Stark Ladder in Solids? A Reply to a Reply

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IN a recent Physical Review Letter by Zak,[1] the existence of a Stark ladder in solids was analyzed. This letter had a twofold purpose. First, to point out that there is actually no correct theoretical prediction for such a ladder (the existing predictions being inconsistent). Secondly, to stimulate a discussion on the subject of a Bloch electron in an electric field. One of the reactions to this letter is a comment by Wannier appearing in this issue.[2] The author of this comment was the first to predict the Stark ladder,[3] and he also was the first to be involved in an unsuccessful attempt to measure this ladder.[4] In his comments, Wannier concentrates on "two errors" in Zak's paper[1] and on their "rectification." These so-called "errors" appear in one paragraph of Ref. 1, where Wannier's "general proof" of the Stark ladder is discussed and proven to be wrong.

In this paper a discussion of Wannier's reply[2] to the Physical Review Letter[1] is given, and it is shown that the claimed "errors" are not errors. The discussion is based on material (in particular equations) that appears in Refs. 1 and 2, to which the reader is referred for details.

The claimed "errors" are as follows. The first "error" is the statement that Wannier's equation appearing as Eq. (13) in Ref. 1 is an approximate one. The second "error" is the statement that ϵ in Eq. (17) of Ref. 1 is arbitrary. We will not discuss the second "error," because it was created by the author of Ref. 2 by leaving out a part of a sentence, which then became unclear. The reader is referred to Ref. 1 for details.

As to the first "error," it is not difficult to prove that it is not an error. The exact equation for a Bloch electron in an electric field was obtained on the basis of the kq representation[5] and is Eq. (12) of Ref. 1. This exact equation contains no band index and has the energy of the problem on the right-hand side. Only if a band index can be assigned to Eq. (12) of Ref. 1 will Wannier's equation [Eq. (13) of Ref. 1], with the function W (see Ref. 1) replaced by the energy ϵ, be correct. For example, the model discussed in Ref. 1 shows that such an assignment of a band index is possible in the extreme tightbinding approximation. It is clear that no band index is meaningful in the other extreme case of a free electron.[1] The approximate nature of Wannier's equation [Eq. (13) of Ref. 1] is therefore obvious.

One should point out that before the kq representation was developed, Wannier's equation [Eq. (13) in Ref. 1] wasn't well understood. Its approximate nature became clear only after the meaning of the variable in this equation was explained by the kq representation. The "rigorous proof" of this equation in Ref. 2 doesn't add anything to either its contents or its understanding. It is not worthwhile to get into details of this proof because we know that this equation cannot be exact [the exact equation is Eq. (12) of Ref. 1]. We would, however, like to make two remarks and shed some light on this "proof." The first remark is that the introduction of a band index in Eq. (4) of Ref. 2 is completely unjustified (this is an important point because the existence of a band index is crucial in the proof of a Stark ladder[1]). This can be seen by pointing out that the eigenvalues of the operator $O(T)$ in Eq. (4) of Ref. 2 are known and are given by $e^{(i/\hbar)\epsilon T}$, where ϵ are the eigenvalues of the energy operator in (1) or (2) of Ref. 2, and T is given by (3) of Ref. 2. Only if the energy spectrum is discrete (this is exactly what one has to prove in order to show that a Stark ladder exists[1]) will Eq. (4) of Ref. 2 contain a band index. The author of Ref. 2 assumes, therefore, what he wants to prove.[6]

The other remark is with respect to the derivation of Eq. (10) from Eq. (9) in Ref. 2. The correct equation for the time development of a wave function is

$$\Psi(t)=0(t)\Psi(0) \tag{1}$$

and not Eq. (9) of Ref. 2. Equation (1) differs from the latter by a phase factor $e^{i\Psi_l(eEt/\hbar)}$. It can be easily seen that Eq. (10) of Ref. 2 becomes the regular time-dependent Schrödinger equation when the correct time-development equation [Eq. (1)] is used. The meaningless $W_l(k)$ function on the right-hand side of Eq. (10) in Ref. 2 is a consequence of the arbitrary phase in Eq. (9) of Ref. 2.

In conclusion, one should point out that Ref. 1 raises the question of whether the Stark ladder in solids exists. There is no general answer to this question today and further investigation of the problem is needed. What is clear from Ref. 1 is that no consistent prediction of the ladder for conduction electrons in solids was given in the past [it is worthwhile to mention that the Stark ladder was usually connected with conduction electrons, and attempts to measure it were performed on crystals

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[2] G. H. Wannier, preceding paper, Phys. Rev. **181**, 1364 (1969).

