Hall Effect in Copper-Base Alloys at Room Temperature

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The Hall coefficient R_H has been measured in the systems Cu-Zn, Cu-Ge, Cu-Sn, and Cu-Al at room temperature. A rigid two-band model is presented, in which it is assumed that the effective-mass anisotropy varies linearly across the α phase in the same manner for all the systems, and there is an anisotropic impurity relaxation time which is independent of composition. This simple model is capable of accounting for the main features of the curves of R_H vs electron-to-atom ratio for all four systems, and in particular accounts for the existence of a minimum in the Cu-Ge and Cu-Sn systems and a monotonic change in the Cu-Zn system. The absolute values are reasonably consistent with the experimental values; the calculated value of the effective-mass ratio is in agreement with qualitative reasoning, and the impurity relaxation-time anisotropies agree with results obtained by other methods.

I. INTRODUCTION

In the free-electron theory, the Hall coefficient R_H is simply related to the number of carriers per unit volume and their charge:

$$R_H = (Nne)^{-1}, \qquad (1)$$

where N is the number of atoms per unit volume, n is the number of carriers per atom, and e is their charge. However, not only does this simple expression fail to predict the correct value of the Hall coefficient for the pure metals, using their nominal valencies; it also fails to predict the general form of the variation of R_H with alloy content. More importantly, the curves of R_H vs the nominal electron-to-atom ratio for the primary solid solutions of the B-subgroup elements in the noble metals Cu, Ag, and Au do not lie even approximately close to one another. For example, $|R_H|$ decreases monotonically in the Cu-Zn α phase as the Zn content increases, whereas in the Cu-Ge α phase $|R_H|$ rises to a marked maximum at a low Ge concentration and then decreases. The anomalous behavior of this first-order effect was first commented on by Coles,[1] and since then there have been many attempts to explain the observed effects. A complete description of the problem and a formal statement of the simple theory is given by Ziman.[2]

It was pointed out by Cooper and Raimes[3] that in order to account for the experimental results it would be necessary to assume phonon and impurity relaxation processes with different anisotropies, and they were able to produce curves having some of the features of the experimental results using a series of cubic harmonics to approximate both the shape of the Fermi surface and the functional form of the relaxation times. Refinement of the model diminished the absolute correspondence with experiment. Ziman[2] produced a simpler model for

the Fermi surface based on the experimental surface of Pippard,[4] and was able with this "eight-cone" model to produce reasonable agreement for the pure metals; but Hagmann and Ricker,[5] using a simplified version of the model to account for the experimental results of Köster and co-workers,[6] had to invoke an anisotropic impurity relaxation time. Hurd[7] has developed this view, suggesting that the Hall coefficient can be regarded as due to two separate effects: one simply due to the change in the electron-to-atom ratio, and the other a contribution attributable to the impurity scattering. Writing an "effective number of electrons per atom" as n^*, defined by

$$n^* = (R_H Ne)^{-1}, \qquad (2)$$

then we have

$$n^* = n_0 + n_i, \qquad (3)$$

where n_0 is the number of electrons per atom for a fictitious alloy, in which the change in band structure on alloying is considered but the effect of impurity scattering is excluded, and n_i is the contribution due to the impurity scattering. Barnard[8] has used a similar approach, and has suggested that n_i should be proportional to the residual resistivity, with the same constant of proportionality for each B period. Agreement was reasonable for Ag-based alloys, less good for Cu-based alloys.

Meanwhile, several investigators were attempting to produce a more analytic approach. Takano[9] suggested a two-band model, in which

$$R_H = \frac{R_e \sigma_e^2 + R_h \sigma_h^2}{(\sigma_e + \sigma_h)^2}, \qquad (4)$$

with the conductivities σ_j given by

$$\sigma_j = Nn_j e^2 \tau_j / m_j^* \quad (j = e, h), \qquad (5)$$

where n_j is the number of carriers per atom, m_j^*

is the carrier effective mass, and τ_j is the relaxation time. The subscripts e and h refer to the electron and hole bands, respectively, and the expressions are given in Wilson.[10]

