THE PHYSICAL REVIEW

A journal of experimental and theoretical physics established by E. L. Nichols in 1893

SECOND SERIES, VOL. **176**, NO. 3 15 DECEMBER 1968

Anisotropic Relaxation Times and the Hall Coefficients of α-Phase Alloys of the I*B* Metals

R. D. BARNARD,* J. E. A. ALDERSON, T. FARRELL,† AND C. M. HURD

Division of Applied Chemistry, National Research Council of Canada, Ottawa, Canada

(Received 16 August 1968)

The Hall coefficient (R_H) of polycrystalline, α-phase alloys of the IB metals has been determined in the range 10–300°K. R_H shows a dependence upon temperature and solute concentration which might be regarded as very unexpected in a system of monovalent constituents with similar electronic structures. However, it is shown that the data can be interpreted semiempirically in terms of a two-band model which includes different anisotropies of the relaxation times associated with impurity and phonon scattering. Estimates of these anisotropies are obtained for each system and are shown to be in relatively good agreement with those obtained from a similar analysis of deviations from Matthiessen's rule.

1. INTRODUCTION

THE electronic structure of the pure group-IB metals has been closely studied for nearly two decades, and there now exists a detailed picture of the geometry of their Fermi surfaces. It is well known, however, that the experimental techniques which provide a direct measurement of this quantity require a long electronic mean free path and in general they are therefore limited to measurements upon very dilute alloys at very low temperatures. Furthermore, electron-transport theory of alloys requires more than a knowledge of the geometry of the Fermi surfaces; it requires some information about how the electronic relaxation time for a given type of scattering $\tau(\mathbf{k})$ varies over the Fermi surface, and up to the present time this has not been forthcoming from the type of experiment referred to above (exceptions to this include work by Deaton and Gavenda,[1] and King-Smith[2]). One is therefore compelled to attempt to obtain such information from the interpretation of more indirect experiments. It is the purpose of this paper to report the results of such an approach to new values of the Hall coefficient R_H determined in the approximate range 10–300°K for the Ag-Au and the α-phase of the Cu-Au and Cu-Ag systems.

Ziman[3] has considered the anisotropy of $\tau(\mathbf{k})$ in the IB metals from a theoretical point of view and has made some estimate of it (for both scattering by phonons and by impurities) by considering what is essentially a two-band model. The electrons in states on the "belly" (denoted by subscript b) of the Fermi surface, which are basically s-like, are considered separately from those on the "necks" (subscript n), which are basically p-like. Perhaps the main feature of Ziman's argument is the prediction that τ_b will tend to increase rapidly at low temperatures due to the freezing out of umklapp processes from the belly as the temperature is reduced. This prediction is supported by the temperature dependence of R_H for the pure IB metals[3,4] and by a recent interpretation of deviations from Matthiessen's rule in certain Cu- and Ag-based alloys by Dugdale and Basinski.[5] These authors have obtained estimates of the ratio of the relaxation times of electrons in the two bands which will be discussed in Sec. 4. The framework of the two-band approach to transport properties of noble-metal alloys, however, immediately suggests that measurements of the Hall effect would probably be more informative than, for example, measurements of the electrical resistivity, for R_H has contributions from the bands which are odd functions of the effective charge of the carrier, while the corresponding contributions

---

* Visiting Scientist, 1968. Permanent address: University of Salford, Salford, Lancashire, England.

† National Research Council Postdoctoral Fellow.

[1] B. C. Deaton and J. D. Gavenda, Phys. Rev. **129**, 1990 (1963).

[2] P. E. King-Smith, Phil. Mag. **12**, 1123 (1965).

[3] J. M. Ziman, Phys. Rev. **121**, 1320 (1961).

[4] J. E. A. Alderson, T. Farrell, and C. M. Hurd, Phys. Rev. **174**, 729 (1968).

[5] J. S. Dugdale and Z. S. Basinski, Phys. Rev. **157**, 552 (1967).

to ρ are even functions of the carrier's charge. Thus R_H depends upon the relative number of *s*- and *p*-type electrons in a manner which ρ does not.

As a starting point we have chosen to study the homologous α-phase alloys of the I*B* metals. The Ag-Au system in particular should be the simplest to analyze since *a priori* it is known that the pseudopotentials of the two constituents must be very similar (e.g., the residual resistivity of each in the other obeys Mott's rule), and there is a continuous range of solid solution with negligible change in lattice parameter. Early measurements of relatively low accuracy exist for R_H in Ag-Au by (temperature of measurement is bracketed) Kammerlingh-Onnes and Beckmann[6] (20, 290°K), Ornstein and van Geel[7] (~300°K), and Flanagan and Averbach[8] (300°K), while more recent results of higher accuracy have been given by Köster *et al.*[9] (90–800°K). R_H for the Cu-Au system has been determined by Flanagan and Averbach[8] (80, 300°K) for the full range of solute concentrations, but there are no previous measurements of its temperature dependence other than for the particular concentration Cu_3Au which has been measured by Love[10] (4–300°K) in the ordered and disordered state, as well as by Komar and Sidorov[11] (~300°K). There are apparently no previous measurements of R_H for α-phase alloys of the Ag-Cu system.

