Crystal Potential Parameters from Fermi-Surface Dimensions

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It is shown that Lee's nonunique phase-shift parameters $\eta_l(\kappa)$, determined from the experimental Fermi surfaces of Cu and the alkali metals, can be transformed into a unique set of parameters consisting of logarithmic derivatives L_l at corresponding atomic radii S_l. The physical significance of these parameters is discussed and it is shown that they give direct information about the conduction electrons in the metal.

Recent discussions[1-3] of Lee's phase-shift analysis of the experimental Fermi surface (FS) of Cu[4] have shown that the phase-shift parameters η_0, η_1, η_2, and κ are nonunique and interdependent, irrespective of whether the augmented-plane-wave (APW) or Korringa-Kohn-Rostoker (KKR) method is used. The position of the Fermi level with respect to the muffin-tin zero (MTZ), $\kappa^2 = E_\mathrm{F} - V_\mathrm{MTZ}$, can apparently be chosen arbitrarily over a range of at least 0.2 Ry,[3] and for each value a different set of phase shifts $\eta_l(\kappa)$ reproduces the FS equally well. This nonuniqueness is also manifested in the analysis of the alkali metals.[4] We shall show, however, that it is possible to transform to a unique set of parameters based on logarithmic derivatives, and that these parameters have direct physical significance.

The η_l define the scattering properties of a single, isolated "muffin-tin atom" embedded in the constant potential V_MTZ. In terms of standing waves, they define unbound MT orbitals[5] for which the radial parts outside the MT are

$$R_l(\kappa, r) = j_l(\kappa r)\cos\eta_l(\kappa) - n_l(\kappa r)\sin\eta_l(\kappa). \tag{1}$$

The phase shifts are good parameters to describe the scattering by a single MT atom. But in a crystal, where the wavelength of the MT orbital is generally large compared with the interatomic spacing and the potential is constant only in a small fraction of the volume, *local* properties of the wave function like the logarithmic derivatives, defined by

$$L_l(\kappa, r) = (r\partial/\partial r)\ln R_l(\kappa, r), \tag{2}$$

are more appropriate. A simple transformation from $\eta_l(\kappa)$ to L_l therefore removes much of the κ dependence but, more significantly, if $L_l(\kappa, r)$ is evaluated as a function of r between the radii S_I and S_E of the inscribed and exscribed spheres of the Wigner-Seitz (WS) atomic cell, using Eq. (1) which is valid in the interstitial region,[5] it is *always* found that there is some unique value S_l at which the κ dependence of L_l vanishes. This is illustrated for Cu in Fig. 1, which has been derived from the phase shifts of Lee.[6] Identical values of S_l and $L_l(S_l)$ were found from an independent set of phase shifts for Cu[3], and similar results, given in Table I, were derived for the alkali metals.[4] In all cases the logarithmic derivatives focus at definite radii between S_I and S_E, which range from −10% to +28% of the WS sphere radius S_WS for fcc structures, and from −12% to +14% of S_WS for bcc structures. The parameters $L_l(S_l)$ and S_l therefore give unambiguous information about the wave function of electrons at the FS, and hence about the crystal potential, from experimental determination of the shape of the FS.

