Effect of pressure on the Fermi surface of noble metals

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We present calculations of the pressure derivatives $A^{-1}dA/dP$ for four Fermi-surface orbits using the *ab initio* linear muffin-tin orbitals method in the atomic-sphere approximation. Calculations are performed with use of various exchange-correlation (XC) potentials. Our calculations indicate that the "belly" orbits are insensitive to the choice of the XC potential while the "neck" orbit is not. We find that the $X\alpha$ exchange-correlation potential (with a variable α) gives the best fit to the experimental data.

I. INTRODUCTION

Although there exist numerous calculations of the Fermi surface (FS) of the noble metals,[1] there is a dearth of calculations on the effect of pressure on the FS of noble metals. This is all the more surprising since the effect of pressure on the Fermi surface provides a valuable check on the reliability of band-structure calculations. The existing calculations of the effect of pressure on the FS of noble metals fall into two broad categories. (i) *Ab initio* calculations such as those of Davis *et al.*[2] for copper using the Korringa-Kohn-Rostoker (KKR) method and those of Ramchandani[3] for gold using the relativistic augmented-plane-wave (RAPW) method. Davis *et al.* did obtain good agreement with experimental data while Ramchandani did not. (ii) Empirical methods such as those of Shaw *et al.*[4] using KKR phase shifts and of Bosacchi *et al.*[5] using the Fourier-series method. The KKR phase shifts and Fourier coefficients are adjusted to fit the FS data.

We present here detailed calculations of the effect of pressure on the FS of noble metals using the linear muffin-tin orbitals (LMTO) method in the atomic-sphere approximation (ASA).[6,7] Unlike the previous *ab initio* calculations, ours is self-consistent, i.e., pressure derivatives of extremal areas ($A^{-1}dA/dP$) are obtained performing self-consistent band-structure calculations at two different radii. We have calculated $A^{-1}dA/dP$ for four FS orbits with various exchange-correlation (XC) potentials.

We have chosen the noble metals for this study because their FS is very simple and also excellent data with which comparison can be made exists. Moreover, since we have already calculated the zero-pressure FS, it is natural to calculate their pressure derivatives.[8]

In Sec. II we briefly give the method used for calculating $A^{-1}dA/dP$. Results and discussions are in Sec. III and conclusions in Sec. IV.

II. METHOD OF CALCULATIONS

We have used the LMTO method within the ASA.[6] We have chosen this method because it is as fast as the empirical methods with the advantage of being an *ab initio* method. Hence the method is very well suited for FS work. The band-structure calculations are done self-consistently, which we take to mean that the change in the potential parameters, between successive iterations, is in the fifth decimal place. Starting with the parameters given in Skriver's book,[7] this requires half a dozen more iterations. This gives eigenvalues converged to 0.1 mRy.

Using these self-consistent parameters, we have calculated FS orbital areas and masses using Stark's area-mass routine.[9] The area and mass of the computed surface in a plane normal to the direction (i.e., the magnetic field) were found by numerical integration of the radii calculated at a fixed interval of rotation in that plane. The areas are calculated for four orbits, "belly (B111)," "belly (B100)," "dog bone (D110)," and "neck (N111)." The numbers denote the direction of the magnetic field. Next, the lattice is expanded by about 0.1%. This is small enough to exclude nonlinear effects and sufficiently large to accurately calculate FS changes. Again, the self-consistent parameters are determined and the FS area calculated. From these two calculations, we obtain dA/A corresponding to a 0.1% change in the lattice constant. Using the values of compressibility[10] 7.39×10^{-4} kbar^{-1} for copper, 10.06×10^{-4} kbar^{-1} for silver, and 5.84×10^{-4} kbar^{-1} for gold, we obtain $A^{-1}dA/dP$. These calculations are done with the $X\alpha$,[11] von Barth–Hedin (BH),[12] von Barth–Hedin–Janak (BHJ),[13] and Vosko-Wilk-Nussair[14] (VWN) exchange-correlation potentials. In the $X\alpha$-XC, α was taken to be 0.77 for copper and silver and 0.693 for gold because these gave a good fit to the zero-pressure FS.[8]

III. RESULTS AND DISCUSSIONS

The $A^{-1}dA/dP$ obtained for the four FS orbits using various XC potentials are given in Tables I–III along with the experimental values and other theoretical calculations. We now discuss each metal separately.

