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Disorder and density-of-states effects on the Hall constant in amorphous transition-metal alloys

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The magnitude of the Hall coefficient R_H of amorphous Cu_xTi_{100-x} and Cu_xZr_{100-x} alloys, prepared by rapid quenching from the melt as well as by sputtering, is found to decrease with increasing temperature. This temperature dependence and the positive sign of R_H are discussed with respect to the presence of d electrons and disorder. Neglecting vertex corrections, we study the effects of a finite spread in the electron's spectral function. Short-range order is included, and hybridization is taken into account in a two-band model. It is shown that under certain conditions lifetime broadening can lead to a positive Hall constant. Below about 25 K the temperature dependence can be described by a $T^{1/2}$ law for the most accurate measurements. This finding gives support to corrections due to electron-electron interaction that are consistent with the low-temperature conductivity and predictions from perturbation theories for coherence effects in disordered conductors.

I. INTRODUCTION

The presence of disorder leads to new features in the electronic transport properties of metals and alloys.[1-5] Due to the strong defect scattering, the resistivity of disordered conductors varies only on a scale of 10^{-2} between 10 and 300 K. A more striking feature may be the sign of its temperature coefficient and the magnetoconductivity measured at low temperatures in glasses based on transition metals as well as on simple metals. There is broad evidence[6] that the underlying mechanisms are quantum interference and electron-electron interaction effects.

Previously we have discussed[7-9] such conductivity anomalies in CuTi and CuZr glasses. Here, we focus on the Hall effect, relying on data taken on the same samples. A preliminary report of some aspects of this work has already appeared.[10] The Hall coefficient R_H is controversial, since the positive[11-14] sign generally observed in transition-metal-based metallic glasses cannot be explained with perturbative corrections to the Boltzmann conductivity assuming a free-electron density of states. On the other hand, given the magnitude and sign, R_H should be affected by the same electron coherence effects[3] that are present in the conductivity and also in the Hall effect of two-dimensional disordered systems.[15] Because disorder as well as the electronic density of states, which is not free-electron-like, are involved, the temperature dependence of R_H has to be discussed with respect to both.

The concept of energy bands in order to classify the single-particle energies has to be modified at least in conductors with resistivities larger than 100 $\mu\Omega$ cm. Since the mean free path, l, of the electrons is of the order of several atomic distances, a considerable width of the electronic spectral function is to be expected. However, model calculations of amorphous systems show that band structure[16,17] is still to be seen. In addition, the measured density of states (DOS), as extracted from photoemission experiments, exhibits very similar results for some crystalline, amorphous, and liquid compounds.[18] This indicates that, although on a large scale the positions of the constituents are uncorrelated, short-range order is present and influences the electronic wave functions.

We will show how the sign of R_H can be related to hybridization between s and d electrons and to a finite spread of the electronic spectral function. We then argue that the temperature dependence does not result from vertex corrections to the conductivity, but from a variation of the width of the spectral function with temperature. In addition, at the lowest temperatures electron coherence and interaction effects will become important. In this paper our main aim will be to describe the transport properties, seen in different temperature regimes with various approximations which, however, must be consistent with each other as well as rely on the same physical parameters.

II. EXPERIMENTAL RESULTS

The Hall resistivity $\rho_H = R_H B$ is related to the longitudinal (σ_{xx}) and transverse (σ_{xy}) conductivities via ($\sigma_{xy} \ll \sigma_{xx}$)

$$\rho_H = \sigma_{xy} / \sigma_{xx}^2 \ . \tag{1}$$

The Hall coefficient R_H was determined by applying the usual dc method, relying on

$$R_H = U_H / IBd \ , \tag{2}$$

where I is the sample current, U_H the Hall voltage, B the magnetic field, and d the sample thickness. The Hall voltage could be measured with a galvanometer amplifier coupled to an integrating microvoltmeter.[14] Contacts were made by pressing Cu wires (0.2 mm in diameter) to taps cut into the samples. This arrangement formed the inner part of a "sandwich" consisting of a sapphire plate, a thin sheet of mica, and a Cu plate which was clamped to a Cu block. Using pressure contacts as compared to soldering has the advantage that the samples are not exposed to higher temperatures which could cause partial crystallization. The contacts were checked to be "Ohmic" and turned out to be stable. During the experiments slow cooling and heating rates (about 30 K/h) were applied to avoid stresses on samples and contacts. For typical dimensions ($8\times0.6\times0.03$ mm^3), a resistivity of 150 $\mu\Omega$ cm, and a current of 0.1 A, the heat dissipation is 6

