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Pressure Dependence of the Fermi Surface of Noble Metals*

B. Bosacchi, J. B. Ketterson, and L. R. Windmiller
Argonne National Laboratory, Argonne, Illinois 60439

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A technique, based on a Fourier expansion, for inverting the pressure dependence of the de Haas–van Alphen areas into corresponding change in the Fermi radii is presented. The technique is applied to construct the pressure dependence of the Fermi surface in the noble metals.

I. INTRODUCTION

Pressure studies of the Fermi surface are of increasing interest in the study of metals, since they provide a valuable check on the reliability of band-structure calculations; in fact, a band scheme which gives a good fit to the Fermi surface can fail in accounting for its pressure variation.[1] Therefore, it turns out to be useful to develop a scheme which allows one to describe analytically the effects of pressure on the Fermi surface and in Secs. II and III of this paper we show that this can be achieved, in the case of cubic crystals, by a simple generalization of the Fourier series representation.[2] In Sec. IV the scheme is applied to the case of the noble metals, where the Fermi surface is well known and relatively simple,[3–10] and where the data[11,12] on the pressure dependence of the principal de Haas–van Alphen (dHvA) orbits may be used to provide a rather complete description of the pressure dependence of the Fermi surface.

II. GENERALIZATION OF THE FOURIER SERIES TECHNIQUE

We now generalize the Fourier series representation to include the effect of hydrostatic pressure, or equivalently, the effect of a change in the lattice constant a on the Fermi surface of a cubic crystal. The techniques to be discussed are easily generalizable to crystals of lower symmetry or to the effect of a more general distortion. In the cubic case the dimensions of the Brillouin zone scale inversely with the lattice constant; for free electrons, the radius of the Fermi sphere would also scale inversely with the lattice constant a. However, for the Fermi surface associated with real energy bands, we expect changes in shape which cannot be accounted for in terms of a simple scaling and it is these changes which represent useful band-structure information.

Roaf[8] and Halse[9] have shown that an accurate Fourier series representation of the Fermi surface in noble metals requires only a small number of expansion coefficients. It has also been shown that a Fourier series expansion is useful for more distorted surfaces such as one encounters in the near noble metals.[2] We will use the following Fourier series to describe a given sheet of the Fermi surface[2]:

$$F(\vec{k}, a) = \sum_{\vec{R}} C_{\vec{R}}(a) e^{i\vec{k}\cdot\vec{R}(a)} = 0 , \qquad (1)$$

where the $\vec{R}$ are position vectors of the atoms of the real space lattice which are in turn directly proportional to the lattice constant a. The changes in the Fermi surface arising from this dependence of $\vec{R}$ on a will be referred to as scaling effects. The (real) expansion coefficients $C_{\vec{R}}$ will in general depend on a. The solution of the implicit Eq. (1) for a given value of a yields the Fermi surface for that particular lattice constant. The vectors $\vec{R}$ of the real space lattice may be factored into sets or "stars" where the members of a given star transform into one another under the operations of the point group. The coefficients $C_{\vec{R}}$ for a given star will all be identical and it is natural to rewrite Eq. (1) in the form[2]

$$F(\vec{k}, a) = \sum_{j=1}^{n} C_j(a) S_j(\vec{k}, a) , \qquad (2)$$

where

$$S_j(\vec{k}, a) = \sum_{\vec{R} \text{ in } j\text{th star}} e^{i\vec{k}\cdot\vec{R}(a)} , \qquad (3)$$

TABLE I. Values of the lattice constants, compressibilities, and coefficients $C_j (j=1,\ldots,6)$ in the expansion (2) for copper, silver, and gold.

	Cu	Ag	Au
a (Å)	3.6030	4.0692	4.0652
χ (10^{-4} kbar^{-1})	7.042	9.200	5.545
C_1	1.00000	1.00000	1.00000
C_2	1.12309	1.56074	4.02836
C_3	0.01557	−0.37551	−1.34024
C_4	−0.23866	−0.70379	−2.52812
C_5	−0.01886	−0.21985	−0.39937
C_6	−0.04236	−0.14801	−0.51176

TABLE II. Values of the coefficients $\partial A_i/\partial C_j$ and $\partial V/\partial C_j$ ($i=1, \ldots, 5$; $j=1, \ldots, 6$) for copper.