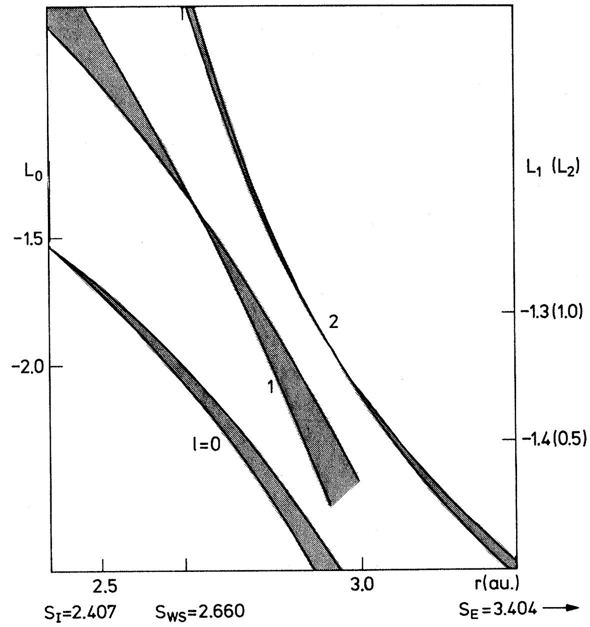

FIG. 1. Radial dependence of the logarithmic derivatives $L_l(\kappa, r) - l$ for Cu as calculated from the phase shifts $\eta_l(\kappa)$ of Ref. 6. In the shaded regions κ^2 ranges from 0.52 to 0.60 Ry. The relatively diffuse focus of L_2 indicates the existence of separate radii for the $\Gamma_{25'}$ and Γ_{12} representations. These might have been found by separate determination of the two corresponding phase shifts.

TABLE I. Crystal potential parameters L_l, λ_l, n_l, and S_l.

Element $k_F\equiv(9\pi/4)^{1/3}/S_{WS}$	Range of Phase-Shift Analysis: $100\cdot(\kappa-k_F)/k_F$	L_ℓ $100\cdot(\lambda_\ell-k_F)/k_F$ n_ℓ			$\sum n_\ell$	$100\cdot(S_\ell-S_{WS})/S_{WS}$		
		$\ell = 0$	$\ell = 1$	$\ell = 2$	Total[d]	$\ell = 0$	$\ell = 1$	$\ell = 2$
Li[a] bcc		- 1.078	- 0.0996	1.955		-2.1	+1.0	+1.0
	-17 - +16	-13.8	+11.7	-71.7				
0.5908 a.u.		0.442	0.502	0.000	0.95			
Na[a] bcc		-2.192	0.256	1.621		+4.	-0.2	-7.1
	- 8 - - 2	+ 4.46	- 4.73	- 9.91				
0.4883 a.u.		0.782	0.244	0.013	1.04			
K[a] bcc		- 1.2005	0.1418	1.1073		-6.6	+1.8	+4.9
	- 5 - + 1	- 5.98	0.00	+18.14				
0.3948 a.u.		0.486	0.328	0.152	0.97			
Rb[a] bcc		- 1.217	0.1880	1.0096		-8.6	+2.9	+4.7
	- 6 - + 5	- 4.41	- 3.95	+23.94				
0.3693 a.u.		0.480	0.290	0.200	0.97			
Cs[a] bcc		- 1.309	0.2822	0.821		-4.0	+2.3	+2.3
	-12 - +21	- 5.19	- 8.41	+37.27				
0.3413 a.u.		0.528	0.229	0.317	1.08			
Cu[b] fcc		- 1.5160	- 0.2153	2.8933		-10.0	+0.9	+10.5
	0 - + 7	+ 6.70	+16.68	+223.69				
0.7214 a.u.		0.597	0.597	10.706	11.9			
Cu[c] fcc		- 1.523	- 0.2046	2.835		-9.4	+0.3	+10.9
	- 5 - +10	+ 6.2	+16.9	+223.0				
0.7213 a.u.		0.599	0.586	10.732	11.9			

[a] Ref. 4.

[b] Ref. 6.

[c] Ref. 3.

[d] The number of electrons with $l>2$ has been set equal to the free-electron value 0.003.

The reason for the existence of these unique parameters may be understood in terms of the classical cellular approach to band theory,[7] in which the FS is determined by the crystal structure and through the boundary condition on the surface of an atomic cell by the wave components transforming according to the ith irreducible representation of the group of the cellular potential, $\psi_{ij}(r)$, and their normal derivatives. These parameters are not limited to MT potentials and they contain no κ. Our parameters $L_l(S_l)$ are those for which the boundary conditions on the WS cell are satisfied when the cellular potential is (almost) spherical and the wave function is expanded in spherical harmonics. By application of the perturbation $-\Delta E=\kappa^2-E+V_{\mathrm{MTZ}}$ in the interstitial region using the MT-orbital formalism,[5] it may be shown that for MT potentials and cubic symmetry the energy dependence of the KKR matrix to first order in ΔE only enters via $L_l(S_l)$, where S_l is determined by the condition that the integral of the charge density R_l^2 be the same in a sphere of radius S_l as in the atomic cell. Corresponding to $L_l>0$, $=0$, and <0, we therefore approximately have $S_l>S_{\mathrm{WS}}$, $=S_{\mathrm{WS}}$, and $<S_{\mathrm{WS}}$, respectively. The radii found in this way agree reasonably with those of Table I found from experiment, but due to the nonflatness of the real potential in the interstitial region there are deviations which require further investigation.