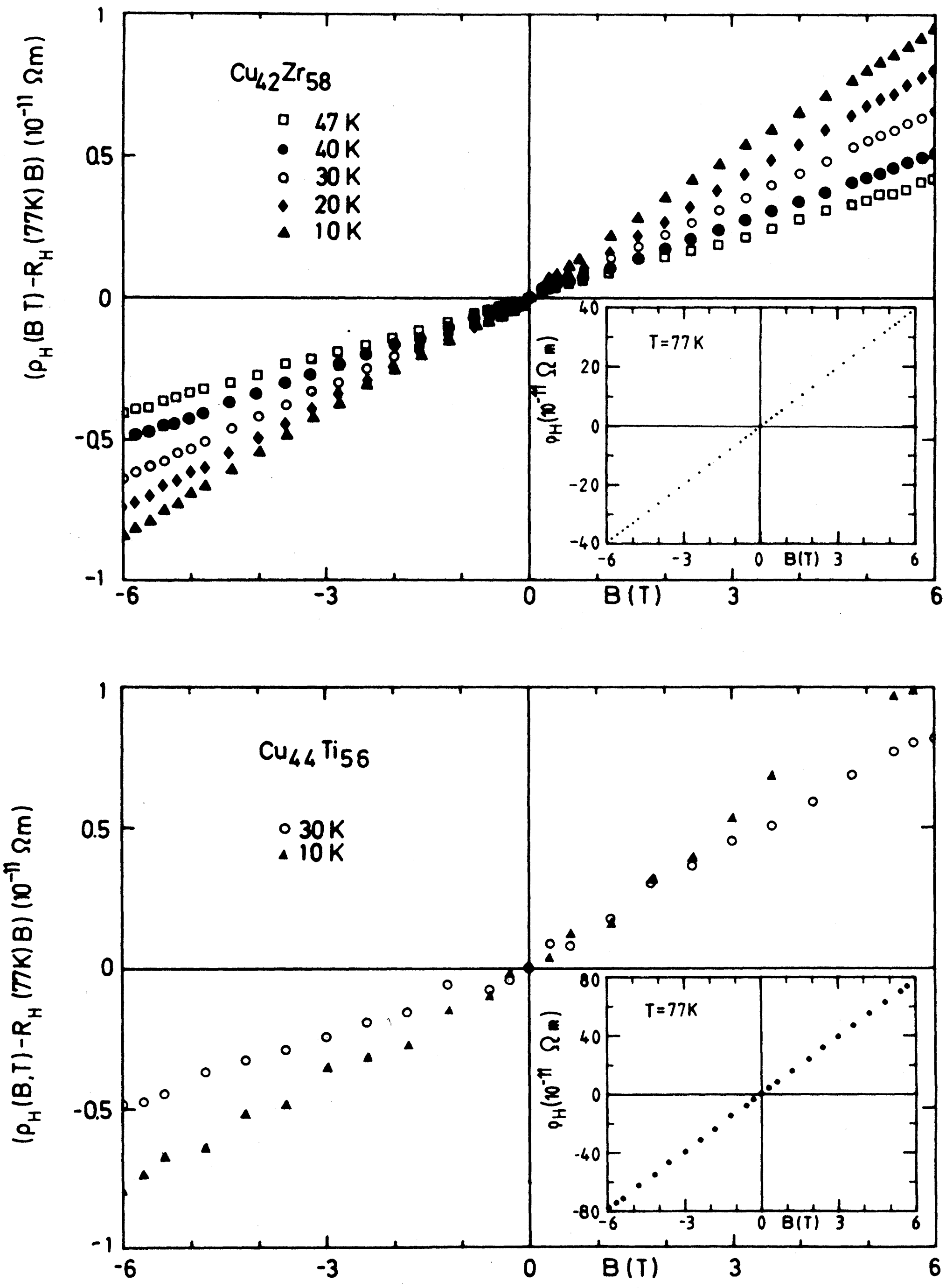

FIG. 1. Magnetic field dependence of the relative change of the Hall resistivity ρ_H for amorphous $Cu_{42}Zr_{58}$ (top) and $Cu_{44}Ti_{56}$ (bottom) at different temperatures. The data points for $\rho_H(B)$ at 77 K are taken as a reference (see insets). The differences in the slopes for negative and positive field directions are caused by magnetoresistivity contributions. They are eliminated by an averaging procedure.

mW. For thinner samples, lower currents (10–50 mA) were used. When drifts occurred the current was set to lower values. A conventional electromagnet ($0<B<1.2$ T) or a superconducting magnet ($0<B<6$ T) supplied the magnetic field B penetrating the sample perpendicular to the ribbon plane. The field setting were calibrated by proton NMR or by a calibrated Hall probe. The errors in the temperature determination, which was performed with the aid of a calibrated carbon glass or a Pt resistor (about 40 K) are smaller than 0.1 K. The error in the temperature dependence of R_H was estimated to be less than 1%, whereas the absolute value is less accurate owing to a 10% uncertainty in the sample thickness. A detailed discussion of systematic errors can be found in Ref. 14.

The amorphous alloys were prepared by melt spinning and dc-magnetron sputtering with typical thicknesses of 30–50 μm and 1.4–3 μm, respectively.[9,19] The conductivities at room temperature are in the range of 5×10^5 $\Omega^{-1}\,\mathrm{m}^{-1}$. A detailed discussion of the resistivity and its temperature and magnetic field dependence is presented in Ref. 9. It should be emphasized that the resistivity is a sensitive marker for the amorphicity of the samples.