	$B(100)$ $\partial A_1/\partial C$	$B(111)$ $\partial A_2/\partial C$	$N(111)$ $\partial A_3/\partial C$	$R(100)$ $\partial A_4/\partial C$	$D(110)$ $\partial A_5/\partial C$	$\partial V/\partial C$
$\partial A/\partial C_1$	0.209 24	0.197 82	0.105 83	−0.219 21	−0.227 49	0.348 21
$\partial A/\partial C_2$	−0.369 65	−0.127 40	−0.043 76	0.110 25	0.243 53	−0.344 58
$\partial A/\partial C_3$	0.371 13	−0.491 44	−0.547 45	0.819 95	0.364 85	−0.537 05
$\partial A/\partial C_4$	−0.966 07	0.122 08	0.087 45	−0.220 50	0.399 16	−0.442 15
$\partial A/\partial C_5$	0.209 51	−0.060 51	0.938 06	−0.705 95	−0.927 81	0.718 06
$\partial A/\partial C_6$	0.625 03	0.450 61	0.226 46	−0.393 79	−0.615 40	1.058 51

where j indexes stars associated with lattice vectors of increasing length, and n is the total number of stars used in the Fermi-surface representation. Alternative to Eq. (1), which is of the form $F=F(\vec{k}, a)$, there exists a function $a=a(\vec{k}, F)$, where the a dependence is explicit. For what follows, it will be useful to have an expression for $\vec{\nabla}a$. This is easily accomplished using the chain rule for the differentiation of implicit functions, i.e.,

$$\left(\frac{\partial a}{\partial k_x}\right)_{F,k_y,k_z} = -\left(\frac{\partial F}{\partial k_x}\right)_{a,k_y,k_z} \bigg/ \left(\frac{\partial F}{\partial a}\right)_{k_x,k_y,k_z}$$

and similarly for the derivatives with respect to k_y and k_z. Thus we have

$$\vec{\nabla}a = -(\vec{\nabla}F)_a \bigg/ \left(\frac{\partial F}{\partial a}\right)_{\vec{k}}, \tag{4}$$

where

$$\left(\frac{\partial F}{\partial a}\right)_{\vec{k}} = \sum_{\vec{R}} \left(\frac{\partial C_{\vec{R}}}{\partial a} e^{i\vec{k}\cdot\vec{R}} + i\vec{k}\cdot\frac{\partial\vec{R}}{\partial a} C_R e^{i\vec{k}\cdot\vec{R}}\right). \tag{5}$$

Since $\vec{R}$ is directly proportional to a, we have immediately $\partial\vec{R}/\partial a = \vec{R}/a$. Noting that $i\sum_{\vec{R}} \vec{R}C_{\vec{R}}e^{i\vec{k}\cdot\vec{R}} = \vec{\nabla}F$, we obtain

$$\vec{\nabla}a = -\vec{\nabla}F \Big/ \left(\sum_j C'_j S_j(\vec{k}) + \frac{1}{a}\vec{k}\cdot\vec{\nabla}F\right), \tag{6}$$

where we have defined $C'_j \equiv \partial C_j/\partial a$.

A technique for determining the C_j from a selected set of dHvA areas A_i (determined at the equilibrium lattice constant) has been given previously.[2] We will now generalize this technique to allow the determination of $\partial C_{\vec{R}}/\partial a$ from a knowledge of $\partial A_i/\partial a$, where the latter are quantities determined by studying the pressure dependence of the dHvA areas. We need to derive an expression for this area derivative as a function of $k_\parallel$, where $k_\parallel$ measures the displacement of an orbit along the magnetic field. Let us split the $\vec{k}$ vector associated with a given point on this orbit into its components parallel and normal to the direction of the magnetic field, i.e.,

$$\vec{k} = \vec{k}_\parallel + \vec{k}_\perp . \tag{7}$$

The area of the ith orbit is given by

$$A_i(k_\parallel) = \tfrac{1}{2}\int_0^{2\pi} k_\perp^2(k_\parallel, \theta)\, d\theta, \tag{8}$$

where θ is an angle in the plane of the orbit measured from some convenient reference point. Differentiating with respect to a, we have

$$\frac{\partial A_i}{\partial a} = \int_0^{2\pi} k_\perp \frac{\partial k_\perp}{\partial a}\, d\theta, \tag{9}$$

where $\partial k_\perp/\partial a$ may be easily evaluated using Eq. (6):

$$\left(\frac{\partial k_\perp}{\partial a}\right)_F = \frac{k_\perp}{\vec{k}_\perp\cdot\vec{\nabla}a}. \tag{10}$$