Consider first the case of copper given in Table I. The pressure derivatives for the B111, B100, and D110 orbits are almost identical for all XC's used except BH-XC. The N111 is the most sensitive to the choice of the XC potential used. On comparison with the exeperimental data of Templeton[15] and of Schirber and Sullivan[16] we

TABLE I. Copper. Experimental and calculated values for $A^{-1}dA/dP$ (10^{-4} kbar^{-1}).

	B111	B100	N111	D111
$X\alpha$-XC ($\alpha=0.77$)	4.4	4.5	22.8	3.9
VWN-XC	4.4	4.5	23.6	3.9
BHJ-XC	4.2	4.6	9.4	4.0
BH-XC	2.3	2.8	4.7	4.8
Gavenda *et al.*[a]	4.11	4.66	16.0	3.79
Davis *et al.*[b]	4.4	4.7	15.5	4.1
Shaw *et al.*[c]	4.26	4.57	16.3	4.08
Bosacchi *et al.*[d]	4.25	4.60	18.97	4.01
Templeton[e] experimental value	4.21±0.03	4.42±0.03	19.8±0.5	4.04±0.02
Schirber *et al.*[f] experimental value	4.25	4.6	18.0	4.0

[a]Reference 17.
[b]Reference 2.
[c]Reference 4.
[d]Reference 5.
[e]Reference 15.
[f]Reference 16.

TABLE II. Silver. Experimental and calculated values of $A^{-1}dA/dP$ (10^{-4} kbar^{-1}).

	B111	B100	N111	D110
$X\alpha$-XC ($\alpha=0.77$)	5.6	6.3	62.2	4.6
VWN-XC	5.6	5.9	90.4	4.6
BHJ-XC	5.7	6.3	41.4	5.7
BH-XC	5.7	6.3	41.4	4.7
Bosacchi *et al.*[a]	5.34	5.61	59.81	4.40
Shaw *et al.*[b]	5.18	5.59	61.2	4.76
Schirber *et al.*[c] experimental value	5.1	5.6	50.0	4.4
Templeton[d] experimental value	5.29±0.03	5.68±0.04	65.0±0.7	4.49±0.03

[a]Reference 5.
[b]Reference 4.
[c]Reference 16.
[d]Reference 15.

TABLE III. Gold. Experimental and calculated values for $A^{-1}dA/dP$ (10^{-4} kbar^{-1}).

	B111	B100	N111	D110
$X\alpha$-XC ($\alpha=0.693$)	3.1	3.8	19.7	2.8
VWN-XC	3.1	3.6	26.2	2.8
BHJ-XC	3.1	3.5	13.1	2.8
BH-XC	2.8	3.6	19.7	2.8
Ramchandani[a]			7.1	
Bosacchi *et al.*[b]	2.90	3.70	22.06	2.75
Schirber *et al.*[c] experimental value	2.8±0.2	3.7±0.3	20±1.0	2.7±0.3
Templeton[d] experimental value	3.06±0.04	3.58±0.3	20.6±0.5	2.70±0.02

[a]Reference 3.
[b]Reference 5.
[c]Reference 16.
[d]Reference 15.

observe that the VWN and the $X\alpha$-XC potentials give good agreement with the data. Also given are the pressure derivatives obtained by Shaw *et al.* and Bossachi *et al.* using phase shifts and Fourier coefficients. These are definitely in better agreement with the data compared to ours because the parameters were adjusted to fit the data. It is indeed heartening to note that the results of Davis *et al.* using KKR also agree with the data except that the N111 derivative is slightly lower than the experimental value. Gavenda *et al.*[17] have used the method of interpolation functions to obtain the pressure derivatives which are consistent with the experimental data and with our calculations. In conclusion, our values for the pressure derivatives for the four FS orbits (using $X\alpha$ and VWN) are in good agreement with the experimental data.

