that such a behavior can be explained by proposing the existence of a relatively small number of holelike carriers together with an electron impurity scattering with a different anisotropy from that of phonon scattering. The treatment has shown that if such differing anisotropies exist then at low temperatures the addition of quite small concentrations of impurity can produce relatively enormous change in n^* (see, for example, the effect at 10°K of the addition of a few at. % Ag into Au, or Au into Cu). This is a direct result of the fact that at low temperatures in the pure material n^* is governed by τ_{np}/τ_{bp} while in the alloy it is governed by τ_{n0}/τ_{b0}.

5. CONCLUSIONS

New values of the Hall coefficient of α-phase alloys of the I*B* metals are reported for the approximate temperature range 10–300°K. In the case of the Cu-Au system the results are markedly different from those previously published, and we believe that our data are the more representative of disordered alloys. We have shown that the dependence of the Hall coefficient of these systems upon temperature and solute concentration can be semiempirically interpreted in terms of a two-band model which includes different anisotropies for the phonon and impurity scattering. Our quantitative estimates of the anisotropy of τ are in order of magnitude agreement with those obtained from a treatment of the deviations from Matthiessen's rule, and also show the same scaling among the alloy systems.

Note added in proof. For completeness in Sec. 1, we should also have mentioned the results of Köster and Storing [Z. Metallk. **57**, 156 (1966)] for the disordered Cu-Au system. These room temperature data are in good agreement with ours presented in Fig. 2.

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Absolute de Haas–van Alphen Frequency Measurements in Potassium*

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A precision value of the de Haas–van Alphen (dHvA) frequency for single crystals of potassium has been obtained. Free-standing samples of known orientation were used to avoid the errors from differential thermal contraction inherent in measurements on encapsulated samples. The oscillations of magnetization were measured using a small Bi magnetoresistive probe with a modulation technique. Accurate field measurements were made by monitoring the Cl^{35} NMR in a NaCl crystal positioned close to the sample in a highly uniform region of the magnetic field. After suitable corrections for the small anisotropy, we obtain the value $F_0=(1.8246\pm0.0006)\times10^8$ G for the dHvA frequency of an equivalent spherical Fermi surface. This value is significantly lower than the free-electron prediction of $F_0=1.832\times10^8$ G, but not by the full 0.8% predicted by Overhauser on the basis of a charge-density-wave (CDW) ground state. However, the lattice constant (5.225±0.002 Å) used in making the theoretical predictions may be in error. A careful redetermination of its low-temperature value would allow a more meaningful test of the CDW theory. Until such a direct measurement is made, the present experiment may be considered as a determination of the lattice constant of potassium with two possible results: 5.236 Å from free-electron theory, or 5.215 Å if the CDW ground state is valid.

I. INTRODUCTION

THIS paper reports the results of dHvA measurements, undertaken with the objective of providing definitive experimental evidence relating to the electronic ground state of potassium. Since the proposal by Overhauser[1,2] of a CDW[3] ground state for potassium on the basis of optical absorption measurements, experimental evidence concerning this model has been inconclusive. In view of the comparatively large predicted distortion of the Fermi surface along the direction of the CDW **Q** vector ($\Delta k\sim7\%$) this ambiguity is perhaps

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[1] A. W. Overhauser, Phys. Rev. Letters **13**, 190 (1964).

[2] A. W. Overhauser, Phys. Rev. **167**, 691 (1968).

[3] Although in the initial paper (Ref. 1), the ground state was described as a spin density wave, more recent calculations (Ref. 2) describe the ground state as a charge-density wave, a modification which does not alter the Fermi-surface topology from the SDW prediction.

surprising. In a number of experiments, however, the interpretation of results is made inconclusive by the possible influence of sample strains.