2. EXPERIMENTAL METHOD

The polycrystalline alloys were prepared from 99.9999% (6*N*) pure starting material[12] of which some trace analyzes have been carried out and published elsewhere.[13] The total mass of the constituents of an alloy casting was in the range 30–50 g, and they were heavily chemically etched before being melted together in a high-purity alumina crucible[14] which had been chemically cleaned in boiling aqua regia. Details of the vacuum-induction furnace have previously been given.[13] The ingot was removed, its surface chemically cleaned, and then recast to improve homogeneity. Sections from the top and bottom of the second cast were chemically analyzed[15] to test homogeneity, and the acceptable ingots were rolled to sheet. (Repeated annealing was necessary for those Cu-Au samples which work hardened rapidly during rolling.) The Hall samples and their electrical leads were cut from the prepared sheet by means of a Servomet spark cutter and fixed template with the shape described previously.[4] Prior to measurement the samples of Ag-Au were degreased after cutting, cleaned with a Wise-Jewett etchant[16] and annealed in vacuum at 550°C for 120 h before slowly cooling to room temperature. After chemical cleaning, the alloys from the Cu-Ag system were annealed for 72 h at 780°C before rapid quenching into iced brine.

TABLE I. Summary of data for the Cu-Au samples.[a]

Au concentration (at. %)	Resistivity of wires at 0°C ($\mu\Omega$ cm) b	c	Lattice parameter of Hall samples[b] (kxu)	Resistivity at 20°C[d] ($\mu\Omega$ cm)
90.2	5.95	···	4.0341	6.00
74.9	10.74	10.73	3.9757	10.90
59.4	12.63	13.29	3.9073	13.65
39.9	12.65	13.41	3.8294	13.60
25.1	10.87	···	3.7443	11.40
15.3	8.24	···	3.6994	8.35

[a] Two Hall-effect samples (Cu+7.2 at. % Au, Cu+19.8 at. % Au) were not analyzed in this way.

[b] Sample vacuum annealed at 550°C for 24 h and quenched in iced brine.

[c] Sample vacuum annealed at 550°C for 168 h and quenched in iced brine.

[d] Interpolated from data of Ref. 17.

The samples of the Cu-Au system were degreased after cutting from the sheet, chemically cleaned where possible, and annealed in vacuum at 550°C for 24 h before being rapidly quenched into iced brine. As we describe in Sec. 3, our Hall-effect results for the Cu-Au system are completely different from those found by previous workers. Since the previous studies show some agreement among themselves, we initially assumed that our results were at fault in some respect. We proposed two possible sources of systematic error in our method: (1) an instrumental source of some kind; and (2) a metallurgical source, probably the presence of some phase other than α in our samples. We had a great deal of evidence to contradict (1). The same apparatus and sample preparation methods had previously been used for the pure group-I*B* metals[4] and the Ag-Au system, the results for which all were in good agreement with those of previous work. Therefore, we intuitively favored (2), although from the previous work[10] on Cu_3Au it is clear that the difference between our results for a disordered alloy and those of Love[10] is in the wrong sense to be explicable in terms of any ordered phase present in our samples.

In view of the large discrepancy between our results for the Cu-Au system and those previously published, and since it is known that R_H for a noble metal is very sensitive to the metallurgical state of the sample,[9] we feel it is appropriate to describe in some detail our attempts to prove the existence in our samples of some phase other than α. To test proposition (2) we prepared wires (0.020 in. diam) from the same ingots used for the Hall samples and subjected them to the same heat treatment (quenched after 24 h at 550°C). The electrical resistivities of these wires are given in Table I, column 2,

---

[6] K. Onnes and B. Beckmann, Proc. Acad. Sci. Inst. **15**, 307 (1912).

[7] L. S. Ornstein and W. C. van Geel, Z. Physik **73**, 488 (1931).

[8] W. F. Flanagan and B. L. Averbach, Phys. Rev. **101**, 1441 (1956).

[9] W. Köster, D. Hagmann, and K. E. Saeger, Z. Metall. **54**, 19 (1963).

[10] W. F. Love, J. Phys. Chem. Solids **9**, 281 (1959).

[11] A. Komar and S. Sidorov, J. Phys. **4**, 552 (1941).

[12] Cu supplied by Gallard-Schlesinger Corp.; Ag and Au supplied by Consolidated Mining and Smelting Co.