[3] G. H. Wannier, Phys. Rev. **117**, 432 (1960).

[4] A. G. Chynoweth, G. H. Wannier, R. H. Logan, and D. E. Thomas, Phys. Rev. Letters **5**, 57 (1960).

[5] J. Zak, Phys. Rev. Letters **9**, 1385 (1967); Phys. Rev. **168**, 686 (1968).

[6] G. H. Wannier and D. R. Fredkin, Phys. Rev. **125**, 1910 (1962).

with relatively high conductivity (for references see Ref. 1)]. Although Wannier concurred in his Comment[2] with the main result of Zak's paper[1] and claims now that "a truly discrete spectrum" for a Bloch electron in an electric field "is unlikely," it is regrettable that he completely overlooked the new development in the dynamics of electrons in solids brought about by the kq representation.

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Addendum to Experimental Determination of the Effect of Hydrostatic Pressure on the Fermi Surface of Copper: Zero-Pressure de Haas–Van Alphen Frequencies*

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Accurate zero-pressure de Haas–van Alphen frequencies associated with the [100] belly, [100] rosette, and [110] dogbone cross sections of the Fermi surface of Cu obtained using *in situ* NMR field determinations are presented.

In a recent paper on the effect of hydrostatic pressure on the Cu Fermi surface,[1] we parenthetically included the values we obtained for the zero-pressure de Haas–van Alphen frequencies associated with cross-sectional areas for fields along principal symmetry directions. Two of the frequencies had been obtained previously[2] with *in situ* NMR field determinations, while the remaining three were obtained less carefully using the current-field calibration of the solenoid. It has come to our attention[3,4] that there is considerable interest, from the standpoint of precise theoretical fits to the Cu Fermi surface, in very accurate absolute values of these other three frequencies. Furthermore, the ratio of the [100] belly to [100] rosette frequencies derivable from our quoted values differed outside of our estimated uncertainty from the directly determined ratio (from the resultant pattern of the two frequencies) of Halse.[4]

We therefore have measured these frequencies using *in situ* NMR field determinations in each case over a minimum of 1000 oscillations using the same procedure as in Ref. 2. Our values for the five cross sections are listed in Table I. The ratio of $B[100]/R[100]$ is now 2.436($\pm$0.003), in excellent agreement with Halse.[4] (We use the notation B for belly, R for rosette, and D for dogbone with the appropriate field direction given in square brackets.) Our underestimate of the uncertainty in our quoted value[1] for $B[100]$ may have stemmed from slight changes in the current-field value for the solenoid which can introduce sizable errors over the short field ranges used in our pressure study. We have also listed directly determined ratios of $B[111]/B[100]$ and $D[110]/R[100]$ obtained by placing two crystals in the holder as well as the directly determined ratio of $B[100]/R[100]$. While these ratios can be determined experimentally to high precision, the relatively large uncertainties quoted stem from the $\sim 1°$ uncertainty in positioning the samples in the field.[5] (Sample orientations were determined relative to the sample holder by back-reflection Laue patterns.) Considering orientation uncertainties, our ratios are in satisfactory agreement with those derivable from the data of Joseph *et al.*[5]

TABLE I. Experimental de Haas–van Alphen frequencies and frequency ratios[a] for Cu. Frequencies are given in G.

Cross section	Frequency
Belly [111] (B[111])	$(5.814\pm0.006)\times10^8$
Neck [111] (N[111])	$(2.177\pm0.002)\times10^7$
Dogbone [110] (D[110])	$(2.514\pm0.003)\times10^8$
Belly [100] (B[100])	$(5.998\pm0.006)\times10^8$
Rosette [100] (R[100])	$(2.462\pm0.003)\times10^8$

[a] $B[100]/B[111]=1.032\pm0.001$, $B[100]/R[100]=2.436\pm0.002$, and $D[110]/R[100]=1.021\pm0.003$.

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[3] M. J. G. Lee (private communication).

[4] D. Shoenberg (private communication, referring to M. R. Halse, Ph.D. thesis, Cambridge University, 1967, and to be published).

[5] We have estimated our probable error using the frequency-versus-angle data from A. S. Joseph, A. C. Thorsen, E. Gertner, and L. E. Valby, Phys. Rev. **148**, 609 (1966).