Hall Coefficients of the β'-AuZn, β'-AgZn, and ζ-AgZn Alloys*

Leonard Muldawer
Temple University, Philadelphia, Pennsylvania 19122

Robert C. Bowe
St. Joseph's College, Philadelphia, Pennsylvania 19131

(Received 24 July 1972)

Hall coefficients (R_H) of the β'-AuZn and β'- and ζ-AgZn systems at room temperature and liquid-nitrogen temperature (77.4 °K) were measured by a standard dc technique. The β' and ζ phases are produced in AgZn by quenching or slow cooling from above 275 °C. The room-temperature coefficients of β'-AuZn and β'-AgZn increase linearly with increasing electron per atom ratio z. From a z of 1.48 to a z of 1.52 the room temperature R_H of β'-AuZn goes from $+0.65\times10^{-11}$ to $+1.70\times10^{-11}$ m^3/C and the R_H of β'-AgZn goes from -0.82×10^{-11} to -0.23×10^{-11} m^3/C. For both systems R_H increases with decreasing temperature. At 77.4 °K, the coefficients of both β'-AuZn and β'-AgZn are positive and increase with increasing z. R_H of ζ-AgZn is positive and peaks at a z of about 1.5 where the values of R_H at room temperature and 77.4 °K are $+0.58\times10^{-11}$ and $+1.76\times10^{11}$ m^3/C, respectively. Results are interpreted in terms of Fermi-surface and scattering effects. In β'-AuZn and β'-AgZn the increase in R_H with increasing z is attributed to an increase in Fermi-surface distortion which results in an increase in a positive holelike contribution to R_H. The temperature dependence of R_H is discussed in terms of a temperature-dependent electron scattering probability. One sample of AuZn undergoes a martensitic transformation slightly above 77.4 °K and shows an anomalous decrease in R_H relative to the β'-AuZn specimens.

I. INTRODUCTION

The gold-zinc and silver-zinc alloy systems possess a CsCl structure near their 50-50 compositions. AgZn must be quenched from above 275 °C in order to have a CsCl structure at room temperature. Slowly cooled AgZn possesses the ζ phase, which has a hexagonal unit cell containing nine atoms. We have measured the Hall coefficient R_H as a function of composition in the CsCl region of these alloy systems at room temperature and at liquid-nitrogen temperature (77.4 °K). The ζ-AgZn system has also been studied. Results are discussed in terms of Fermi-surface and scattering effects. These factors have been used by other workers[1–4] in interpreting Hall data on the noble-metal alloys.

Rapidly quenched AgZn shows the β' phase free of the ζ phase. It is believed that, at room temperature and below, it is the ζ and not the β' phase which is metastable. As shown by Annaka[5] and confirmed by one of us,[6] cold-worked filings of ζ material convert to β' after a period of days at room temperature.

It is generally agreed that the Hall coefficient of an alloy is sensitive to changes in the shape of its Fermi surface. A distorted Fermi surface can give rise to regions where one or more components of the effective mass may become negative. The more the Fermi surface deviates from a sphere, the more we would expect R_H to deviate from its free-electron value, that is, become less negative. R_H may even become positive if there is a preponderance of holelike regions with negative-effective-mass components. The neck areas of the Fermi surfaces of Au and Ag are holelike. Since the ratio of the neck to belly area of the Fermi surface of Au is larger than that for Ag,[7] it is expected that the R_H of Au would be less negative (less electronlike) than the R_H of Ag. This is the case. The R_H of Au is about -7×10^{-11} m^3/C, while the R_H of Ag is about -9×10^{-11} m^3/C. The interpretation of much of our Hall data is along these same lines, that is, in terms of Fermi-surface effects.

At low temperatures, β'-AuZn undergoes a martensitic transformation. Pops and Massalski[8] have reported the start temperature of this transformation as a function of composition. Only one of the alloys we studied, that containing 52 at.% Zn, was in the composition range where this transformation is to be expected at or above 77.4 °K. An anomalous effect was observed in R_H for this alloy.

The alloys studied here are β-brass-type alloys (high diffusion rates) and are expected to order readily to the maximum allowable. Even in the ternary alloys $AgAuCd_2$, $AgAuZn_2$, and $CuAuZn_2$, it was difficult to preserve any noble-metal disorder by quenching[9]; binary ordering is expected to be still more rapid and must be complete even with relatively mild anneals. It is therefore assumed that the only disorder in these β' alloys is that associated with the up-to-2-at.% deviation from stoichiometry. The case of ζ-AgZn may be

different. The ζ phase is hexagonal and partially ordered,[10] but since its structure is similar to that of β', the diffusion rate should still be high.