[13] C. M. Hurd, Cryogenics **6**, 264 (1964); J. Phys. Chem. Solids **27**, 1371 (1966).

[14] Supplied by McDanel Refractory Porcelain Co.; grade 997.

[15] The chemical analyzes were made by the Analytical Section of this Division.

[16] E. M. Wise, *Gold* (D. Van Nostrand Co., Inc., Princeton, N. J., 1964), p. 360.

and comparison with the values interpolated from those of Johansson and Linde[17] for 20°C (Table I, column 5) shows that our samples containing 59.4 and 39.9 at.% Au were significantly lower than those of Johansson and Linde[17] while our results at other concentrations were in excellent agreement. This evidence supported (2) in that it is known[17] that the presence of a second phase can reduce the resistivity, but against this it must be pointed out that there is also a wide spread of resistivity values quoted in the literature for ostensibly α-phase alloys. For example, ρ for disordered Cu_3Au has been given as (in $\mu\Omega$ cm, together with the temperature of measurement) 11.35 (20°C),[17] 12.7 (?),[10] 11.25 (~20°C),[11] 11.3 (~20°C),[18] and 10.87 (0°C).[19] (There seems to be no correlation of these results with either annealing time or temperature, and in fact there are contradictory conclusions in the literature relating to the effect of heat treatment of Cu_3Au. For example, Damask[20] finds from resistivity measurements that increasing disorder takes place with increasing quenching temperature from 390 to ~485°C, while Kuczynski *et al.*[21] find exactly the opposite from measurements of Young's modulus.)

Following these results, Calvert of our x-ray section kindly undertook the following work. Two photographs of each Hall sample in the Cu-Au series were taken in a Debye-Scherrer camera of 114.3 mm diam with Cu radiation. One was a back-reflection oscillation exposure for a lattice parameter determination and the other a glancing-angle oscillation exposure for a metallurgical phase determination. No sample showed evidence of any detectable amount of any phase other than α, and in each case the lattice parameter (given in Table I, column 4) was in excellent agreement with that expected from the measured composition. However, the x-ray results give information only about the surface of the sample, and to check that the bulk of the sample was in the same phase as the surface we took a wire sample drawn from the same ingot as produced a Hall sample (in fact Au+39.9 at.% Cu) which, after the same heat treatment given to the Hall samples, was x-ray photographed. The surface showed only the α-phase. The wire was then etched (in boiling aqua regia) to half its original diameter and then rephotographed. The new surface showed the original α phase plus a fcc phase with (to within the limits of precision of the experiment) the same lattice parameter as pure Au. Further x-ray work using Cr and Mo radiations, which have different penetration depths from that of Cu, gave evidence from the 220, 311, and 222 lines that the Au was localized on the surface, having probably been replated there during the etching. This proposition was supported by the evidence from the 111 and 200 lines which showed that the Au had randomly oriented texture while the bulk α-phase showed well-aligned drawing texture. The lattice parameter determined for the α phase of this wire sample was in agreement with that expected from the concentration. Thus, although the x-ray results were not *entirely* conclusive in the matter of Au found on the surface of the etched sample, there was no evidence in any of this work of the presence of any phase other than the α, either upon the surface or within the bulk of the material.

We found in the course of this work that the annealing time can affect the resistivity (but not R_H to within our accuracy) of Cu-Au alloys. Three wire samples, including the two whose resistivities previously did not agree with the results of Johansson and Linde, were reannealed in vacuum at 550°C for 168 h before rapid quenching into iced brine. The resistivities were redetermined and are given in Table I, column 3. Comparison shows that the resistivity of two of these samples increased significantly such that the results for all samples are in excellent agreement with those of Johansson and Linde. We can presently offer no explanation of this effect, but we can report that a similar treatment of the Hall samples of corresponding concentrations did not significantly alter the value of R_H or its temperature dependence.

In view of these unexplained resistivity results we must admit the possibility that the degree of disorder of our Cu-Au samples is not necessarily the same as that of α-phase alloys studied by previous workers. However, we have found no direct evidence of any phase other than α to be present in our samples, and if we are to explain the discrepancy between our values of R_H and those in the literature in terms of metallurgical effects it is clear[10,11] that a very significant degree of order is required in our samples. Furthermore, taking the Cu_3Au composition as a test case, our values of R_H are found to be more negative than those previously found for a disordered alloy,[10] while ordering brings about a large positive increase in R_H.[10,11] Hence these data support the proposition that our results are in fact more representative of disordered alloys than those previously available.

The Hall-effect measurements were made by a dc technique which has been described in connection with similar measurements upon the pure group-IB metals.[4] In the following the results for the pure elements are taken from this previous work, although Fig. 2 actually shows new results for a pure Cu sample quenched in iced brine after a vacuum annealing at 550°C for 24 h. The results are not significantly different from those for a sample slow-cooled from 550°C.[4] The thickness of a sample was measured as described previously[4] and for samples of the Ag-Au series was in the range 0.023–0.026 in., and in the range 0.017–0.023 in. for a Cu-Au or Ag-Cu sample. All other details of the experimental method are identical to those described previously.[4]

---

[17] C. H. Johansson and J. O. Linde, Ann. Physik 25, 1 (1936).