In the simple theory, we have

$$R_e = - (Nn_e|e|)^{-1}, \quad R_h = (Nn_h|e|)^{-1}. \tag{6}$$

Tentatively, Takano identifies the "electron band" with the belly, and the "hole band" with the necks, of the experimental Fermi surface, recognizing the difficulties of this interpretation. Then the two components of m_j^* and τ_j^* can be regarded as representing the anisotropies of the Fermi surface and the relaxation time, respectively. The values of n_e and n_h can then be calculated directly from Ziman's eight-cone expression for the surface, and varies as the total electron-to-atom ratio increases. In the detailed calculation, Takano assumes a rigid band; that is, that the band gap across the $\{111\}$ faces of the Brillouin zone remains constant. It remains to take account of the phonon and impurity scattering, and Takano writes

$$\tau_j^{-1} = \tau_{jp}^{-1} + \tau_{ji}^{-1}, \tag{7}$$

where the subscripts p and i refer to the phonon and impurity processes, respectively. Then, the τ_{jp} are regarded as constants for a given temperature and independent of concentration of the alloy element, while the τ_{ji} are related to the solute concentration c through Nordheim's rule.

This model again gives fair agreement with experiment in some respects, but conspicuously it predicts a maximum in $|R_H|$ vs n for all solutes, and in fact predicts a much more marked maximum for Cu-Zn than for Cu-Ge.

Matsuda[11] has extended this type of approach in an attempt to understand the temperature dependence of the Hall coefficient. Again, the basis of the analysis is the expression for R_H in Ziman's paper, but expressed as a function of τ_N/τ_B, where now the subscripts refer to the neck and belly of the surface, respectively. Now, the temperature dependence of R_H in pure Cu suggests that $A_p = \tau_{Np}/\tau_{Bp}$ is less than 1 at 100 °K, but approximately 1 at room temperature. Matsuda suggests that the form of the R_H-vs-n curve is largely determined by the magnitude of $A_i = \tau_{Ni}/\tau_{Bi}$, and concludes that for Zn, $A_i \simeq 1$; whereas for Ge, $A_i < 1$. This suggests that the form of the R_H-vs-n curves will be a function of temperature at low temperatures, but not at room temperature and above where A_p is effectively constant.

Finally, a most elegant calculation has been performed by Dugdale and Firth.[12] Following Tsuji,[13] they write

$$R_H = \frac{12\pi^3 \int \langle 1/\rho \rangle V^2 \, ds}{ec(\int V \, ds)^2}, \tag{8}$$

where $\langle 1/\rho \rangle = \frac{1}{2}(1/\rho_1 + 1/\rho_2)$, and ρ_1 and ρ_2 are the principal radii of curvature of the Fermi surface at the point indicated. At room temperature, they assume that the phonon scattering is reasonably isotropic, and perform the integration above over the experimentally determined Fermi surfaces using velocity maps calculated from cyclotron resonance data. The numerical agreement with the experimental values for Cu and Ag is excellent and it is shown that, because the principal radii of curvature in the neck regions are of opposite sign and thus tend to cancel, and also because the electron velocities are small in the neck regions, the contribution of the necks to the Hall effect in the pure metal is very small. This is surprising because many of the earlier qualitative analyses based on two-band models had concluded that the influence of the necks was very important. However, Dugdale and Firth point out that in the Cu the Fermi surface bulges noticeably towards the $\{100\}$ surfaces of the zone, and there are thus regions of high curvature in these regions making a large contribution to the Hall coefficient; they then use a two-band model again, with two terms representing the belly and the necks, but estimate the relative importance of the $\{100\}$ bulges.

Again, the major effect of the impurity elements is considered to be on the scattering anisotropy. It is assumed that the scattering in the "pure" metal is dominated by residual impurities, and that the solute scattering gradually becomes more important. By calculating τ_B/τ_N and plotting against the inverse solute concentration, extrapolation enables τ_{Bi}/τ_{Ni} for the solute atom to be determined; for Ge in Cu this is 5. They estimate that for Zn, the corresponding value will be 1; de Haas–van Alphen results suggest 1.2 ± 0.1.

It is clear that the problem is far from a complete solution, but it appears that the results for copper-base alloys are more difficult to analyse than those for silver base; and furthermore that the systems Cu-Zn and Cu-Ge represent extremes of behavior. Any truly satisfactory theory must therefore be capable of interpreting these systems. In the present investigation, the Hall effect in these two systems, together with Cu-Al and Cu-Sn, have been studied.