Substituting Eq. (10) into Eq. (9) we have

$$\frac{\partial A_i}{\partial a} = -\sum_j C'_j \int \frac{k_\perp^2 S_j(\vec{k})}{\vec{k}_\perp\cdot\vec{\nabla}F}\, d\theta - \frac{1}{a}\int k_\perp^2\, d\theta - \frac{1}{a}\int k_\perp^2 \frac{\vec{k}_\parallel\cdot\vec{\nabla}F}{\vec{k}_\perp\cdot\vec{\nabla}F}\, d\theta . \tag{11}$$

TABLE III. Values of the coefficients $\partial A_i/\partial C_j$ and $\partial V/\partial C_j$ ($i=1, \ldots, 5$; $j=1, \ldots, 6$) for silver.

	$B(100)$ $\partial A_1/\partial C$	$B(111)$ $\partial A_2/\partial C$	$N(111)$ $\partial A_3/\partial C$	$R(100)$ $\partial A_4/\partial C$	$D(110)$ $\partial A_5/\partial C$	
$\partial A/\partial C_1$	0.102 56	0.098 53	0.058 67	−0.130 72	−0.128 56	0.178 33
$\partial A/\partial C_2$	−0.181 79	−0.069 83	−0.012 74	0.057 63	0.115 85	−0.173 22
$\partial A/\partial C_3$	0.168 98	−0.242 85	−0.326 57	0.532 11	0.288 92	−0.298 50
$\partial A/\partial C_4$	−0.438 10	0.076 73	0.025 47	−0.115 27	0.184 36	−0.206 10
$\partial A/\partial C_5$	0.071 32	−0.035 47	0.604 95	−0.590 55	−0.638 31	0.405 42
$\partial A/\partial C_6$	0.324 54	0.233 31	0.070 91	−0.200 11	−0.308 50	0.513 38

TABLE IV. Values of the coefficients $\partial A_i/\partial C_j$ and $\partial V/\partial C_j$ ($i = 1, \ldots, 5$; $j = 1, \ldots, 6$) for gold.

	$B(100)$ $\partial A_1/\partial C$	$B(111)$ $\partial A_2/\partial C$	$N(111)$ $\partial A_3/\partial C$	$R(100)$ $\partial A_4/\partial C$	$D(110)$ $\partial A_5/\partial C$	$\partial V/\partial C$
$\partial A/\partial C_1$	0.039 62	0.030 60	0.015 21	−0.034 56	−0.039 00	0.057 67
$\partial A/\partial C_2$	−0.084 84	−0.017 33	−0.005 66	0.014 97	0.050 37	−0.063 45
$\partial A/\partial C_3$	0.094 35	−0.075 98	−0.079 91	0.130 76	0.040 18	−0.069 16
$\partial A/\partial C_4$	−0.194 70	0.013 44	0.011 32	−0.029 94	0.086 22	−0.093 54
$\partial A/\partial C_5$	0.101 09	−0.011 03	0.139 28	−0.114 89	−0.183 52	0.139 04
$\partial A/\partial C_6$	0.048 22	0.064 63	0.029 77	−0.054 59	−0.067 63	0.147 91

The second term of this equation is clearly twice the area divided by the lattice constant. It is easy to show that the integral in the first term of Eq. (11) may be rewritten as $-\partial A_i/\partial C_j$,[2] while the last term may be written as $-(k_\parallel/a)\,\partial A/\partial k_\parallel$. With these substitutions Eq. (11) becomes

$$\frac{\partial A_i(k_\parallel)}{\partial a} = \sum_j C_j' \frac{\partial A_i(k_\parallel)}{\partial C_j} - \frac{2A_i(k_\parallel)}{a} + \frac{k_\parallel}{a}\frac{\partial A_i(k_\parallel)}{\partial k_\parallel} . \tag{12}$$