The characteristics of the FS are not immediately transparent from the set of numbers L_l. However, using the nearly-free-electron wave numbers λ_l, which we define by $\eta_l(\lambda_l)=0$, or equivalently

$$L_l\equiv l-x_l j_{l+1}(x_l)/j_l(x_l), \tag{3}$$

with the smallest root $x_l=\lambda_l S_l$, a free-electron FS may be recognized as one for which all λ_l are equal to k_{F}. Small deviations among the λ_l imply FS anisotropy, as illustrated in Table I. If, for instance $\lambda_2>\lambda_1\approx\lambda_0$, the FS radii will be greater in those directions where the character of the wave functions is more d like. However, the variation in λ_l is much greater than the FS anisotropy. A substantial deviation of a particular λ_l

(e.g., λ_2) indicates a resonance (e.g., a d band), and under these circumstances L_l rather than λ_l is a more significant parameter, since the band extends approximately from $L_l = 0$ to $-\infty$. This is the case, for example, in Cu.

From the relation[8]

$$L_l = S_l^{-1}\int_0^{S_l}[V(r)-E_{\mathrm{F}}][R_l(r)/R_l(S_l)](r/S_l)^l r^2\,dr + l, \tag{4}$$

we find that in a first-principles calculation with a MT potential, $\lambda_l \to \kappa$ for $l \gg x_l$. In a FS fitting, the fundamental uncertainty of κ is equivalent to the uncertainty of the λ_l of large l, but in contrast to the phase shifts this uncertainty does not influence the λ_l of small l. Since partial waves of zero phase shift do not contribute in the KKR matrix, the determination of the range of κ in a phase-shift analysis with a KKR matrix truncated at $l=2$,[3] or with $\eta_l \equiv 0$ for $l>2$ using the APW method,[4,5] is actually a determination of λ_3. In Table I a column has been headed "Range of phase-shift analysis" rather than λ_3 since the limits of the κ range were not explored in Refs. 3–5.

Although any set of FS parameters determines the volume of the FS by $\vec{k}$ space integration, it is useful to derive a simple, approximate sum rule for the number of states. For the alkali metals, Lee[6] calculated the Friedel sum $\sum(2l+1)\eta_l(\kappa)/\pi$ and found it to vary by typically 0.3 over the κ range considered. A more satisfactory approximate sum rule may be obtained by noting that λ_l^2 is the distance from the Fermi level above the bottom of the square-well pseudopotential of radius S_l appropriate to the lth partial wave. If hybridization could be neglected, or if all the λ_l were equal, then the l-dependent pseudopotential would be constant throughout space and the number of states per atom n_l could be calculated by integrating the product of the free-electron density of states and the probability that the electron is within the sphere of radius S_l. The result is

$$n_l = [2(2l+1)/\pi]x_l\{j_l^2(x_l)[L_l(L_l+2)-l(l+2)+x_l^2]-(2l+1)\sum_{k=l+1}^{\infty} j_k^2(x_l)\}. \tag{5}$$

As may be seen in Table I, the sum of states for the alkali metals is very close to 1, while the increase in the number of d electrons and the simultaneous decrease in the number of p electrons in the series K, Rb, and Cs is apparent. The experimental results for Li are rather uncertain[4] and the parameters for Na, the radii in particular, fall outside the general pattern.[9] Because of the d resonance, the approximations used in deriving Eq. (5) are not very satisfactory for Cu.