II. EXPERIMENT

A. Experimental Procedure

The alloys were prepared by induction melting under argon from starting materials of 99.99% purity or better. Ingots of approximately 200-g weight were cast and homogenized in vacuum for approximately 4 days at 700 °C. The homogenized ingots were then rolled to sheet approximately 0.5 mm thick, and annealed. Lattice parameters
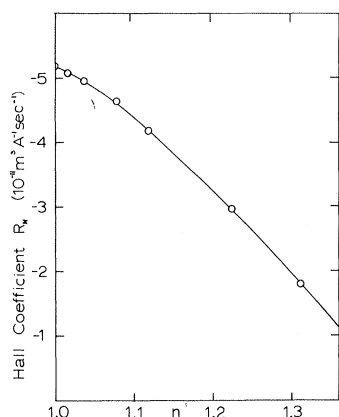
FIG. 1. Variation of Hall coefficient with electron-
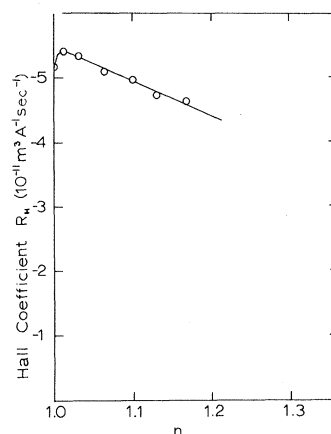to-atom ratio n for the system Cu-Zn at 20 °C.

FIG. 3. Variation of Hall coefficient with electron-
to-atom ratio n for the system Cu-Sn at 20 °C.

were determined for all the alloys using a conven-
tional Debye-Scherrer technique, and the electrical
resistivities were determined over a wide range of
temperatures. Since these properties have been
established for these systems, they acted as a
check on composition and metallurgical condition.
In addition, the majority of specimens were chemi-
cally analyzed. The Hall effect was determined by
the two-probe dc technique described by Lane et al.[14]
using a field of 18 kG. Measurements were carried
out several times on each specimen, and on several
specimens from each alloy to eliminate the possi-
bility of statistical errors. The absolute repro-
ducibility was about 3-4% of the mean, which
agrees well with the calculated error. The major
source of error is the measurement of the thickness
of the specimen for a thin specimen, and the mea-
surement of the Hall voltage for a thick specimen.
For the dc technique, without a major refinement
in the method of producing uniform thickness speci-
mens and measuring their dimensions accurately,

the optimum absolute reproducibility is not better
than 2%; this is consistent with the results in the
literature, where some papers contain appreciably
larger systematic errors. The results are shown
in Figs. 1–4; the points are the mean of the ex-
perimental data.

B. Experimental Results

Hall-coefficient measurements have been carried
out on these systems at room temperature by a
number of investigators. The results for the Cu-Zn
system are in very close agreement with those of
Frank[15] obtained using an ac technique, but the
values for more concentrated alloys are somewhat
lower than those obtained by Köster and Rave.[6]
However, the results of Barnard and Sumner[16] for
concentrated alloys show that the value of the Hall
coefficient can be strongly dependent on the previous
heat treatment. For example, the value for a slow-
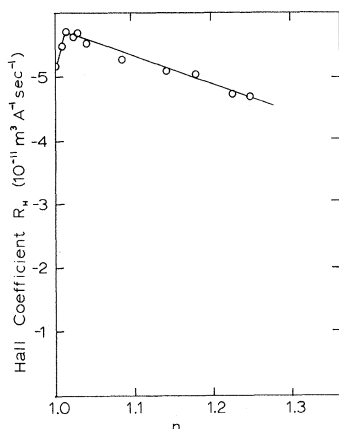cooled alloy containing 28.16-at.% Zn was approxi-

FIG. 2. Variation of Hall coefficient with electron-
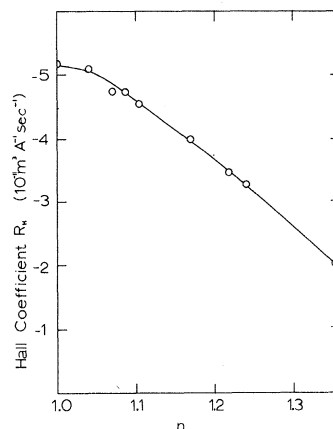to-atom ratio n for the system Cu-Ge at 20 °C.

