-\infty$ to ∞. However, for a finite N (we cannot assume that the N atoms form a part of an infinite chain when $E \neq 0$) $\psi_{nk}(x)$ is no longer a Bloch function. In the absence of an electric field one can make $\psi_{nk}(x)$ to be a Bloch function by bending the chain into a circle[13] and the result (21) will hold. This, however, is impossible when an electric field is present because the potential of the field will become discontinuous. In order to use Bloch functions in the tight-binding approximation when an electric field is present, therefore, one has to deal with an infinite chain. This will lead to an infinite number of levels in the Stark ladder (19) [see also result (8)] which is meaningless because the ladder then covers the whole energy range from $-\infty$ to $+\infty$. It follows therefore that in the considered tight-binding model the one-band derivation of the Stark ladder[1,5,8] [formulas (5)-(11)] is incorrect.

In conclusion let us point out that the previous derivations of a Stark ladder for conduction electrons in solids are inconsistent. Both the free-electron and the tight-binding models testify against the existence of such a ladder. This therefore casts doubts whether the experimental attempts to find effects connected with the Stark ladder for conduction electrons[2] will be successful.

The authors would like to thank P. N. Argyres and L. Gruenberg for a very illuminating discussion and helpful criticism. Thanks are due to H. Praddaude, J. Hanus, M. Reine, F. Arntz, and J. N. Churchill for a discussion of the paper. The author is in particular indebted to B. B. Schwartz for reading the manuscript and for valuable suggestions. It is a pleasure to thank the Physics Department and the Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, for very kind hospitality.

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†Supported by the U. S. Air Force Office of Scientific Research.

[1]Gregory H. Wannier, Phys. Rev. 117, 432 (1960).

[2]A. G. Chynoweth, G. H. Wannier, R. A. Logan, and D. E. Thomas, Phys. Rev. Letters 5, 57 (1960); B. B. Snavely, Bull. Am. Phys. Soc. 10, 344 (1965); V. S. Vavilov, V. B. Stopachinskii, and V. S. Chanbarisov, Fiz. Tverd. Tela 8, 2660 (1966) [translation: Soviet Phys.-Solid State 8, 2126 (1967)].

[3]Petros N. Argyres, Phys. Rev. 126, 1386 (1962); Yizhak Yacoby, Phys. Rev. 140, A263 (1965); W. Franz, Phys. Status Solidi 1, K4 (1961); B. B. Snavely, Solid State Commun. 4, 561 (1966); Yu. A. Kurskii and V. B. Stopachinskii, Fiz. Tech. Poluprov. 1, 106 (1967) [translation: Soviet Phys.-Semicond. 1, 81 (1967)]; Yu. A. Bychkov and A. M. Dykhne, Zh. Eksperim. i Teor. Fiz. 48, 1174 (1965) [translation: Soviet Phys. -JETP 21, 783 (1965)].

[4]Gregory H. Wannier, Rev. Mod. Phys. 34, 645 (1962).

[5]Joseph Callaway, Phys. Rev. 130, 549 (1963).

[6]M. Chester and L. Fritsche, Phys. Rev. 139, A518 (1965).

[7]D. E. Aspnes, Phys. Rev. (to be published).
[8]E. O. Kane, J. Phys. Chem. Solids 12, 181 (1959).
[9]L. Fritsche, Phys. Status Solidi 13, 487 (1966).
[10]J. Zak, Phys. Rev. Letters 19, 1385 (1967); Phys. Rev. 168, 686 (1968).
[11]L. D. Landau and E. M. Lifshitz, Quantum Mechanics (Pergamon Press, New York, 1958).
[12]A. H. Wilson, The Theory of Metals (University Press, Cambridge, England, 1965).
[13]H. Jones, The Theory of Brillouin Zones and Electronic States in Crystals (North-Holland Publishing Company, Amsterdam, The Netherlands, 1960).

MEASUREMENT OF THE s-d ADMIXTURE FOR Mn IN Cu †

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Measurements of the spin-resonance linewidth for Mn in dilute copper alloys provides evidence of the extended nature of the magnetic impurity wave function in the metal and allows a straightforward determination of the s-d admixture $V_{dk} \simeq 1$ eV. A theoretical treatment of the local moment spin relaxation via the distant impurity spin-orbit interaction is given.

Recently, measurements of the electron spin-resonance linewidth of Mn in copper have confirmed that the s-d exchange interaction is the mechanism responsible for the observed line broadening with increasing temperature.[1] The linewidth increases linearly with temperature, as predicted for a "bottlenecked" system by Hasegawa.[2] However, we have observed that the linewidth becomes temperature independent at sufficiently low temperatures. Moreover, when nonmagnetic impurities are added, the residual linewidth increases linearly with impurity concentration. Figure 1 shows the residual linewidth for various concentrations of Si and Al added as impurities to 0.1% Mn in copper.[3] The arc-melted alloys were prepared in our laboratory and were subsequently annealed and quenched from 1000°C. Metallographic inspection showed no precipitation. The quoted impurity concentrations were obtained from chemical analysis. All measurements were made on powder samples (<30 μ) at 30 GHz. The linewidths shown in Fig. 1 are temperature independent for $T < 4.2$°K.

We propose that the mechanism responsible for this temperature-independent residual linewidth arises from the admixture of conduction-

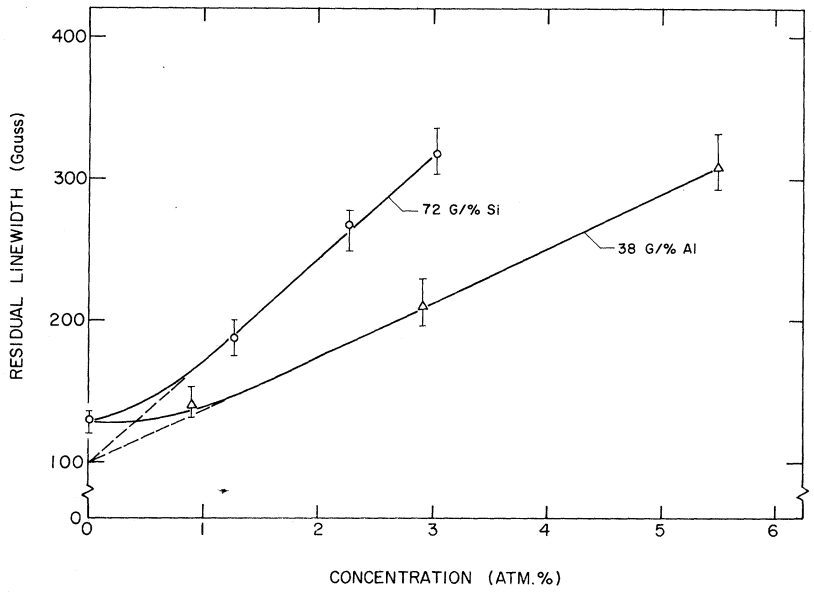

FIG. 1. Mn spin-resonance linewidth versus concentration of Si and Al impurity in copper. The pure-sample linewidth (i.e., no added impurity) is caused by surface relaxation. The linewidth increases at the rate of 72 G/% Si or 38 G/% Al. The measured widths are temperature independent below 4.2°K.