We have therefore shown that the wave numbers λ_0, λ_1, and λ_2 (or L_2) and the radii S_0, S_1, and S_2 are unique parameters, which may be derived from FS dimensions, and which characterize the cellular potential and the boundary conditions on the wave functions. These parameters have the physical significance of indicating approximately the character of the conduction-band wave functions and the distortion of the FS. From these, and an assumed value of the wave number κ,[10] consistent with the range of λ_3, the logarithmic derivatives $L_l(\kappa, r)$ at any radius between S_{MT} and S_E and the previously used phase-shift functions $\eta_l(\kappa)$ can be derived. These results are valid for cubic crystals in general, including both simple and transition metals, and we believe that they will prove useful also for crystals of lower symmetry. Taken as function of energy our parameters uniquely determine the band structure and may therefore be used in connection with photoemission and optical experiments.

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[8] This relation may be derived from a standard formula in P. Roman, *Advanced Quantum Theory* (Addison-Wesley, Reading, Mass., 1965), Sect. 3-3.

[9] The parameters derived from the most recent set of phase shifts *do* follow this general trend [M. J. G. Lee, Phys. Rev. B 4, 673 (1971)].

[10] Since the bottom of the free-electron-like band falls in the vicinity of $V_{\rm MT}$, the range of κ usually includes $[(n_0+n_1)9\pi/4]^{1/3}/S_{\rm WS}$.

Motion of Electron-Hole Drops in Pure Ge

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We study the motion of electron-hole drops in pure Ge at 2°K. An analysis of their luminescence by a time- and space-resolved technique yields their diffusion coefficient (150 cm^2/sec) and their lifetime (40 μsec). We also measure the formation time (0.1–0.7 μsec) of drops containing about 10^6 electron-hole pairs. A discussion of these new results is given.

Between approximately 10 and 70°K, the luminescence spectrum of pure germanium exhibits only emission lines due to the phonon-assisted decay of free excitons.[1,2] Below 10°K, new radiation peaks arise and grow rapidly when the temperature is further decreased.[3,4] Their maxima all fall about 5 meV below the LA, TO, and TA phonon replicas of the free exciton. Similar data have been obtained[5] in Si at low temperature and have been interpreted in terms of the recombination of excitonic molecules which were predicted by Lampert[6] in 1958. It has also been proposed[4,7] that one interpret the new emission lines observed in pure Ge as arising from the radiative annihilation of excitonic molecules. However, following an idea of Keldysh,[8] Pokrovskii and co-workers[3,9,10] have suggested explaining these results by the condensation of excitons into electron-hole drops (hereafter called EHD). In fact, it is now quite clear[11-13] that EHD are responsible for the low-energy emission lines observed in pure Ge at low temperature.

We wish to report here some new experiments performed in Ge to investigate the motion of EHD and the formation time of drops containing approximately 10^6 electron-hole pairs. To our knowledge, these measurements provide the first determination of the diffusion constant of EHD and they also yield the first data obtained on their time of formation.

Motion of EHD.—In these experiments, the light emitted by a pulsed GaAs laser was focused onto a 50-Ω-cm Ge sample at 2°K so that the excitation spot was a thin horizontal line whose width was less than 50 μm. The pulse length was 1.5 μsec with a fall time smaller than 0.1 μsec and the repetition rate was 300 cps; the peak power of the laser used was approximately 10 W. The recombination light emitted from the irradiated face of the Ge sample was sent onto a rapid detector by means of a very good elliptic mirror. During the experiment, the positions of the GaAs laser and of the sample were left unchanged, but the detector, which was a Ge photodiode with a fall time of 0.2 μsec, could be displaced in a vertical plane. It was therefore possible to observe the light emitted at a distance x from the exciting spot. With this apparatus, we were able to separate entirely the light coming from two points separated vertically by 100 μm on the sample. Besides, the photodiode was followed by a boxcar integrator to analyze the detected signals as a function of time.

As shown for example in Ref. 10, the only radiation which can be observed in Ge at 2°K is due to the EHD. Figure 1 represents the measured luminescence decays of the EHD at 2°K for different points of the sample. These results can be explained quite well by a diffusion of the EHD with a total lifetime $\tau \sim 40$ μsec and a duffusion constant $D \sim 150$ cm^2/sec. This interpretation is supported by the variation with x of the time delay t_M corresponding to the maximum of the different curves given in Fig. 1. Indeed, from Fig. 2 it can be seen that t_M varies as x^2. Let us add that Pokrovsky, Kaminsky, and Svistunova failed[10]