FIG. 4. Variation of Hall coefficient with electron-
to-atom ratio n for the system Cu-Al at 20 °C.

mately -2.15×10^{-11} m^{3}A^{-1}sec^{-1}; for a quenched alloy of the same composition the value was approximately -1.95×10^{-11}m^{3}A^{-1}sec^{-1}. The same behavior was found for an alloy of 18.17-at.% Zn, although the difference was not nearly so marked.

The results for the Cu-Ge system agree very well with those obtained by Köster and Rave.[6] The maximum of $|R_H|$ occurs at approximately 0.6-at.% germanium and the value of $|R_H|_{max}$ is some 10% greater than the value of $|R_H|$ for pure copper. The results for the Cu-Sn system indicate a peak in $|R_H|$ at approximately 0.5-at.% Sn with $|R_H|_{max}$ some 5% larger than the pure copper value. This is a little different from the behavior found by Köster and Rave. Their results indicate a smaller and broader maximum at about 1.5-2.0-at.%Sn. However, they carried out no measurements on alloys containing less than 1-at.% Sn, and thus it is not possible to fix very accurately the position of the maximum from their data. The results for the Cu-Al system give the same behavior as those obtained by Köster and Rave and also those by Matsuda,[11] but the absolute values are somewhat higher than those obtained by these workers. The fact that the values of Matsuda may be systematically 3% lower than the true values, as evidenced by his values for other systems, is not sufficient to explain the discrepancy. The possibility of the Hall coefficient being dependent on the previous heat treatment, as for the Cu-Zn system, cannot be ruled out however.

III. DISCUSSION

Using the two-band model we can write an expression for n^*:

$$n^* = \frac{n_B n_N (1 + \sigma_N/\sigma_B)^2}{n_N - n_B (\sigma_N/\sigma_B)^2} . \tag{9}$$

Now if the conductivities in the two bands are expressed in terms of the appropriate effective masses m_B^* and m_N^*, and in terms of the relaxation times τ_B and τ_N in the two bands, we have for the ratio of the conductivities

$$\frac{\sigma_N}{\sigma_B} = \frac{n_N}{n_B} \frac{m_B^*}{m_N^*} \frac{\tau_N}{\tau_B} . \tag{10}$$

Therefore, we have

$$n^* = n_B n_N \left(1 + \frac{n_N}{n_B} \frac{m_B^*}{m_N^*} \frac{\tau_N}{\tau_B} \right)^2 \Big/ \left[n_N - n_B \left(\frac{n_N}{n_B} \frac{m_B^*}{m_N^*} \frac{\tau_N}{\tau_B} \right)^2 \right]. \tag{11}$$

To use Eq. (11) we need to know how (i) n_B and n_N vary with electron-to-atom ratio n, (ii) the effective mass ratio m_B^*/m_N^* varies with n, (iii) the total relaxation time ratio varies with n.

To calculate n_B and n_N the model of Ziman[2] is used. The procedure used by Takano[9] is applied and the proportional constant A [Eq. (5) of Takano's

analysis] is given the value 3. This is a reasonable value since only one of the three components of the effective-mass tensor in the neck regions is positive.

The scattering in the alloys is entirely by phonons and impurities. For the two regions of the Fermi surface we write

$$(\tau_N)^{-1} = (\tau_{Ni})^{-1} + (\tau_{Np})^{-1} , \tag{12a}$$

$$(\tau_B)^{-1} = (\tau_{Bi})^{-1} + (\tau_{Bp})^{-1} , \tag{12b}$$

where the subscripts i and p apply to impurity and phonon scattering, respectively. Now the total relaxation time ratio can be written

$$\frac{\tau_N}{\tau_B} = \frac{\tau_{Bi} + \tau_{Bp}}{\tau_{Bi} \tau_{Bp}} \frac{\tau_{Ni} \tau_{Np}}{\tau_{Ni} + \tau_{Np}} . \tag{13}$$

This is a good measure of the actual anisotropy of the relaxation time, provided the actual relaxation time does not vary too strongly in each region. If the phonon scattering is isotropic at room temperature, then $\tau_{Np}/\tau_{Bp} = 1$. Matsuda[11] presents evidence from various sources to show that this is approximately so. In addition, if the electrical resistivity is dominated by belly scattering, then it is reasonable to assume that $\tau_{Bi}/\tau_{Bp} \simeq \rho_p/\rho_i$, where ρ_p and ρ_i are the phonon and residual resistivities, respectively.