Some comments on Eq. (12) are in order: (a) For the extremal orbits measured in a dHvA experiment $\partial A_i(k_\parallel)/\partial k_\parallel = 0$ and thus the last term vanishes; (b) the quantities $\partial A_i/\partial C_j$ for extremal orbits may be obtained during the inversion of the zero-pressure dHvA data.[2] The quantities $\partial A_i/\partial a$ may be related to $\partial A_i/\partial P$ (the experimentally measured quantities) through the compressibility χ with the relation

$$\frac{\partial A_i}{\partial a} = -\frac{3}{a\chi}\frac{\partial A_i}{\partial P} , \tag{13}$$

where

$$\chi = -\frac{1}{V}\frac{\partial V}{\partial P} . \tag{14}$$

Integrating (12) with respect to $k_\parallel$ one has

$$\frac{\partial V}{\partial a} = \sum_j C_j' \frac{\partial V}{\partial C_j} - \frac{2V}{a} + \frac{1}{a}\int k_\parallel \frac{\partial A}{\partial k_\parallel}\, dk_\parallel . \tag{15}$$

Integration by parts of the last term shows that it is equal to $-V/a$ and, therefore,

$$\frac{\partial V}{\partial a} = \sum_j C_j' \frac{\partial V}{\partial C_j} - \frac{3V}{a} . \tag{16}$$

On the other hand, the scaling law, which in view of the distortion does not hold for the variation of the radii and the areas, must be valid for the variation of the volume (in the case where the Fermi surface consists of a single carrier), since it reflects the invariance of the number of carriers; thus

$$\frac{\partial V}{\partial a} = -\frac{3V}{a} . \tag{17}$$

A comparison of (16) and (17) gives

$$\sum_j C_j' \frac{\partial V}{\partial C_j} = 0 , \tag{18}$$

which is a relation that the coefficients C_j' must satisfy.

III. DETERMINATION OF THE C_j' COEFFICIENTS

We now discuss the numerical fitting technique used to obtain the C_j' coefficients from measured dHvA areas together with their pressure derivatives. We rewrite Eq. (12) for extremal orbits:

$$\frac{\partial A_i}{\partial a} = \sum_j C_j' \frac{\partial A_i}{\partial C_j} - \frac{2A_i}{a} \quad \text{(extremal orbits only).} \tag{19}$$

Let us define

$$Q_i = \frac{\partial A_i}{\partial a} + \frac{2A_i}{a} , \quad i = 1, \ldots, N \tag{20}$$

TABLE V. Experimental and calculated values for A_i and $(1/A_i)(\partial A_i/\partial P)$ ($i = 1, \ldots, 5$) for copper, silver, and gold.

	Cu				Ag				Au			
	A(a.u.)		$\frac{1}{A}\frac{\partial A}{\partial P}$ [10^{-4} kbar^{-1}]		A(a.u.)		$\frac{1}{A}\frac{\partial A}{\partial P}$ (10^{-4} kbar^{-1})		A(a.u.)		$\frac{1}{A}\frac{\partial A}{\partial P}$ (10^{-4} kbar^{-1})	
	Expt	Calc	Expt	Calc	Expt	Calc	Expt	Calc	Expt	Calc	Expt	Calc
1 $B(100)$	1.603	1.602	4.6 (±0.2)	4.60	1.269	1.268	5.6(±0.2)	5.61	1.296	1.295	3.7(±0.3)	3.70
2 $B(111)$	1.554	1.552	4.25(±0.2)	4.27	1.231	1.232	5.1(±0.2)	5.34	1.202	1.201	2.8(±0.2)	2.90
3 $N(111)$	0.058	0.058	18.0 (±2.0)	18.97	0.024	0.023	50.0(±10.0)	59.81	0.041	0.041	20.0(±1.0)	22.06
4 $R(100)$	0.658	0.657	4.3 (±0.3)	4.31	0.525	0.524	5.2(±0.3)	5.27	0.535	0.534	3.7(±0.3)	3.70
5 $D(110)$	0.672	0.669	4.0((±0.2)	4.01	0.539	0.537	4.4(±0.3)	4.40	0.518	0.515	2.7(±0.3)	2.75

TABLE VI. Pressure dependence coefficients for copper, silver, and gold.