A key experiment which motivated a number of subsequent measurements was the dHvA effect investigation of the alkali metals by Shoenberg and Stiles.[4] The primary purpose of that work, carried out by rotating a sample in the fixed field of a superconducting solenoid, was to investigate the small anisotropic departures in extremal Fermi-surface area from a free-electron sphere. The anisotropy observed by Shoenberg and Stiles,[4] ($\sim$0.1%) recently confirmed by Lee and Falicov,[5] is considerably smaller than that to be expected for a "lemon-shaped" CDW Fermi surface. Interpretation of these results within a CDW framework requires the **Q** vector to be aligned along a sufficiently high magnetic field.[6] The extremal orbits observed experimentally would then be normal to **Q** and hence always circular and only slightly smaller than those predicted by the free-electron model. Because of this possibility, later direct attempts to test the CDW–Fermi-surface topology have primarily been experiments which measure linear dimensions along the magnetic field direction and hence the comparatively large distortion from sphericity along **Q**. A variety of acoustic[7–9] and rf size-effect results[10,11] are in reasonable agreement with free-electron theory, whereas measurements of the helicon Kjeldaas edge[12] and positron-annihilation measurements[13] are better explained by the CDW model. The apparent discrepancies among these results are consistent with an assumption that extreme thermal straining caused by sample preparation, acoustic bonding or by protective coatings can be dominant in determing the local orientation of the CDW at the lower magnetic fields ($\leq$20kG) typical for such experiments. The possibility of complications due to sample strains has also been used[14] to explain anomalous electron-spin-resonance results[15] as well as optical experiments on thin films[16,17] which fail to reproduce the optical absorption anomaly found for single crystals.[18]

Apparently a definitive test of the CDW model requires conditions such that a unique **Q** vector of known orientation is to be expected. In this respect perhaps the least ambiguous experiment is the dHvA effect in large magnetic fields, where interpretation in terms of the CDW model requires field alignment of the **Q** vector. If one assumes a CDW with **Q** along the direction of the magnetic field, the extremal area normal to **Q** should be 0.8% lower than the free-electron value.[19] This prediction cannot be checked in the dHvA data published to date. Although Shoenberg and Stiles[2] made such a measurement of the absolute dHvA frequency, the estimated error in field calibration was 1–2%. Pulsed field measurements by other workers[20] also had estimated uncertainties which were larger than the magnitude of the predicted CDW distortion. There is also a serious objection to the use of samples cast in the sealed off containers used in previous dHvA investigations. As Dugdale and Gugan[21] have emphasized, such constraint can produce dilations equivalent to negative pressures of up to 2000 atm making capillary specimens unsuitable for any precise comparison with theory. The measurements reported here were therefore made using free-standing samples.

II. EXPERIMENTAL TECHNIQUE

Although the magnitude of the largest departure from sphericity of the Fermi surface of potassium found by the rotating sample technique of Shoenberg and Stiles[4,5] is small in comparison with the effect of a possible CDW distortion investigated here, it was considered desirable to work with oriented single-crystal specimens in the hope that use could be made of the published anisotropy measurements to establish experimentally the field alignment of a possible CDW. Ten single crystals of potassium of known orientation were investigated in the present work. The specimens had been cut by a string saw from two single-crystal boules grown from 99.97% nominal-purity bulk potassium metal.[22] The boules had been optically oriented along the required crystallographic directions, and transmission x-ray photographs were taken of a thin slice to check the alignment before the experimental samples were cut. Orientation errors are estimated to be $\pm 3°$. The specimens were in the form of thin discs approximately $\frac{3}{8}$ in. in diameter, 1–2 mm thick, with parallel faces in the (100), (110), or (123) crystallographic planes. Upon receipt, they were lightly etched, dried, and stored in liquid nitrogen until used.

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[18] M. H. El Naby, Z. Physik **174**, 269 (1963); H. Mayer and M. H. El Naby, Physik **174**, 289 (1963); H. Mayer and B. Hietel, in *Proceedings of the International Colloquim on Optical Properties and Electronic Structure of Metals and Alloys* (North-Holland Publishing Co., Amsterdam, 1966), p. 47.
[19] A. W. Overhauser (private communication).
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[21] J. S. Dugdale and D. Gugan, J. Sci. Instr. **40**, 28 (1963).
[22] Obtained from the MSA Research Corporation, Collery, Pa.

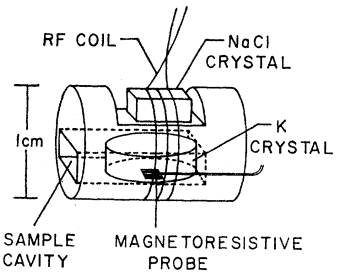

FIG. 1. Schematic diagram of sample holder.