II. PROCEDURE

Alloys were made by melting appropriate quantities of Au and Zn and Ag and Zn in evacuated quartz tubes. The molten metals were mixed and water quenched. The resulting alloy slugs were given a homogenization anneal at 600 °C for 24 h and slow cooled. A 2-mm slab cut from the slug was rolled down to a thickness of 0.2 mm. Hall samples were then cut from the 0.2-mm sheet on a lathe. The AgZn Hall samples were slow cooled or quenched from about 350 °C to produce either the ζ or β' phase, respectively.

Three AuZn compositions [52-48, 50-50, and 48-52 (in at.%)] and four AgZn compositions (52-48, 50-50, 49-51, and 48-52) were studied. The AuZn alloys were analyzed at the U.S. Assay Office and the compositions were found to deviate less than 0.1 at.% from nominal. Samples are weighted after melting and, assuming the weight loss is exclusively from zinc, maximum deviations from nominal are obtained. By this procedure, AgZn compositions were found to fall within 0.1 at.% of nominal. One specimen of each composition was utilized in the R_H measurements; the measurements, however, were carried out several times in a systematic way.

Current and potential leads were spot welded to the Hall samples. A standard dc technique was used to measure Hall voltages. A dc field of 10 000 G and a dc current of about 4.5 A were used. The Hall voltages were amplified and recorded with fields alternately in the normal and reversed directions. The recorded output resembled a square wave. The Hall voltage was taken as half the recorded peak-to-peak voltage.

The usual procedure in making measurements was to obtain a room-temperature value, then one at 77.4 °K, and then another at room temperature. Often two liquid-nitrogen-temperature measurements were taken. In the case of the AgZn alloys, the same specimens were used for both the β' and ζ measurements. The standard procedure was to quench from near 300 °C (giving β'), take measurements at room and liquid-nitrogen temperatures, reheat and slow cool (giving ζ), take measurements, reheat and quench, and take measurements. The reproducibility was about 0.01×10^{-11} m^3/C for AuZn and $\pm0.015\times10^{-11}$ m^3/C for AgZn.

III. RESULTS AND DISCUSSION

Figures 1 and 2 show the results of our Hall studies on the β'-AuZn and β'-AgZn systems. Our room-temperature R_H values for the AgZn alloys agree to within about 0.15×10^{-11} m^3/C with those

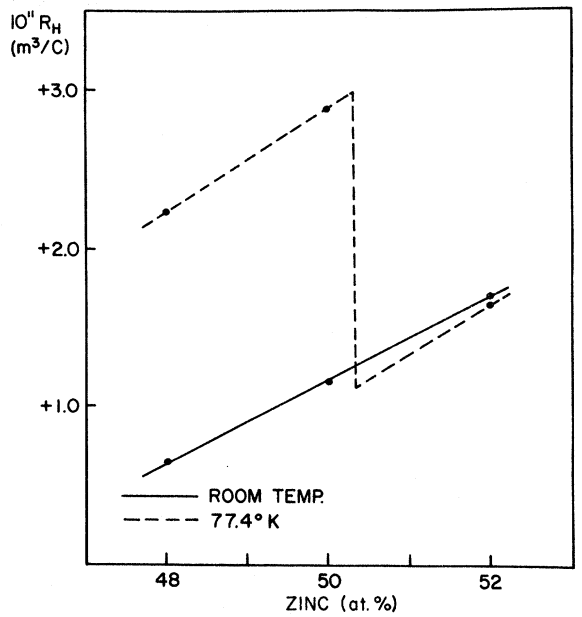

FIG. 1. R_H of AuZn vs composition at room temperature and at 77.4 °K. Dots are experimental values. The dashed curve connects 77.4 °K points and takes account of transformation (see text).

of Takano[1] and Jan.[11] Takano's data indicate, as do ours, that the room-temperature R_H of β'-AgZn is negative and becomes less negative with increasing electron-per-atom ratio $\mathfrak{z}$. Jan measured the room-temperature R_H for the β' and ζ phases of a single sample containing 49.26-at.% Zn. His results are in good agreement with ours. Noguchi's[12] R_H data on the β' and ζ phases of AgZn agree with ours in regard to sign but not magnitude or trend with $\mathfrak{z}$. It is believed that our paper contains the first published data of R_H vs $\mathfrak{z}$ for β'-AuZn.