[18] C. Sykes and F. W. Jones, Proc. Roy. Soc. (London) A157, 213 (1936).

[19] See Table I.

[20] A. C. Damask, J. Phys. Chem. Solids 1, 23 (1956).

[21] G. C. Kuczynski, M. Doyama, and M. E. Fine, J. Appl. Phys. 27, 651 (1956).

From repeated measurements upon samples which have been removed from the apparatus, chemically reduced in thickness and replaced, we estimate the accuracy of any R_H value as ±1.5%. This is slightly lower accuracy than we estimate for earlier measurements of the pure metals made with the same apparatus[4] but, we think, it includes some systematic error introduced from metallurgical effects incurred during cleaning and handling the alloy samples (particularly Cu-Au) which is not present with the pure metals. The electrical resistance of each sample was measured potentiometrically at the ice point using knife-edge potential contacts. The samples, which were in wire form with a diameter of ~0.040 in., were cut at the knife-edge marks and weighed with a high-precision Mettler balance. Their diameters were determined with a light wave micrometer,[4] and their lengths from their densities, which were obtained from lattice parameter data. In this manner the form factor of the specimen, and ultimately its resistivity, was determined with an accuracy of 0.25%. To determine departures from Matthiessen's rule, a wire sample of pure Au and one of Au+1 at. % Cu were mounted together in a suitable holder with soldered potential leads, and in this case the form factors for the two samples were determined from their resistances at the ice point (the resistivities being known). Hence the resistivity of the sample could be determined at chosen temperatures.

3. EXPERIMENTAL RESULTS

Our results for the Ag-Au system are shown in Fig. 1. (We choose to present the data graphically. The tabulated results are available upon request.) These agree well with the recent similar work[9] in their common temperature region (80–300°K) except for a detail shown by Köster *et al.* at the gold-rich end of the system. From data obtained at 300°K, Köster *et al.* interpolate that R_H has a local minimum at about Au+5 at. % Ag (Fig. 4 of Ref. 9 or Fig. 1 of Hurd[22]). Our data, which in this region are more closely spaced than the earlier results, do not confirm this interpolation but show rather (insert to Fig. 1) that R_H varies approximately linearly with solute concentration as Ag is added to Au up to about 20 at. %. (To avoid overcrowding in the main part of Fig. 1 we have omitted the results for Ag+95 at. % Au.) We think it is important to note that for temperatures above 300°K the data of Köster *et al.* show more conclusively that such a local

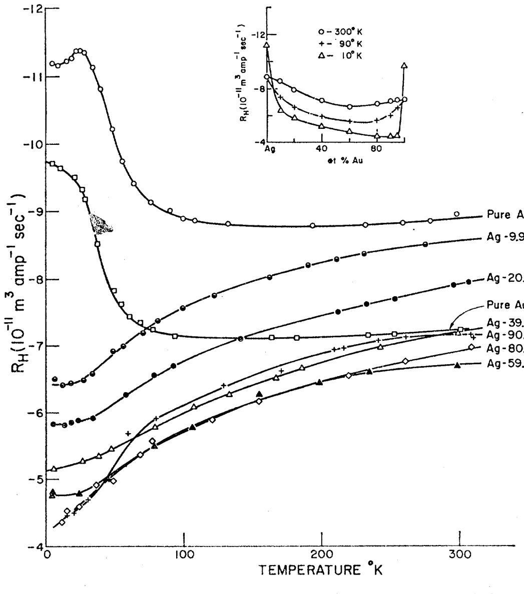

FIG. 1. Temperature dependence of the Hall coefficient of polycrystalline alloys of the Ag-Au system.

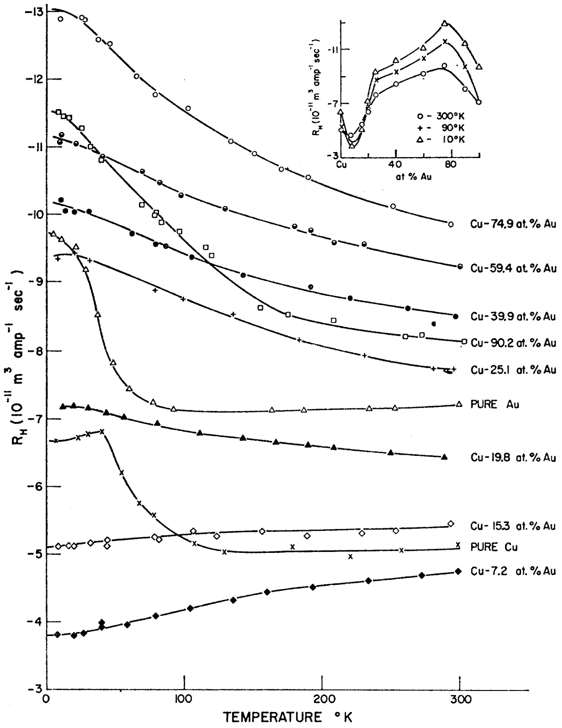

FIG. 2. Temperature dependence of the Hall coefficient of polycrystalline, α-phase alloys of the Cu-Au system.