Each sample selected for measurement was etched in a dilute solution of absolute alcohol in dry xylene, carefully dried, placed in the sample holder cavity (Fig. 1), and located in position by a loose packing of tissue paper between the specimen and the open slot of the cavity. The sample holder was then quenched in liquid nitrogen before being transferred to a Dewar prefilled with liquid helium. In this last process the usual procedure was to drain the sample holder of liquid nitrogen, which on freezing might have strained the sample, while holding it in a stream of helium gas at the top of the Dewar before lowering it into the liquid-helium bath. The Dewar temperature was reduced to approximately 1.1°K before making measurements.

The magnetization of the potassium was monitored by a small bismuth magnetoresistive probe[23] glued to the base of the sample cavity directly below the sample under investigation (see Fig. 1). A fixed current in the range 10^{-5}–10^{-3} amp was supplied to the probe and the voltage drop across the probe was monitored by a Princeton model HR-8 lock-in amplifier whose reference channel was used to drive an audio amplifier providing a 2–15-Hz current for the field modulation coils. A 60-kG Varian superconducting magnet provided the dc field. Because of hysteresis effects on the solenoid wire, the field could not be predicted reliably from the known current to better than 0.1%. To obtain the dHvA frequency to the precision necessary to see anisotropy the magnetic field strength was monitored directly at the sample throughout each run. This was done by placing a NaCl crystal close to the sample as shown in Fig. 1. An rf coil was wound around the small holder containing the K sample and the NaCl crystal. In this configuration, both crystals were located within a region of the solenoid where the field was uniform to better than 1 part in 10^4. The applied field was measured by observation of the Cl^{35} NMR line using a Robinson marginal oscillator and an EMC lock-in amplifier. To optimize the NMR signal, the reference channel of the EMC lock-in amplifier was made coherent with a 280-Hz modulation current through the modulation coils, allowing modulation-amplitude control independent of the low-frequency dHvA modulation current.

[23] Purchased from American Aerospace Corporation, Farmingdale, N. Y.

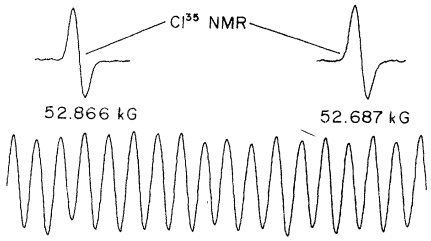

FIG. 2. Portion of a recorder tracing of raw data.

In a typical run the solenoid field was swept linearly in H^{-1} from 58 to 50 kG or in some cases to as low as 40 kG. One run made with field increasing with time indicated that no systematic error was involved. After observing an NMR line, the frequency of the Robinson oscillator was adjusted to a value corresponding to a resonance field 200–300 G lower so that as the field passed through the new resonance value the NMR line was again recorded by one pen of a two-pen strip chart recorder. The second pen of the recorder was used to display the dHvA oscillations. By repeating this procedure and recording the resonance frequencies as measured on a Hewlett-Packard model 5245L frequency counter, continuous traces giving up to 1400 oscillations and 125 field calibrations could be obtained. A portion of such a trace is reproduced in Fig. 2.

III. RESULTS

The data for each sample were processed using a digital computer to make a linear least-squares fit to oscillation count (estimated to 0.01 cycle) corresponding to the reciprocal magnetic field values at each NMR calibration. The field was calculated from the NMR frequency using a Larmor frequency of 4.1716×10^6 Hz at 10 kG.[24] The large number of calibrations allowed a check for flux jumps which in some cases have limited the accuracy of dHvA experiments to 0.5% in similar superconducting solenoids.[25] Flux jumps could possibly lead to a miscount in the number of oscillations but would be detected as a large deviation in the dHvA frequency, which was computed for the local field interval. The recorder tracings contained several instances where the oscillations locally were nonperiodic in time, probably because of variations from linearity of the H^{-1} field sweep but also possibly from flux jumps: No actual miscounts were detected.

Overhauser has suggested[19] that a CDW, through the introduction of heterodyne band gaps, may produce additional side band frequencies in the dHvA oscillations. With this possibility in mind, field sweeps were made for several samples over a much larger range of H^{-1} than would have been necessary for precision measurement of a single dHvA frequency. No beats

[24] Obtained from relative measurements [Yu Ting and Dudley Williams, Phys. Rev. 89, 595 (1953)] and the value for H^1 from the tabulation of Varian Associates.