	Cu	Ag	Au
C_1'	0.0	0.0	0.0
C_2'	−9.519	3.639	−508.094
C_3'	4.737	−3.432	239.620
C_4'	6.425	−4.021	391.001
C_5'	1.400	−1.644	67.730
C_6'	1.039	−1.083	77.670

(where N is the number of experimental data), and

$$Q_i^{(C)}=\sum_j C_j'\frac{\partial A_i}{\partial C_j}\,,\quad i=1,\ldots,N \tag{21}$$

the $Q_i^{(C)}$ being the calculated quantities which correspond to the experimental Q_i. The coefficients C_j' may be determined, as long as $n \le N$, by minimizing the rms error

$$\Delta^2(C_j')=\frac{1}{N}\sum_i\frac{1}{Q_i^2}(Q_i^{(C)}-Q_i)^2\,. \tag{22}$$

Minimizing Eq. (22) with respect to C_j', we obtain the following set of equations:

$$\sum_i\frac{1}{Q_i^2}(Q_i^{(C)}-Q_i)\frac{\partial Q_i^{(C)}}{\partial C_j'}=0\,. \tag{23}$$

Now $\partial Q_i^{(C)}/\partial C_j'=\partial A_i/\partial C_j$, and substituting this in Eq. (23) and using Eq. (21) we have

$$-\sum_i\frac{1}{Q_i}\frac{\partial A_i}{\partial C_j}+\sum_i\sum_l\frac{1}{Q_i^2}\frac{\partial A_i}{\partial C_j}\frac{\partial A_i}{\partial C_l}C_l'=0\,. \tag{24}$$

If we put

$$X_j=\sum_i\frac{1}{Q_i}\frac{\partial A_i}{\partial C_j} \tag{25}$$

and

$$T_{jl}=\sum_i\frac{1}{Q_i^2}\frac{\partial A_i}{\partial C_j}\frac{\partial A_i}{\partial C_l}\,, \tag{26}$$

then Eq. (24) may be rewritten in the compact form

$$-X_j+\sum_l T_{jl}C_l=0\,. \tag{27}$$

The vector and tensor coefficients X_j and T_{jl} may be easily built and, by simply inverting the matrix T_{jl}, we obtain

$$C_l'=\sum_j (T)_{jl}^{-1}\cdot X_j\,. \tag{28}$$

The set of coefficients (28) must satisfy relation (18), and this condition, once the $\partial V/\partial C_j$ are known,[10] may be used as a test for the consistency of the experimental results.

Alternatively, one can require that Eq. (18) be satisfied *a priori*; this amounts to include it as a further constraint in the minimization of (22), which is performed through the equation

$$\frac{\partial\Delta^2(C_j')}{\partial C_j'}+\lambda\frac{\partial V}{\partial C_j}=0\,, \tag{29}$$

where λ is a Lagrangian multiplier. Equation (27) now becomes

$$-X_j+\lambda\frac{\partial V}{\partial C_j}+\sum_l T_{jl}C_l'=0\,, \tag{30}$$

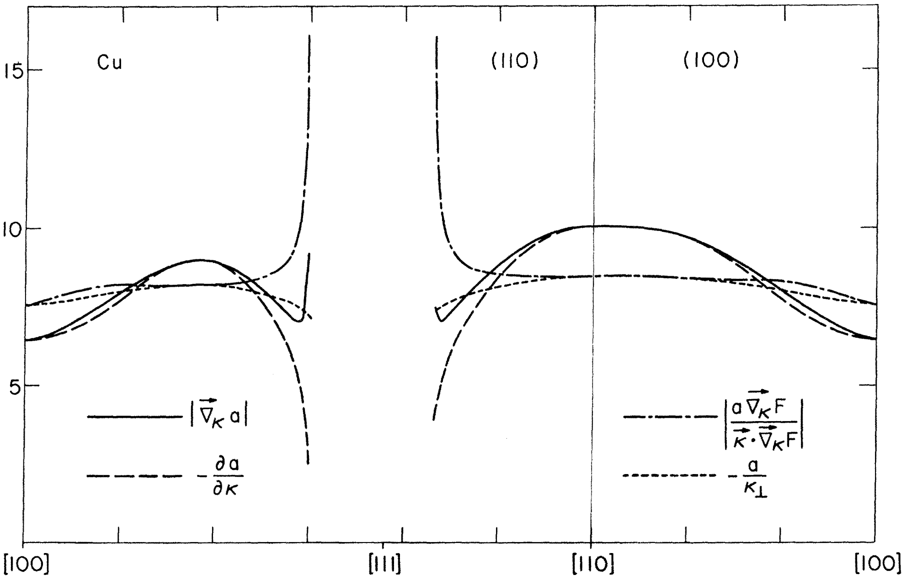

FIG. 1. Angular dependence of $|\partial a/\partial\vec k|$, $-\partial a/\partial k$, $|a\vec\nabla F/\vec k\cdot\vec\nabla F|$, and $a/k_\perp$ for the (100) and (110) planes in copper. The lines extend somewhat farther in the neck region than indicated in the figure, as the exact position of the zone contact of the neck does not fall on the grid used to calculate these quantities.

