ism. Also, the formulation in terms of an effective-mass operator allows an extension of the theory beyond the Hartree-Fock approximation, treating the difference between effective-mass operator and pure metal Hartree-Fock potential as a perturbing potential. This new potential can then be determined from a diagramatic expansion of the effective-mass operator, which may be of more complicated form than the Hartree-Fock potential.

If temperature dependence is considered, since the Fermi function only differs from a step function over a range of energy or order $KT\approx 0.002$ Ry at room temperature, dependent effects are probably quite small since the level widths are of the order of 0.02 Ry.

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Precision Measurements of ⟨111⟩ de Haas–van Alphen Frequencies in Copper, Silver, and Gold

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Precise measurements have been made of ⟨111⟩ neck de Haas–van Alphen frequencies and belly/neck ratios in copper, silver, and gold, using deuterium resonance for magnetic field calibration. All three metals were studied in a superconducting solenoid using a field-modulation technique; the neck in gold was also measured by the torque method in a conventional electromagnet. The results are believed to have an absolute accuracy of better than ±0.2%, and show discrepancies of up to 1.6% when compared with earlier published figures.

INTRODUCTION

THE de Haas–van Alphen effect in the noble metals has been studied extensively over the past few years, notably by Shoenberg[1] and by Joseph, Thorsen, and co-workers (JT)[2–4]. Band-structure calculations have been made for copper by Segall[5] and Burdick,[6] but Zornberg and Mueller[7] in combining JT's data with Burdick's calculation found an apparent discrepancy in the absolute volume contained by the Fermi surface, which could be resolved on the assumption that JT's data for Fermi-surface cross sections in copper were in error by some +0.4%.

In the course of some recent experimental studies in this laboratory of the effect of hydrostatic pressure on the noble-metal Fermi surfaces,[8] and some continuing work on the effect of alloying,[9] we had occasion to make measurements of the ⟨111⟩ de Haas–van Alphen frequencies with rather high precision. It became apparent that there were discrepancies of the order of 1% between our figures and the most reliable (in terms of their claimed absolute accuracy) of the figures from other laboratories. Our figures were obtained using a superconducting solenoid, whereas Shoenberg used pulsed fields and JT the torque method. Since superconducting solenoids have a reputation for a degree of nonlinearity and hysteresis in their field-current relationship we at first attributed the discrepancies to this cause. However, further investigations, to be described below, seem to substantiate our figures.

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EXPERIMENTS

The first discrepancies observed were in the ⟨111⟩ neck frequency of gold, where a difference of about 1.6% was found between our results and those reported in JT.[3] Because of the doubt, mentioned above, about the accuracy obtainable when using a superconducting solenoid, we decided to use the torque method to give an independent check of our figure.

Gold is a particularly suitable material for such a test since the neck oscillations are strong and of a frequency which is easily measured with either the torque or the field-modulation technique. Furthermore, since it is possible in the superconducting solenoid to measure the ratio between neck and belly oscillations with very high precision (~1 in 5000) this provides also a transfer calibration of the *belly* frequency.

A. Torque Balance Measurements

The sample was a rod of approximately $1\times1\times3$ mm, with its main axis in the ⟨110⟩ direction. It was mounted vertically, allowing a horizontal magnetic field to be swept across the ⟨111⟩ direction in a {110} plane. As the torque ideally vanishes in the ⟨111⟩ direction, seven recordings were taken at intervals of 1° in that neighborhood. The quartz suspension fiber and the sample holder were designed for mounting on a Laue back-reflection x-ray camera, and the uncertainty on the orientation, checked before and after the runs, was less than 1°, corresponding to a systematic error of less than 0.05% on the neck frequency.[3]

The torque balance was of the type described by Condon and Marcus[10]; the field was provided by a 12-in. Harvey-Wells magnet, with a maximum of 22 kG. It was monitored by a Siemens FC32 Hall probe, mounted against a pole face, close to the Dewar tail. The presence of a type-304 stainless-steel Dewar filled with liquid helium modifies the field at the Hall probe by 17 G at 22 kG. Since it was not known how much the field in the interior of the Dewar might be changed, it was felt safer to use a Pyrex Dewar. It was later found, however, that there is no significant difference between the results obtained with either Dewar.

The Hall probe was linearized between 15 and 22 kG by the method described by Lerner,[11] and its output was displayed on the x axis of a recorder; the torque was plotted along the y axis. At least 100 oscillations were recorded for each crystal orientation, between 18.5 and 22 kG. Each sheet of recorder paper was calibrated at both minimum and maximum field before and after recording. For this, the cryostat was removed from the magnet gap and replaced by a NMR deuterium probe, whose resonance frequency was measured by a Model 5245L Hewlett-Packard frequency counter. The deuterium frequency used in the calibration was 653.575 Hz/G.

To determine the de Haas–van Alphen frequency, the output of the Hall probe was read from the recordings at intervals of 10 oscillations, and the slope of the straight line, obtained by plotting the oscillation number in function of reciprocal field, was determined by the method of least squares. A plot was then made of the frequency in function of crystal orientation, and a parabola of the second degree was fitted to the points, also by the method of least squares. The minimum of the parabola gave the ⟨111⟩ neck frequency of gold as $(1.532\pm0.001)\times10^7$ G.