[25] Joseph J. Vuillemin, Phys. Rev. 144, 396 (1966).

were observed in these runs, but a small systematic variation in the computed frequency was detected in the form of nonrandom deviations from the least-squares linear fit to the experimental data. These deviations, only slightly larger than our random errors, were of the order of ± 0.1 oscillation over a few hundred oscillations and resulted typically in fluctuations of 0.05% in the measured dHvA frequency. The published anisotropy measurements indicate that a rotation of 20° from [110] is required to produce a change of this magnitude in the dHvA frequency so that it is not likely that mosaic structure in the samples is responsible for this effect. A possible explanation is the presence of harmonic distortion found at high fields. The field dependence of this distortion would, of itself, lead to systematic errors in estimating the phase of the signal. Further, an instrumental source of systematic error may result from the modulation technique employed. Since the modulation amplitude is fixed, the resulting signal is proportional to $J_1(2\pi F H_m B^{-2})$, where F is the dHvA frequency, B is the magnetic induction in the sample, and H_m is the modulation amplitude. The first zero of the Bessel function J_1 occurs at almost twice the argument corresponding to its maximum value, so that for a given value of B, H_m can be adjusted to produce a signal with low second-harmonic content. However, as the field is swept to a lower value ($\sim$10 kG lower for a 59-kG initial field), the relative amplitude of second-harmonic content will rise to that given by the second maximum in the Bessel function. This change will be reflected experimentally as a corresponding systematic error in estimates of the signal phase and nonrandom deviations from a least-squares linear fit.

There does remain some evidence in apparent conflict with the above explanation, in that neither of the (100) samples showed any significant field variation of the dHvA frequency, whereas the effect was present in the four other samples which were investigated over a sufficiently large range of magnetic field. An alternative explanation may lie in the possible presence of heterodyne frequencies predicted on the basis of a CDW model. An analysis by Shoenberg[26] suggests that magnetic interaction effects can considerably reduce the amplitude of the resulting beat pattern when one frequency is dominant. Thus, our failure to observe beats directly in the raw data does not rule out the possibility that extra frequencies are present. The detection of the observed frequency changes was, however, too marginal to allow any firm conclusions as to physical origin.

The results of the present measurements are summarized in Table I. The value of $(F_{100}-F_{110})/F_0 = 17.9\pm 1.6\times 10^{-4}$ derived from these results is in satisfactory agreement with the value $(18.80\pm 0.47)\times 10^{-4}$, cited by Lee and Falicov. In addition, a 20° angular rotation of one of our (100) samples with respect to the applied magnetic field resulted in $\Delta F/F_0 = 12\times 10^{-4}$, also in good agreement with the data of Lee and Falicov. The fact that these differences in our absolute dHvA frequencies among a number of different samples are in such good agreement with the inherently more accurate relative determinations leads to the conclusion that if a CDW is present in these samples it must be aligned by the external magnetic field. As a specific check on the effect of thermal cycling, sample 1 (H along [100]) was warmed to 170°K and later to room temperature, without removing the sample from its holder. Subsequent runs gave the same value of the dHvA frequency to within the experimental error of $<0.01\%$. For both of the (100) samples agreement among the runs was consistent with the small differences (0.02%) to be expected from possible alignment errors. For the other samples the frequency-variation effect already discussed was larger than the changes in the average value obtained for different runs or indeed among samples. This consistency is a good indication that systematic errors arising from possible sample strain are negligible.

TABLE I. Experimental dHvA frequencies in potassium.