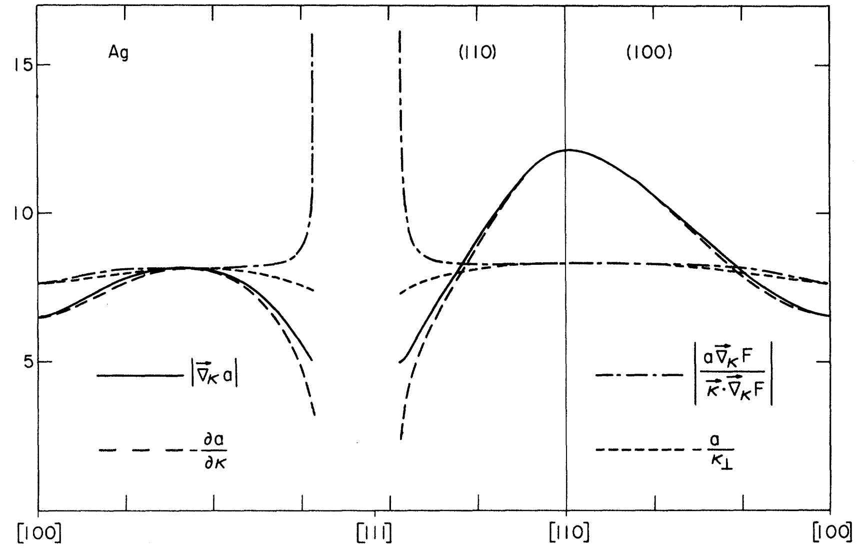

FIG. 2. Angular dependence of $|\partial a/\partial \vec{k}|$, $-\partial a/\partial k$, $|a\vec{\nabla}F/\vec{k}\cdot\vec{\nabla}F|$, and $a/k_\perp$ for the (100) and (110) planes in silver. The lines extend somewhat farther in the neck region than indicated in the figure, as the exact position of the zone contact of the neck does not fall on the grid used to calculate these quantities.

from which

$$C_l' = \sum_j (T)^{-1}_{jl}\left(X_j - \lambda \frac{\partial V}{\partial C_j}\right). \tag{31}$$

Substituting Eq. (31) in Eq. (18), we get

$$\lambda = \sum_{jl} \frac{\partial V}{\partial C_l} (T)^{-1}_{jl} X_j \Big/ \sum_{jl} (T)^{-1}_{jl} \frac{\partial V}{\partial C_j} \frac{\partial V}{\partial C_l} \tag{32}$$

and, finally,

$$C_j' = \sum_l (T)^{-1}_{jl}\left[X_j - \frac{\partial V}{\partial C_j}\left(\sum_{m,n} \frac{\partial V}{\partial C_n}(T)^{-1}_{mn} X_m \Big/ \right.\right.$$
$$\left.\left.\sum_{m,n} (T)^{-1}_{mn} \frac{\partial V}{\partial C_m} \frac{\partial V}{\partial C_n}\right)\right]. \tag{33}$$

Since we have $C_1 = 1$ in Eq. (1) for any representation (and therefore also for that of the deformed surface), we shall perform the above inversion by keeping $C_1' = 0$ (the condition $n \leq N$ then becomes $n \leq N+1$).

IV. APPLICATION TO THE NOBLE METALS

The scheme developed in Secs. II and III will now be applied to the case of the noble metals. Here the situation appears to be particularly favorable in view of the following circumstances:

(a) The Fermi surfaces of these metals are well known and Fourier series representations exist which are very successful in reproducing the experimental cross sections[8-10]; the coefficients C_j are therefore well known. For a given set of C_j,