Equation (13) can now be simplified:

$$\frac{\tau_N}{\tau_B} = \frac{\tau_{Ni}}{\tau_{Bi}} \left(\frac{1 + \rho_p/\rho_i}{1 + \tau_{Ni}/\tau_{Bi}(\rho_p/\rho_i)} \right). \tag{14}$$

If the anisotropy of the impurity relaxation time τ_{Ni}/τ_{Bi} is known, then it is possible to calculate the anisotropy of the composite relaxation time τ_N/τ_B using Eq. (14) and electrical-resistivity data.

The first part of the calculation is to make an estimate of m_B^*/m_N^* for pure copper. This is done by substituting the experimental value of n^* for pure copper into Eq. (11). All the other parameters in this equation have been estimated and it is found that $m_B^*/m_N^* = 1.35$ for pure copper. We would have expected intuitively that $m_B^*/m_N^* > 1$ because of the negative component of the inverse mass tensor in the neck regions. Next, considering the Cu-Zn system, various values are given to τ_{Ni}/τ_{Bi}, and using Eq. (14) the values of τ_N/τ_B are calculated at $n = 1.30$.

Again, using the experimental value of n^* at $n = 1.30$, the values of m_B^*/m_N^* corresponding to these values of τ_N/τ_B are calculated at this composition. For charged impurities in copper there is much evidence to show that $\tau_{Ni}/\tau_{Bi} < 1$, and for Zn in Cu it is thought that this ratio does not differ appreciably from 1 (see, for example, Matsuda[11]). Accordingly, the values 0.8, 0.9, and 1.0 were chosen for τ_{Ni}/τ_{Bi} for Zn. Using these values the
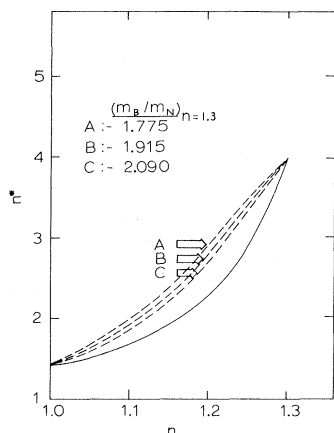
FIG. 5. Variation of effective number of electrons per atom n^* with n for the system Cu-Zn at 20 °C. (Solid line: from experimental R_H value; dashed lines: calculated.)
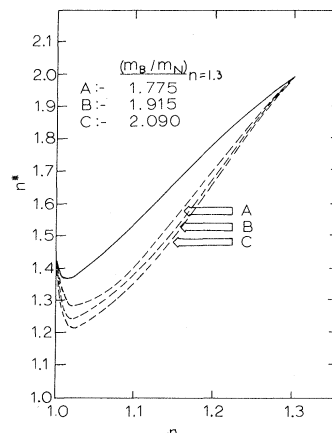
FIG. 7. Variation of effective number of electrons per atom n^* with n for the system Cu-Sn at 20 °C. (Solid line: from experimental R_H value; dashed lines: calculated.)

respective calculated values of m_B^*/m_N^* at $n = 1.30$ were 2.090, 1.915, and 1.775. In calculating the values of n^* between $n = 1.0$ and $n = 1.30$ it is assumed that the ratio m_B^*/m_N^* varies linearly in this region. The corresponding values of τ_N/τ_B are obtained from Eq. (14). The calculated curves for n^* for the Cu-Zn system are shown in Fig. 5, together with the experimental curve. For the other three systems the same three values of m_B^*/m_N^* at $n = 1.3$ are used in order to keep a consistent model throughout and because this would be expected from a rigid-band approach. As before, using the experimental value of n^* at this composition, values of τ_N/τ_B at $n = 1.3$ can be calculated and hence the values of τ_{Ni}/τ_{Bi} can be obtained. n^* is calculated as for Cu-Zn. The re-

sults of these calculations are shown in Figs. 6–8 together with the experimental curves. In Table I are given the values of τ_{Ni}/τ_{Bi} for the four systems for each value of m_B^*/m_N^* at $n = 1.3$, together with estimates by other workers.