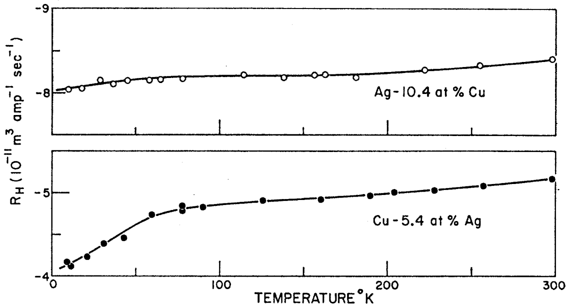

FIG. 3. Temperature dependence of the Hall coefficient of polycrystalline, α-phase alloys of the Cu-Ag system.

---

[22] C. M. Hurd, Phil. Mag. **12**, 47 (1965).

minimum exists, but unfortunately we cannot check this as our present apparatus does not function above 300°K.

Our results for α-phase Cu-Au alloys are shown in Fig. 2. They are in disagreement with previous similar work in almost every respect, and this naturally has been a source of some concern to us as the description in Sec. 2 indicates. First, consider the dependence of R_H upon solute concentration. The only previous similar data were obtained by Flanagan and Averbach[8] and these show R_H to have a practically linear dependence upon solute concentration with apparently no significant difference between results obtained at 80 and 300°K. Our results, on the other hand (insert to Fig. 2), indicate a local maximum in the R_H versus solute concentration curve at about Au+90 at.% Cu (of which there is also evidence in some results of von Neida and Gordon[23]) together with a broader local minimum at about Au+25 at.% Cu. Furthermore, we find a very appreciable temperature dependence of R_H.

Second, consider this temperature dependence of R_H. The only data available for comparison are the results obtained by Love in the range 4.2–300°K for an ostensibly disordered sample of Cu_3Au. These show that R_H is relatively independent of temperature in the range 80–300°K, and that it increases slightly as the temperature is reduced below 80°K. Our results (Fig. 2) for Cu+25 at.% Au are completely different; they show that R_H is strongly temperature-dependent over the whole temperature range and increases monotonically as the temperature is reduced. Furthermore, our value of R_H at any temperature is a factor of 1.5–2.0 smaller than the corresponding value obtained by Love. We tentatively attribute this discrepancy to metallurgical effects in the sample. We pointed out in Sec. 2 that from Love's own work,[10] and that of Komar and Sidorov,[11] the sign of this discrepancy supports the proposition that our results are more representative of the disordered state than those obtained by Love. Unfortunately it appears that no special examination was made of the metallurgical state of Love's sample.

Figure 3 shows our results for quenched *Ag*-Cu and *Cu*-Ag samples. There are no previous data available for comparison.

The electrical resistivity results are summarized in Table II which contains values of the deviation from Matthiesson's rule Δ divided by the residual resistivity ρ_0.

TABLE II. Summary of resistivity results for Cu in Au.[a]

Temperature (°K)	Δ/ρ_0
66	0.10
77	0.10
131	0.13
167	0.13
273	0.15

[a] Δ is the deviation from Matthiessen's rule; ρ_0 is the residual resistivity. ρ_0 for Au+1 at. % Cu was 0.37 $\mu\Omega$ cm, and for pure Au was 0.0036 $\mu\Omega$ cm. These data have not been corrected for changes in atomic volume produced by alloying and by thermal expansion. These corrections become increasingly insignificant as the temperature is reduced (Ref. 5) and it is the datum at 66°K which was used in the calculation of σ_{n0}/σ_{b0} of Table V.