B. Superconducting Solenoid Measurements

i. Calibration

Because of the difficulty, in this case, of making a sufficiently precise direct measurement of magnetic field in the solenoid during an experiment, a number of calibrations of field versus current were made in a separate run. A deuterium NMR probe was constructed to operate in a room-temperature insert in the tail of the inner (normally 1°K helium) Dewar. The solenoid current at each calibration point was measured by the same manganin resistor and digital voltmeter system as was used during the de Haas–van Alphen experiments, and the deuterium resonance frequency was measured by a Hewlett-Packard 5245L frequency counter. Each point was measured several times, approaching slowly from higher and lower fields, to minimize any hysteresis effects. In the range 5 to 50 kG the calibration constant was found to lie within ±0.1%.

ii. de Haas–van Alphen Measurements

The equipment used was the same as that used in the pressure experiments described by Templeton.[8] No provision was made for changing the orientation of the specimen since our earlier experiments had shown that it was possible to locate the samples relative to the magnetic field to within a small fraction of a degree of their orientation as cut. To achieve the required precision of de Haas–van Alphen frequency measurement, the modulation level was set to the optimum for the low end of the field range to be used (~13 to 22 kG for gold); and while the field was swept slowly (~20 G/sec) in either direction over the range, the de Haas–van Alphen oscillations were both recorded on an X-Y recorder and counted on a Hewlett-Packard 5214L counter. At 10-cycle intervals the solenoid current was read automatically by a H-P 3440A digital voltmeter and its value printed out by a H-P 562A digital recorder. Later in the experiments the D.V.M. readings were punched directly onto computer cards via a suitable interface unit and an IBM 526 card punch. A simple computer program was used to make a least-squares fit of a straight line to the 50 or so points representing number of oscillations as a function of reciprocal field. After taking the mean of up- and down-sweep results (which themselves only differed by a few tenths of 1%) the values obtained were consistent within a run to a few hundredths of a percent, and from run to run to at least 0.1%. Since the samples were all within 1° of ⟨111⟩, the orientation correction was less than 0.05%. The linearity of the solenoid field with current could also be checked by computing the error in the assumed linear relationship between number of oscillations and reciprocal current. The probable error in the slope of the line was found to be of order 0.01%.

The final figure for the neck frequency in gold was found to be $(1.531_5\pm0.001_5)\times10^7$ G, in very satisfactory agreement with that obtained by the torque method. This contrasts rather sharply with the figure of $(1.508\pm0.009)\times10^7$ G published in JT.[3]

RESULTS

Table I lists the results for copper, silver, and gold. The neck frequencies and belly/neck ratio are as measured directly, while the belly figures are the products of the neck and ratio values. It seems likely that any

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TABLE I. Neck frequencies and belly/neck ratios as measured, and derived belly frequencies for copper, silver, and gold.

Material	F_N (G)	F_B/F_N	F_B (G)
Cu[a]	$(2.174\pm0.002)\times10^7$	26.72 ± 0.02	$(5.809\pm0.006)\times10^8$
Ag	$(8.921\pm0.01)\times10^6$	51.56 ± 0.05	$(4.600\pm0.005)\times10^8$
Au	$(1.532\pm0.001)\times10^7$	29.33 ± 0.03	$(4.493\pm0.004)\times10^8$

[a] Similar figures for copper, supplied to Dr. E. Zornberg, resulted in an improved fit to a 1-electron-per-atom model (Ref. 7). However, it is not necessarily suggested that the figures in JT (Ref. 3) are *all* in error by +0.6%, as Zornberg assumed.

errors due to hysteresis in a superconducting solenoid will be rather small where a relatively large field interval is involved. This is not generally the case in a direct measurement of a belly frequency. We have found, indeed, that a value of F_B obtained by sweeping the field over an interval of some 1% may be 1 or 2% high in comparison with that derived from $F_N(F_B/F_N)$. However, if a 10% interval is used this error is reduced to less than +0.3%. It is even possible in this way to calibrate the error for a particular 10% or so field interval for use in measuring a de Haas–van Alphen frequency in which no transfer via a ratio can be made.

Note added in proof. Since submitting this paper we have become aware of the work published by O'Sullivan and Schirber.[12] Of the noble metals they give figures for copper only: these figures agree with ours to within our combined experimental errors of ±0.2%.

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Annealing Studies of Irradiated Platinum*

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A field-ion microscope operated at 4.2°K has been used to study defects introduced into 99.9998% pure platinum by fast-neutron irradiation. Damaged or depleted zones have been identified and their concentration and size have been studied as a function of dose and annealing temperature. Direct observations indicate a distribution of zone sizes up to approximately 40 Å in diameter. The density of these zones is linear with dose in the range from 10^{16}–10^{18} n/cm^2 ($E>1.45$ MeV). Field-ion–microscope studies also reveal that upon annealing through stage-IV recovery, the small depleted zones (<15 Å) grow, causing an increase in the density of zones in the range between 15–30 Å. Simultaneously, the largest of the depleted zones present collapse to form dislocation loops lying on {110} planes. The remaining depleted zones are removed at temperatures corresponding to that of self-diffusion. Stage-III recovery in platinum has also been studied by examining specimens irradiated at temperatures above and below stage-III recovery. Direct observation indicates that some form of interstitial-atom motion must be associated with this recovery stage. The possibility of vacancies moving in this temperature range is specifically ruled out by energy considerations.

I. INTRODUCTION

IRRADIATION of metals with energetic particles can introduce local displacements of atoms, leading to nonequilibrium concentrations of Frenkel defects and various combinations of vacancies and of interstitials.[1] At very low temperatures, it is expected that such defects would be immobile except for close pair annihilation of Frenkel defects, which are separated by less than a minimum distance.[2] Various annealing studies of irradiated materials above such low temperatures have revealed five distinct stages of recovery in many of the fcc and bcc metals investigated.[3] Further correlation of these recovery stages with such material parameters as individual melting points of the materials involved, indicate that similar processes might be taking place in corresponding temperature ranges, using the melting point as the scaling factor.[4] This is most likely a consequence of the fact that the energetics of the process do not involve the fine detail of the specific lattice. However, the detailed interpretation of the observed spectrum, within the general framework of imperfection theory, has not been agreed upon by

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