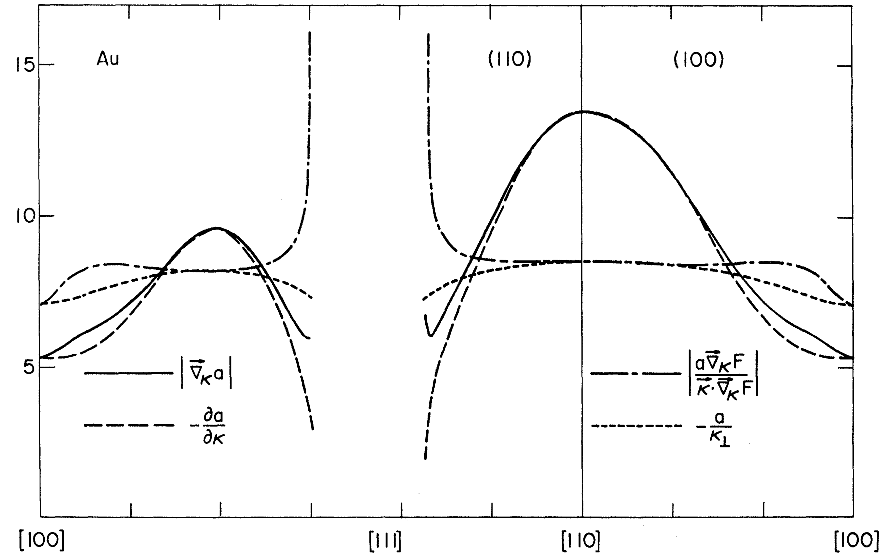

FIG. 3. Angular dependence of $|\partial a/\partial \vec{k}|$, $-\partial a/\partial k$, $|a\vec{\nabla}F/\vec{k}\cdot\vec{\nabla}F|$, and $a/k_\perp$ for the (100) and (110) planes in gold. The lines extend somewhat farther in the neck region than indicated in the figure, as the exact position of the zone contact of the neck does not fall on the grid used to calculate these quantities.

also $\partial A_i/\partial C_j$ and $\partial V/\partial C_j$ may be easily obtained.[10]

(b) The experimental situation is better than for most other metals. The areas of the extremal cross sections are known with high accuracy and reproductibility[3-7] and data for their pressure dependence along symmetry directions also exist. In particular, those of Schirber and O'Sullivan,[12] in view of the simplicity of the Fermi surface of the noble metals, may be considered sufficiently complete to provide a meaningful representation for the pressure effects on the over-all surface.

The values of the various parameters which have been used to find the set of coefficients (33) for Cu, Ag, and Au are reported in Tables I–V. In Table I, the values of the lattice constants are taken from Halse[9]; those of the compressibility at 0 °K have been obtained starting from the stiffness constants[13-15]; the coefficients C_j of Eq. (21) are the equivalent of those reported by Halse for his representation.[9]

Tables II–IV report the coefficients $\partial A_i/\partial C_j$ and $\partial V/\partial C_j$ for copper, silver, and gold, respectively. These coefficients have been obtained by applying our procedures[10] to Eq. (2) with the C_j of Table I.

The experimental data of Table V are taken from Schirber and O'Sullivan[12]; in this table are also shown the corresponding values for both A_i, calculated with Eq. (8), and $(1/A_i)(\partial A_i/\partial p)$, the latter have been obtained by using the set of coefficients (33) which are reported in Table VI. Since condition (18) is included in (33), the agreement of Table V between experimental and calculated values for $(1/A_i)(\partial A_i/\partial p)$ suggests that the sets of data of Ref. 12 are consistent.

The coefficients of Table VI, through Eqs. (6) and (12), allow one to know the variation with pressure for any point and any cross section, and in this sense we may say they provide a complete description of the initial effect of the pressure on the geometrical properties of the Fermi surface. In Figs. 1–3, we have reported the angular variations in the planes (100) and (110) for copper, silver, and gold, respectively, of the following quantities:

$$|\vec{\nabla}_k a|\,,\quad -\frac{\partial a}{\partial k}\,,\quad \left|\frac{a\vec{\nabla}_k F}{\vec{k}\cdot\vec{\nabla}_k F}\right|\,,\quad \text{and } \frac{a}{k_\perp}\ .$$

All these quantities have been obtained from Eq. (6), the latter two corresponding to the first two when $\sum C_j' S_j(\vec{k})$ vanishes. Therefore, the latter reflect the distortion introduced by the scaling effect alone, whereas the former contain also the effect of the pressure through changes in the band structure.

V. CONCLUSIONS

As shown in Figs. 1–3, one gets a rather detailed knowledge of the pressure dependence of the Fermi surface of noble metals starting from only a limited number of experimental data. For more distorted surfaces, which would require correspondingly more terms in the Fourier expansion, data for field directions other than those parallel to crystallographic axis of high symmetry would be required. These data are somewhat more difficult to obtain, however, as a small tipping of the crystal with pressure can introduce an error into the measurements.