4. DISCUSSION

The Fermi surfaces of Ag, Au, and Cu are now well known and possess the same basic features including zone boundary contact with the Brillouin zone in the $\langle 111\rangle$ directions. Since the effect of the band structure and of the anisotropy of the electronic relaxation times are known to be the principal contributors to R_H for noble-metal alloys, we interpret the striking difference between the concentration dependences of R_H for the Ag-Au and Cu-Au systems as evidence that the anisotropy of the relaxation times must be markedly different in these two systems. In the interpretation of the data we shall follow Ziman[3,24] and consider a simple two-band model in which it is assumed that states on the neck regions of the Fermi surface possess holelike properties while those on the belly regions are electronlike. We assume further that these two regions are characterized by their own effective masses m_n and m_b and by their relaxation times τ_n and τ_b. This is a gross simplification of reality. Only one component of the effective-mass tensor is known to be negative in the neck regions,[24] and interband transitions are explicitly excluded from the two-band formulation. However, the two-band model has aided our understanding of various electron-transport properties of the noble-metal alloys, including the Hall effect, where such a model has already been applied with some success to the Ag-Au system[25,26] and to noble metals with charged impurities,[27] but no information on the anisotropy of the electron relaxation times was obtained from either analysis. Indeed the analysis given by Takano[27] was unable to account for the Hall-effect behavior in the Ag-Au system.

R_H is given by the two-band model as

$$R_H=\frac{1}{N}\left(\frac{\sigma_b{}^2}{n_b ec}-\frac{\sigma_n{}^2}{n_n ec}\right)(\sigma_b+\sigma_n)^{-2}=\frac{1}{Nn^*ec}, \tag{1}$$

where N is the number of conduction electrons per unit volume, and σ_n and σ_b are the neck and belly conductivities, respectively.

Writing

$$A=\sigma_n/\sigma_b \tag{2}$$

then

$$n^*=\frac{n_b n_n(1+A)^2}{n_n-n_b A^2}. \tag{3}$$

---

[23] A. R. Von Neida and R. B. Gordon, Phil. Mag. **7**, 1129 (1962).

[24] J. M. Ziman, Advan. Phys. **10**, 1 (1961).

[25] D. Hagmann and K. E. Saeger, Z. Metall. **54**, 650 (1963).

[26] E. Krautz and H. Schultz, Z. Naturforsch. **12a**, 710 (1957).

[27] K. Takano, J. Phys. Soc. Japan **23**, 1234 (1967).

TABLE III. Number of electrons per atom in neck states (n_n) and belly states (n_b) for different $k=m_n/m_b$.

k	Ag n_n	Ag n_b	Cu n_n	Cu n_b	Au n_n	Au n_b
1.0	0.08	0.92	0.15	0.85	0.16	0.84
0.9	0.10	0.90	0.18	0.82	0.19	0.81
0.8	0.13	0.87	0.23	0.77	0.24	0.76
0.7	0.17	0.83	0.28	0.72	0.29	0.71
0.6	0.23	0.77	0.36	0.64	0.37	0.63
0.5	0.34	0.66	0.48	0.52	0.49	0.51

Further simplification may be obtained by expressing

$$A=\frac{\sigma_n}{\sigma_b}=\frac{n_n}{n_b}\frac{m_b}{m_n}\frac{\tau_n}{\tau_b}=\frac{n_n}{n_b}kx, \tag{4}$$

where

$$k=\frac{m_b}{m_n} \quad\text{and}\quad x=\frac{\tau_n}{\tau_b}.$$

For the Ag-Au, Cu-Ag, and Cu-Au alloys considered here

$$n_n+n_b=1 \tag{5}$$

and thus

$$n^*=\frac{[1-n_n(1-kx)]^2}{1-n_n(1+k^2x^2)}. \tag{6}$$

At room temperature, where for the pure noble metals phonon scattering is assumed to be isotropic ($x=1$), the values of n^* for Ag, Au, and Cu are 1.20, 1.46, and 1.44, respectively. Values of n_n (and hence n_b) can thus be calculated for a given k, and such are given in Table III. To proceed further it is necessary to fix a value of k, which unfortunately [as shown by (6)] is inextricably bound with the scattering anisotropy. However, we have estimated k in the following manner. It can be shown that the smallest positive value of n^* is n_b, and this occurs when $kx=0$. In the Cu-Au system the smallest value of n^* observed is 0.74 (Cu+74.9 at.% Au at ~10°K) and it can be judged from Table III that the maximum possible value for k in this system is therefore about 0.75. We feel that a value of k of about 0.6 or less would be unrealistic in view of the resulting numbers of electrons and holes, while our present estimates for the Cu-Au system of $k=0.70$, $n_n=0.29$, and $n_b=0.71$, which will be used in the following, seem reasonable in view of what is known of the Fermi surfaces of the materials. Clearly then, our interpretation of the data is semi-empirical and this must be borne in mind when considering Fig. 4, where the agreement between the calculated and experimental values of n^* for Cu+74.9 at.% Au at 10°K is implicit to the treatment.