Our results show that the R_H of β'-AuZn and β'-AgZn are considerably more positive than the R_H of pure Au or Ag. This would indicate that the Fermi surface of these alloys is more anisotropic than that of either Au or Ag. Evidence exists to support this implication. β'-CuZn, β'-AgZn, and β'-AuZn are believed to have a similar Fermi-surface topology,[13] so that what could be said concerning β'-CuZn should also hold for β'-AgZn and β'-AuZn. Ordered CuZn is expected to have a Fermi surface more distorted than that of disordered CuZn. Disordered CuZn has a somewhat free-electron Fermi surface, but ordering produces a cubic Brillouin zone which cuts into the Fermi surface and results in holelike regions at the corners of this cubic zone. We believe these holelike regions are responsible for the positive sign of the R_H of β'-AuZn and of β'-AgZn at 77.4 °K. Similarly, we feel the low negative values for

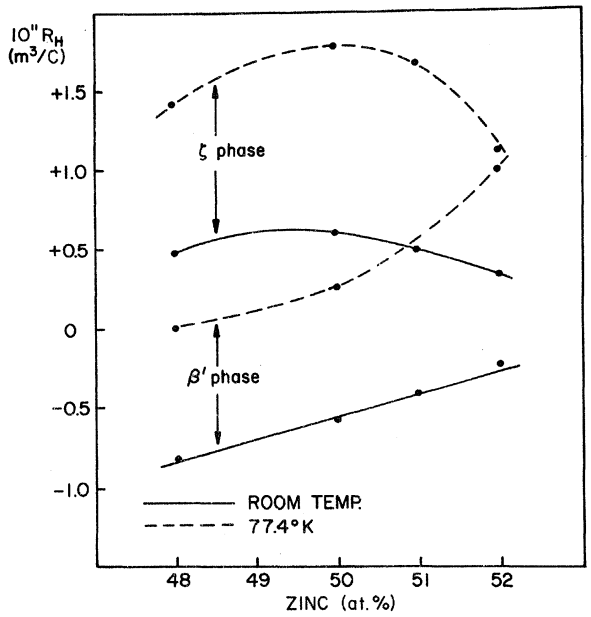

FIG. 2. R_H of AgZn vs composition at room temperature and at 77.4 °K. No value was taken at 77.4 °K for β'-AgZn.

β'-CuZn, β'-AgZn, and β'-AgCd at room temperature[1] arise from a similar cause. Since the R_H of β'-AuZn is more positive than the R_H of β'-AgZn, the Fermi surface of β'-AuZn is more holelike and probably more distorted than the Fermi surface of β'-AgZn.

The higher holelike character of β'-AuZn can be expected from the results of optical studies of β'-CuZn, β'-AgZn, and β'-AuZn.[14] The main electron transition moves to lower energy as we go from CuZn to AuZn, thus probably indicating a raising of the lower band which crosses the Fermi surface. This would increase the amount of hole character for β'-AuZn. In addition, the relativistic band splitting expected in β'-AuZn because of the gold should lead to the creation of extra hole pockets.[15]

Figures 1 and 2 show that the R_H of β'-AuZn and β'-AgZn increase with increasing $\mathfrak{z}$ both at room and liquid-nitrogen temperatures. It is suggested that with increasing $\mathfrak{z}$ the expanding Fermi surface, already in contact with the Brillouin-zone boundary, becomes even more distorted, and this results in an increase in the positive holelike contributions to R_H. The behavior of the 52-at.%-Zn AuZn at 77.4 °K is anomalous. As has been pointed out in the Introduction, this alloy is no longer β' and is expected to behave differently from the other two alloys, which are still β' at 77.4 °K. This is the reason we have connected the points as shown in Fig. 1.

As is clear from the data for β'-AuZn and β'-AgZn, the variation of R_H with composition is linear at room temperature. Inasmuch as there must be some disorder due to the 2% deviation from stoichiometry, this indicates that limited disorder is negligible relative to the changes in $\mathfrak{z}$. On the other hand, ζ-AgZn does show a maximum at stoichiometry.

R_H for both β'-AgZn and β'-AuZn becomes more positive with decreasing temperature. Fermi-surface distortion and anisotropy of relaxation time have been suggested as factors which may be most closely associated with the temperature dependence of R_H.[1] Distortion of the Fermi surface with decreasing temperature may conceivably contribute to the more positive R_H observed at 77.4 °K. Most probably, however, the anisotropy of relaxation time, or, equivalently, the variation of the electron scattering probability over the Fermi surface, is of more importance. It has been suggested that the scattering probabilities on the neck and belly regions of the Fermi surface are different.[4] Suppose the change in R_H with temperature is due to changes in positive holelike and negative electronlike contributions. If there is a temperature-dependent electron scattering probability which is greater on the holelike region than on the electronlike region of the Fermi surface, it might be expected that with increasing temperature the decrease in the positive holelike contribution to R_H would be greater than the decrease in the negative electron contribution. If this were the case, R_H would decrease (that is, become less positive) with increasing temperature, just as observed.