Figures 5–8 show that the two-band model can explain the differences of the Hall-effect behavior in the α phase of the systems Cu-Zn, Cu-Ge, Cu-Sn, and Cu-Al, providing impurity relaxation times with different anisotropies are used for the systems. The model predicts a minimum value of n^* at low impurity concentrations in the systems Cu-Ge and Cu-Sn. Although the predicted minima are deeper than those found experimentally, the predicted depth in the Cu-Ge system is larger than that predicted for the Cu-Sn system, as found experimentally. For
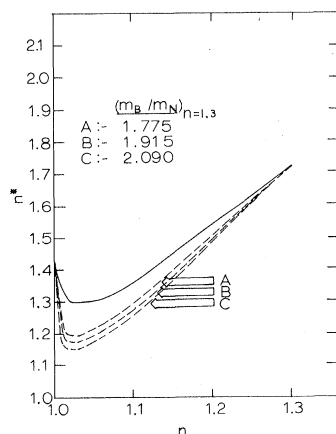
FIG. 6. Variation of effective number of electrons per atom n^* with n for the system Cu-Ge at 20 °C. (Solid line: from experimental R_H value; dashed lines: calculated.)
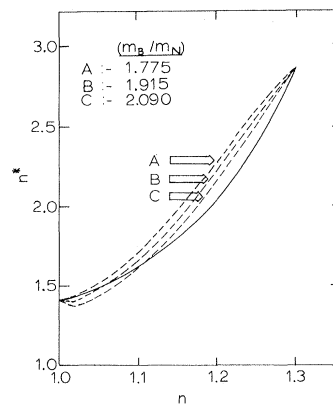
FIG. 8. Variation of effective number of electrons per atom n^* with n for the system Cu-Al at 20 °C. (Solid line: from experimental R_H value; dashed lines: calculated.)

TABLE I. Values of τ_{Ni}/τ_{Bi} used in the present work for each system as a function of $(m_B^*/m_N^*)_{n=1.3}$.

$\left(\dfrac{m_B^*}{m_N^*}\right)_{n=1.3}$	Cu-Zn	Cu-Ge	Cu-Sn	Cu-Al
1.775	1.00	0.501	0.611	0.832
1.915	0.90	0.464	0.565	0.764
2.090	0.80	0.424	0.515	0.692
Estimates by other workers				
	$\simeq 1^a$	$< 1^a$	$\simeq 1^a$	$\simeq 1^a$
	$> 1^b$	0.2^b		0.65^c
	0.85^d			

[a]Reference 11.   [c]Reference 18.
[b]Reference 12.   [d]Reference 17.

the Cu-Al system a very shallow minimum is found and it is possible that this exists experimentally (Köster and Rave[6]), although in the present investigation its presence could not be demonstrated because no very dilute alloys of Cu-Al were studied. The calculated behavior of the Cu-Zn system shows a monotonic rise in n^* with composition, as found experimentally. Table I shows that the anisotropy of the impurity relaxation time increases with increasing valency difference between the solute and copper, as predicted by earlier workers.

IV. CONCLUSIONS

This appears to be the first model to describe successfully the shapes of the R_H-vs-n curves for Cu-base alloys and to explain the absence of a turning point in the Cu-Zn system and its presence in the other systems in a quantitatively consistent fashion. It is also in qualitative agreement with the *order* of the magnitudes of the minima observed in the other systems. Although the absolute agreement is still not altogether satisfactory, it would be surprising if a model as simple as this were to give better results: The absolute disagreement is only two or three times the experimental reproducibility. It is possible that the introduction of a third band, as suggested by Dugdale and Firth,[12] would improve the agreement, but at the expense of additional parameters to be arbitrarily determined by the experiment. It is felt that this would complicate the model to the point where its main features are obscured.

It appears, therefore, that a rigid-band model is capable of accounting for the observed composition dependence of the Hall effect in a number of Cu-based systems, assuming a simple linear change in the effective-mass anisotropy across the phase field, and an anisotropic impurity relaxation time which is independent of concentration. The values of the calculated effective-mass anisotropy are not inconsistent with values expected on qualitative reasoning; and the values of the impurity-scattering anisotropy are consistent with results obtained by other methods.

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