In alloys for which the solute concentration exceeds a few percent the impurity scattering will certainly be dominant at 10°K. For these circumstances we can write

$$x=x_0=\tau_{n0}/\tau_{b0}, \tag{7}$$

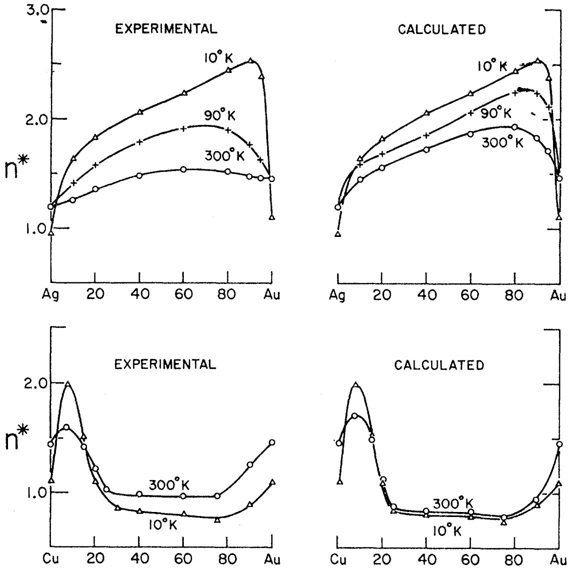

FIG. 4. Calculated and experimental values of the parameter n^*.

where the subscript 0 refers to impurity scattering. Equation (6) then becomes

$$n^*=\frac{(n_b+n_nkx_0)^2}{(n_b-n_nk^2x_0^2)}. \tag{8}$$

Given k, we can then calculate from (8) values of τ_{n0}/τ_{b0} from the observed values of n^* at 10°K. In the absence of any better alternative we have applied throughout this treatment the value $k=0.7$ obtained for the Cu-Au system to the Ag-Au and Cu-Ag systems, and a linear interpolation between the values of n_n and n_b for the pure components was made in calculating these quantities for the alloys. (Some justification for this is shown by the results for the Ag-Au system in Fig. 4. The model gives the correct qualitative dependence of n^* upon solute concentration and is certainly an improvement upon the results of previous similar attempts.[25,26,27]) The calculated τ_{n0}/τ_{b0} are given in Table IV. In the Ag-Au system τ_{n0}/τ_{b0} is approximately constant while in the Cu-Au system τ_{n0}/τ_{b0} is small and reasonably constant for the high-concentration alloys but changes quite markedly for the low-concentration alloys. At present we can see no reason for this change. It is clear from Table IV that the addition of small quantities of Ag to Au and Au to Ag produce the same impurity anisotropy. Therefore it might be expected that small additions of either Ag or Au to Cu would produce similar changes in the Hall coefficient and give rise to similar values of τ_{n0}/τ_{b0}. Table IV shows that this is found to be the case. For small amounts of Au in Cu τ_{n0}/τ_{b0} is 1.28, while it is 1.22 for small amounts of Ag in Au.

The value of τ_{n0}/τ_{b0} for Cu+7.2 at.% Au (1.28) is low compared with the value (2.7) obtained by Dugdale

TABLE IV. Ratio of relaxation times for impurity scattering.

at. % Au in Ag	$\frac{\tau_{n0}}{\tau_{b0}}$	at. % Au in Cu	$\frac{\tau_{n0}}{\tau_{b0}}$	at. % Cu in Ag	$\frac{\tau_{n0}}{\tau_{b0}}$
10	1.49	7.2	1.28	10.4	1.05
20	1.58	15.3	1.03	94.6	1.22
40	1.59	19.8	0.65		
60	1.57	25.1	0.30		
80	1.53	39.9	0.25		
90	1.51	59.4	0.23		
95	1.45	74.9	0.07		
		90.2	0.35		

TABLE V. Comparison between the ratio of the neck and belly conductivities determined from resistivity and Hall-effect data.

System	σ_{n0}/σ_{b0} (Resistivity)	σ_{n0}/σ_{b0} (Hall effect)
Au in Cu	0.46[a]	0.37
Ag in Cu	...	0.34
Au in Ag	0.34[a]	0.21
Cu in Ag	...	0.16
Ag in Au	0.55[b]	0.42
Cu in Au	0.11	0.07

[a] Obtained from Ref. 5.
[b] Obtained from Ref. 26.