Since the pressure derivatives provide a valuable check on the reliability of a band-structure calculation,[12] it is hoped that the inversion scheme developed here will encourage further measurements. We point out in passing that for closed surfaces having inversion symmetry and with a single-valued radius vector a variation of the Fermi-velocity inversion technique of Ketterson, Windmiller, Hörnfeldt, and Mueller[16] allows inversion of $\partial A/\partial a$ to $\partial a/\partial\vec{k}$. This follows on substituting a for E in the relevant equations.

From a knowledge of the detailed shape of the Fermi surface, one can determine the phase shifts $\delta_l(E_F)$ used to parametrize the potential in an augmented-plane-wave or Korringa-Kohn-Rostoker calculation. To determine how $\delta_l(E)$ changes with energy we need additional information. Fermi-velocity determinations are relevant but complicated by the fact that they include many-body effects. Pressure derivatives on the other hand look quite attractive since this offers a way of varying the Fermi energy and thus a way of obtaining $[\partial\delta_l(E)/\partial E]_{E=E_F}$ without considering the complicating many-body effects.

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Accurate Resonance-Parameter Approach to Transition-Metal Band Structure

D. G. Pettifor*
Cavendish Laboratory, Cambridge, England

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The position E_d and width W of the d resonance are shown to be good physical parameters, in that the *same* pair of parameters ($E_d = 0.540$, $W = 0.088$ Ry) is capable of reproducing Wood's band structure of fcc and bcc iron to within a rms error of 0.006 Ry. The energy levels were obtained by diagonalizing an improved hybrid nearly-free-electron tight-binding model Hamiltonian that includes explicitly the nonorthogonality of the basis functions.

The band structure of all transition and noble metals is characterized by the presence of a fairly tightly bound d band, which overlaps and hybridizes with a broader nearly-free-electron s-p band. Hodges *et al.*[1] and Mueller[2] set up a model Hamiltonian based on this hybrid nearly-free-electron tight-binding (H-NFE-TB) picture and successfully fitted the first-principles band structure of copper[3] to within a rms error of 0.01 Ry. Subsequently, Heine,[4] Hubbard,[5] and Jacobs[5] derived from first-principles model Hamiltonians of essentially this H-NFE-TB form by manipulating the basic Korringa-Kohn-Rostoker (KKR)[6] equations. The numerous[1,2] TB overlap integrals and hybridization matrix elements could now be expressed[7] analytically in terms of only *two* fundamental parameters E_d and W,[8] which are, respectively, the position and width of the resonance associated with the $l = 2$ phase shift,[9] namely,

$$\tan\eta_2 = \tfrac{1}{2}W(E)/(E_d - E) \quad . \qquad (1)$$

This phase shift is accurately represented over the entire width of the d band if the energy dependence of the resonance width is expressed explicitly in the form[7]

$$W(E) = \{[Kj_2^2(Kr_i)]/[K_d j_2^2(K_d r_i)]\}W \quad , \qquad (2)$$

where $K^2 = E$ and r_i is the inscribed sphere radius. The width of the d band is proportional to W, whereas the hybridization is proportional to $W^{1/2}$. The latter is not unexpected,[4] since $W/\hbar$ gives the probability of a localized d-electron tunneling through the centrifugal barrier into plane-wave states, provided that the resonance energy E_d is measured with respect to the bottom of the conduction band.

In the present paper we shall substantiate our argument given previously[10] that E_d and W, *taken together*, are good constant parameters for describing the band-structure energy *about the absolute position* of the resonance under a change of volume or crystal structure. This very important property arises because they always appear in the TB and hybridization matrix elements *combined together* in a certain ratio[10] that remains invariant, to a high degree of accuracy, from one volume[10] or structure to the next, even though the resonance parameters themselves do change individually. It must be stressed, however, that they are *not* good physical parameters if E_d is measured with respect to the muffin-tin plateau[6] instead of the bottom of the conduction band. For example, in the former case E_d and W (measured in rydbergs) have the values (0.608, 0.108) and (0.649, 0.122)[11] for fcc and bcc iron,[12] respectively, whereas in the present paper we have reproduced the identical fcc and bcc band structure by using the same set of parameters (0.540, 0.088) in both cases.

Furthermore, we shall present an improved H-