Table II gives our results for silver along with the experimental values of Schirber and Sullivan[16] and Templeton[15] and the empirically adjusted values. Unfortunately, we are not aware of any *ab initio* calculations. Once again we observe that the B111, B100, and D110 are not sensitive to the choice of the XC potentials, whereas N111 is. For silver only the $X\alpha$ ($\alpha=0.77$) gives agreement with the experimental data. Our previous work[8] on silver indicates that $X\alpha$ ($\alpha=0.77$) gives the best fit to the zero-pressure FS data.

Values of $A^{-1}dA/dP$ for gold are given in Table III. We are aware of only one *ab initio* calculation by Ramchandani[13] who used the RAPW method to obtain $A^{-1}dA/dP$ for N111 which is $\frac{1}{3}$ of the experimental value. Again the B111, B100, and D110 are not influenced much by the XC potentials; only the N111 is. Our calculations indicate that the $X\alpha$ ($\alpha=0.693$) and BH-XC's give good agreement with the experimental data. Our previous work[8] for gold indicates that these XC's give the best fit to the zero-pressure FS data.

As mentioned above, the pressure derivatives were obtained by performing self-consistent band calculations at the equilibrium lattice constant and at a lattice constant increased by 0.1%. This is small enough to exclude nonlinear effects and sufficiently large to accurately calculate the FS changes. We have also calculated the band structure at a lattice constant 0.4% larger than the equilibrium value. This yields $A^{-1}dA/dP$ within 10% of the values given in the tables. This could be due to the nonlinear variation of FS area with pressure.

IV. CONCLUSIONS

Our calculations of $A^{-1}dA/dP$ for the noble metals suggest that the LMTO method gives values that are in good agreement with experiment. Our results show that B111, B100, and D110 orbits are insensitive to the choice of XC used, while the N111 orbit is greatly influenced by the XC. Hence the pressure data can be used to determine the most appropriate XC potential. Our calculations indicate that the $X\alpha$ (α variable) gives correct values of $A^{-1}dA/dP$ for all the noble metals as does VWN for copper and BH for gold. It would seem interesting to compare this with our zero-pressure results,[8] which show that no single XC potential gives a good representation for the FS of noble metals. The $X\alpha$ method with a variable α gives the best agreement with the experimental data for all the noble metals.

Our calculations give better agreement with the data than obtained with previous *ab initio* methods. Perhaps this reflects the need and importance of self-consistency in band-structure calculations. Also, our values of $A^{-1}dA/dP$ are in no way inferior to the values obtained by the empirical methods. In fact, they are as good and obtained with no adjustable parameter.

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[1]See, for example, O. Jepsen, D. Glötzel, and A. R. Mackintosh, Phys. Rev. B **23**, 2684 (1981), and references cited therein.
[2]H. L. Davis, J. S. Faulkner, and H. W. Joy, Phys. Rev. **167**, 601 (1968).
[3]M. G. Ramchandani, J. Phys. F **2**, 297 (1972).
[4]J. C. Shaw, J. B. Ketterson, and L. R. Windmiller, Phys. Rev. B **5**, 3894 (1972).
[5]B. Bossachi, J. B. Ketterson, and L. R. Windmiller, Phys. Rev. **132**, 3025 (1970).
[6]O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).
[7]H. L. Skriver, in *The LMTO Method,* Vol. 41 of *Springer Series in Solid State Sciences,* edited by M. Cardona, P. Fulde, and H. J. Queisser (Springer, Berlin, 1984).
[8]R. Ahuja, A. K. Solanki, T. Nautiyal, and S. Auluck (unpublished).
[9]R. W. Stark, private communication.
[10]C. Kittel, *Introduction to Solid State Physics,* 4th ed. (Wiley, New York, 1971).
[11]J. C. Slater, Int. J. Quantum Chem. **5S**, 403 (1971).
[12]U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).
[13]J. F. Janak, Phys. Rev. B **12**, 1257 (1975).
[14]S. H. Vosko, L. Wilk, and M. Nussair, Can. J. Phys. **58**, 1200 (1980).
[15]I. M. Templeton, Can. J. Phys. **52**, 1628 (1974).
[16]J. E. Schirber and W. J. O'Sullivan, in *Les Proprietes Physiques des Solides Sous Precersion* (Centre National de la Recherches Scientifique, Paris, 1970), p. 113.
[17]J. D. Gavenda, W. M. Theis, and B. Mulvaney, Phys. Rev. B **21**, 2096 (1980).