and Basinski[5] from observations of deviations from Matthiessen's rule for some dilute Cu-Au alloys. However, the corresponding conductivity ratios σ_{n0}/σ_{b0} calculated from (4) compare quite favorably, (present investigation: 0.37, Dugdale and Basinski: 0.46). We believe it is more realistic to compare the ratios of conductivities for in the case of deviations from Matthiessen's rule it avoids the rather arbitrary choice of ratios of velocities and areas of Fermi surface for the neck and belly regions. It is clear from Table IV that the Hall-effect data predict a considerable difference between the conductivity ratio for a small amount of Cu in Au and that for corresponding amount of Au in Cu. To test this prediction we have examined the deviations from Matthiessen's rule for Au+1 at. % Cu. A summary of the conductivity ratios determined by the Hall effect and resistivity are shown in Table V. The values determined for Au in Cu and Au in Ag from resistivity measurements are those given by Dugdale and Basinski.[5] It should be pointed out that in the determination of σ_{n0}/σ_{b0} from resistivity data two solutions exist, since σ_{n0}/σ_{b0} appears squared in the relation given by Dugdale and Basinski.[5] The two values obtained for Au+1 at. % Cu were 0.13 and 0.61. We have rejected the latter value since it predicts n^* to *increase* substantially (even more strongly than in Au-Ag alloys) when Cu is added to Au, whereas in fact n^* strongly *decreases*. We feel that the agreement between the results of columns 2 and 3 of Table V is very encouraging, bearing in mind the approximations involved in their derivation. The two sets of results are in order of magnitude agreement and are scaled in the same manner among the alloy systems. Both results indicate that the anisotropy of the relaxation times must be considerably different for Cu in Au from that for Au in Cu.

It is of some interest to apply the two-band model in an examination of the temperature dependence of the Hall coefficient or n^* in Ag-Au and Cu-Au alloys. For the three pure noble metals it is noted that n^* is approximately constant in the temperature interval 90–300°K. This is indicative of isotropic phonon relaxation times between these two temperatures. At lower temperatures, τ_{np}/τ_{bp} (the subscript p refers to phonons) is thought to decrease due to the suppression of umklapp processes from the belly and this accounts for the decrease of n^* observed in the noble metals at such temperatures. The equality of τ_{np} and τ_{bp} between 90 and 300°K, we have assumed, prevails in all the alloys. Thus, for the alloys at 90 and 300°K, Eq. (6) is applicable but with

$$x=\frac{\tau_{n0}}{\tau_{b0}}\frac{\tau_{np}}{\tau_{bp}}\frac{(\tau_{b0}+\tau_{bp})}{(\tau_{n0}+\tau_{np})} \tag{9}$$

and with

$$\frac{\tau_{np}}{\tau_{bp}}=1.$$

Assuming $\tau_{b0}/\tau_{bp}\approx\rho_p/\rho_0$, where ρ_p and ρ_0 are the phonon and residual resistivities, respectively, then Eq. (9) may then be rearranged to give

$$x=x_0\left[\frac{\rho_p/\rho_0+1}{x_0(\rho_p/\rho_0)+1}\right]. \tag{10}$$

To determine values of n^* at a given temperature, it is clear from (6) that we require n_n, k, and x. Values of n_n, k, and x_0 have already been determined from the values of n^* at ~10°K, and the corresponding value of x can therefore be determined from (10) and the values of ρ_p and ρ_0 obtained from experimental values of the resistivities.[17,28] The results of such a calculation at 90 and 300°K are shown in Fig. 4, together with the experimental values of n^*. In Fig. 4 the variation of n^* with concentration at 90°K has been omitted for the Cu-Au system since the calculated variation is almost identical to that obtained at 10°K. Fig. 4 shows that the numerical agreement between the experimental and calculated values of n^* is only fair, which perhaps is not surprising in view of the approximations implied by a two-band model, but clearly the treatment predicts the correct form of the temperature and concentration dependence of n^*. We feel that this alone is an encouraging result, since at first sight the observed dependence of n^* upon solute concentration (Fig. 4) seems a rather strange behavior to be found for an alloy system consisting of homovalent constituents with similar electronic structures (particularly the behavior observed in the Cu-Au system), and yet we have shown

---

[28] H. Auer, E. Riedl, and H. J. Seeman, Z. Physik **92**, 291 (1934).

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.

ACKNOWLEDGMENTS

We are grateful to Dr. L. D. Calvert and Miss F. Hui for their x-ray work carried out on our behalf, to J. A. H. Desaulniers of the Analysis Section in this Division who carried out the chemical analyses, and to F. Turner for his careful preparation of the samples. One of us (R. D. B.) wishes to express his appreciation to the National Research Council of Canada for his appointment as Visiting Scientist, and to the members of the Division of Applied Chemistry who provided the agreeable atmosphere in which this work was done.

PHYSICAL REVIEW VOLUME 176, NUMBER 3 15 DECEMBER 1968

Absolute de Haas–van Alphen Frequency Measurements in Potassium*

R. L. Thomas and G. Turner
Department of Physics, Wayne State University, Detroit, Michigan

(Received 31 July 1968)

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 $F_0 = (1.8246 \pm 0.0006) \times 10^8$ G for the dHvA frequency of an equivalent spherical Fermi surface. This value is significantly lower than the free-electron prediction of $F_0 = 1.832 \times 10^8$ 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 ($\Delta k \sim 7\%$) this ambiguity is perhaps

---

* Research sponsored by the U. S. Air Force Office of Scientific Research, Office of Aerospace Research, under AFOSR Grant No. 68-1494.

[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.