It is observed from Fig. 3 that ΔR_H, the change in R_H between 77.4 °K and room temperature, is greater for those alloys with the more positive R_H. The observed ΔR_H increases with increasing R_H in

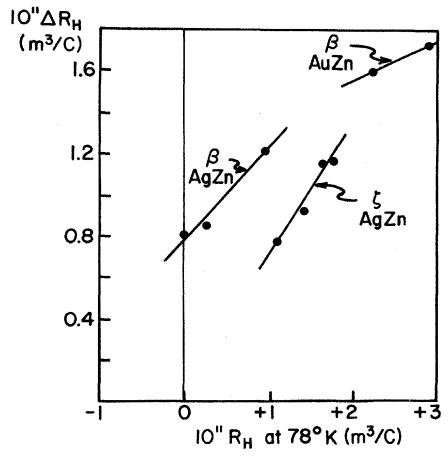

FIG. 3. Differences between room-temperature and liquid-nitrogen-temperature values of the Hall coefficient plotted as a function of R_H at 77.4 °K for the alloys.

both the β'-AuZn and β'-AgZn systems. Also, the ΔR_H observed in the β'-AuZn system (AuZn possessing the more positive R_H) is larger than that observed in the β'-AgZn system. These results are consistent with the speculation presented in the preceding paragraph concerning the role played by electron scattering. A larger R_H implies a larger holelike area of the Fermi surface and thus a greater amount of scattering on this area. With increasing temperature it might then be expected that a greater decrease in the positive holelike contribution to R_H would occur and thus account for the greater ΔR_H observed.

Figure 3 shows ΔR_H vs R_H at 77.4 °K for the alloys we have studied. Results from the AgZn alloys show a linear relationship; in particular, this linearity is well observed for ζ-AgZn with the order of the points being from alloys of 52, 48, 51, and 50 at.% Zn. We are puzzled by the extrapolation of the ζ-AgZn curve going approximately to $R_H = 0$; we would have expected it to go to a large negative value as do β'-AgZn and β'-AuZn. However, such an extrapolation is tenuous due to the limited range of data.

The decrease in R_H that occurs during the martensitic transformation in $Au_{48}Zn_{52}$ suggests that the Fermi surface of the martensite is more electronlike than the Fermi surface of the parent CsCl phase. β-brass-type alloys generally undergo martensitic transformations which increase the nearest-neighbor spacing as well as the coordination number, i.e., make the alloy more nearly close packed.[16] The Brillouin zone just beyond the Fermi surface for these ordered alloys is the second which corresponds to a bcc first zone. When these alloys transform, this chief zone tends to correspond to that of the fcc first zone. This zone is more nearly spherical than that of the bcc lattice, and hence the Fermi surface should be less distorted and more electronlike; this would have the effect of reducing R_H. This speculative argument is in keeping with our observations.

It is not clear why the R_H of ζ-AgZn attains a maximum near $\mathfrak{z}$ of 1.5, whereas the R_H of β'-AgZn increases linearly with $\mathfrak{z}$. The R_H of ζ-AgZn is more positive than the R_H of β'-AgZn. In view of the partial disorder of the ζ phase, and the structural similarity of the ζ and β' phases, just the opposite might have been expected. However, the peak in the R_H of ζ-AgZn vs composition is in keeping with the idea of greater scattering in the holelike regions of the Fermi surface which might arise from disorder.

New data have been presented here and some conclusions regarding the Fermi surfaces of these alloys have been drawn. However, it is clear that there are still a number of unanswered questions.

ACKNOWLEDGMENTS

We are grateful for informative conversations with Dr. K. H. Johnson and Dr. N. Berk and for experimental assistance from George Kemmerer and the Temple University Physics shop.

*Work at Temple University supported by the U. S. Atomic Energy Commission.

[1]K. Takano, J. Phys. Soc. Jap. **26**, 362 (1969).
[2]K. Takano, J. Phys. Soc. Jap. **23**, 1234 (1967).
[3]C. M. Hurd, Philos. Mag. **12**, 47 (1965).
[4]J. M. Ziman, Adv. Phys. **10**, 1 (1961).
[5]S. Annaka, J. Phys. Soc. Jap. **9**, 354 (1954).
[6]L. Muldawer, AFOSR Report No. TR58-140, 1958 (ASTIA Document No. AD 204 553) (unpublished).
[7]D. Shoenberg, Philos. Trans. R. Soc. Lond. A **255**, 85 (1962).
[8]H. Pops and T. B. Massalski, Trans. Metall. Soc. AIME **233**, 728 (1965).
[9]L. Muldawer, Acta Crystallogr. **20**, 594 (1966).
[10]I. G. Edmunds and M. M. Qurashi, Acta Crystallogr. **4**, 417 (1951).
[11]J. P. Jan, Helv. Phys. Acta **35**, 425 (1962).
[12]S. Noguchi, J. Phys. Soc. Jap. **17**, 1844 (1962).
[13]H. Amar, K. H. Johnson, and K. P. Wang, Phys. Rev. **148**, 672 (1966).
[14]L. Muldawer, Phys. Rev. **127**, 1551 (1962).
[15]K. H. Johnson (private communication).
[16]L. Muldawer, Bull. Am. Phys. Soc. **13**, 442 (1968).