Nominal direction of **H**, crystallographic orientation	Run	F in units of 10^8G	F corrected to an equivalent sphere (average value)[a] units of 10^8G
[100] (Sample 1)	1–3	1.82741 ± 0.00020	1.82461
(Sample 2)	7, 8	1.82694 ± 0.00010	
(Sample 3)[b]	4, 17	1.82461 ± 0.00100	
(Sample 4)	5	1.82349 ± 0.00040	1.82466
[110] (Sample 5)	12	1.82394 ± 0.00015	
(Sample 6)[b]	14	1.82352 ± 0.00200	
(Sample 7)	6	1.82411 ± 0.00015	
(Sample 8)	9	1.82439 ± 0.00021	1.82449
[123] (Sample 9)[b]	15	1.82365 ± 0.00080	
(Sample 10)[b]	16, 18, 19	1.82406 ± 0.00150	
F_0, the dHvA frequency for an equivalent spherical Fermi surface		$(1.8246\pm 0.0006^c)\times 10^8$G	

[a] Corrections made were derived from Refs. 4 and 5, as explained in the text.
[b] The errors quoted for these samples reflect the maximum variation in frequency with field as discussed in the text, and greatly exceeded the standard deviation of the least-squares constant-frequency fit to the data, or the spread among the runs.
[c] The error quoted includes some allowance for systematic errors.

To allow comparison with the theory we have corrected our values for different crystallographic orientations to give the dHvA frequency of a spherical Fermi surface containing the same number of electrons. This was done using the deviations from such a spherical surface obtained by Shoenberg and Stiles[4] after scaling[27] these according to the more accurate results of Lee and Falicov.[5] In taking average values each sample was weighted equally but for a given sample extra weight was given to runs over larger field sweeps.

[26] D. Shoenberg (to be published).

[27] The data of Ref. 5 uses the (110) frequency value as an origin, and therefore cannot be used directly. Simple scaling using the data of Ref. 4, which has a zero corresponding to the equivalent sphere, should be reasonable [M. J. G. Lee (private communication)], but the differences are not critical for our purpose.

After the corrections have been made we obtain a value of $(1.8246\pm0.0006)\times10^8$G for the absolute dHvA frequency corresponding to a spherical Fermi surface. The values obtained for the three crystallographic directions investigated show a spread of only a part in 10^4, comparable to the precision of field calibration. The larger error quoted reflects a guess at the possible error introduced by the frequency fluctuations already discussed.

IV. DISCUSSION

Assumption of the free-electron model, coupled with Barrett's[28] experimental value for the lattice constant of potassium at 5°K (5.225±0.002 Å), leads to a predicted dHvA frequency of 1.832×10^8G, or 0.4% higher than our experimental result. This discrepancy is considerably larger than our estimated experimental uncertainty.

The dHvA frequency is thought to be unaffected by the electron-electron interaction[29] and such a discrepancy, if real, is not therefore easily explained. It should be pointed out, however, that some doubt exists as to the reliability of Barrett's absolute value for the lattice constant, since the primary purpose of Barrett's work was to investigate possible martensitic transformations. Analysis of specific-heat data has lead Martin[30] to suggest the possibility of systematic experimental errors. Certainly a possible source of error would be the the 0.5% (~1 at.%) Na contained in the potassium used by Barrett. Martin's analysis, however, indicates that it is impossible to correct Barrett's data with confidence, and it would be premature to speculate on the existence of a CDW ground state in potassium on the basis of our results together with Barrett's lattice constant. Should a precision low-temperature lattice-constant measurement for pure potassium become available, however, these results would provide a reliable test of the CDW hypothesis, as the conditions required for the observation of the CDW would appear to have been satisfied. Our measured anisotropy of the Fermi surface obtained from the difference of absolute measurements on a large number of different samples is in good agreement with the available relative data, indicating that the objective of aligning any CDW present along the magnetic field had been achieved. The use of free-standing samples and precision field calibration in our opinion gives a value of the dHvA frequency sufficiently free from possible systematic errors for any deviations from free-electron theory to be meaningful, while also satisfying the low-strain requirements for observation of a CDW. It might be interesting to note that at present our results, suitably inverted, constitute a determination of the lattice constant. From free-electron theory our measurements give a value of 5.236 Å for the lattice constant, whereas, if the CDW model represents the correct ground state of potassium, a value of 5.215 Å is obtained.

Note added in proof. An experimental determination of the lattice constant has recently been carried out at 5.2°K by S. A. Werner and A. Arrott (private communication) using neutron diffraction. The preliminary result (5.233±0.002 Å) is in good agreement with the value inferred from the present work using free-electron theory.

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[29] J. M. Luttinger, Phys. Rev. **121**, 1251 (1961).
[30] Douglas L. Martin, Phys. Rev. **139**, A150 (1965).

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