The magnetic field dependence of the Hall resistivity for $Cu_{44}Ti_{56}$ and $Cu_{42}Zr_{58}$ at different temperatures is reproduced in Fig. 1. As in our previous measurements,[14] no nonlinearities in $\rho_H(B)$ are observed over normal and reverse directions of the magnetic field within the experimental error. The Hall coefficient is calculated from least-squares fits of straight lines to the data for normal and reverse directions of the magnetic field. Averaging over both field directions eliminates the contribution of the magnetoresistivity due to the imperfect alignment of the Hall probes. The sign of R_H is positive, but the order of magnitude is characteristic for metals with charge carrier densities of 10^{22} cm^{-3}.

The temperature dependence of the Hall coefficient R_H is shown in Figs. 2 and 3. R_H decreases with increasing temperature for samples prepared by melt spinning as well as by sputtering. The relative change of R_H between 10 and 77 K amounts to about 2%. Results for $R_H(T)$ with a lower resolution are reproduced for $Cu_{41}Ti_{59}$, $Cu_{50}Ti_{50}$, $Cu_{39}Zr_{61}$, and $Cu_{25}Zr_{75}$ in Fig. 2. Very accurate measurements could be performed for $Cu_{44}Ti_{56}$, $Cu_{42}Zr_{58}$, and $Cu_{28}Zr_{72}$ (Fig. 3). For these alloys the Hall voltage was also measured as a function of temperature at constant magnetic field. In the latter case, the Hall coefficient is obtained by averaging measurement for normal and reverse directions of B. With this method, more data points and a better resolution of the temperature dependence are attainable. The absolute values of R_H agree with previous results,[11–14] the temperature dependence is beyond the resolution quoted by other authors.[11–13]

Measurements taken after annealing a $Cu_{41}Ti_{59}$ sample for 12 h at 468 K in 99.998%-pure Ar showed no significant change in $R_H(T)$ (Fig. 2). The T dependence can be described by a $T^{1/2}$ law below about 25 K, whereas at higher temperatures R_H decreases more rapidly. These findings have to be discussed on the same footing as the positive sign of R_H. Because of $R_H \approx \sigma_{xy}/\sigma_{xx}^2 B$, the quantity R_H/ρ_{xx}^2 should be equal to σ_{xy}/B within the same approximation. Therefore, we have plotted R_H divided by the square of the normalized resistance (4.2 K) for constant fields in the insets of Fig. 3. Above about 25 K σ_{xy} increases with rising temperature. Thus, the temperature dependence of R_H is not only due to that of σ_{xx}. The measured resistance which has been used for the calculation of σ_{xy} contains all the contributions to the temperature dependence. In the case of $Cu_{44}Ti_{56}$, σ_{xy} is approximately constant in just that temperature range, where $R_H \sim T^{1/2}$ is observed. This behavior is predicted by leading-order perturbation theory for the electron-electron interaction.[20] The variation of roughly 1% between 4 and 25 K is about twice as large as the T dependence measured by Bergmann in two-dimensional disordered Au films,[21] which was also explained by the Coulomb anomaly.

The Hall constant is shown as a function of the Cu concentration for Cu_xZr_{1-x} and Cu_xTi_{1-x} in Fig. 4. For

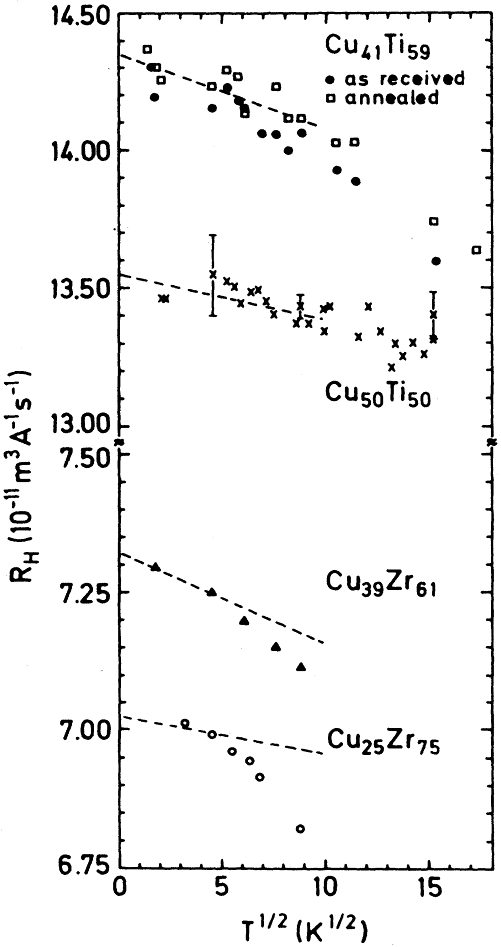

FIG. 2. Temperature dependence of the Hall constant R_H for amorphous $Cu_{41}Ti_{59}$ (see text for annealing procedure), $Cu_{50}Ti_{50}$, $Cu_{39}Zr_{61}$, and $Cu_{25}Zr_{75}$. The dashed lines correspond to the correction due to electron-electron interactions as expected from the conductivity. (See also Table I.)

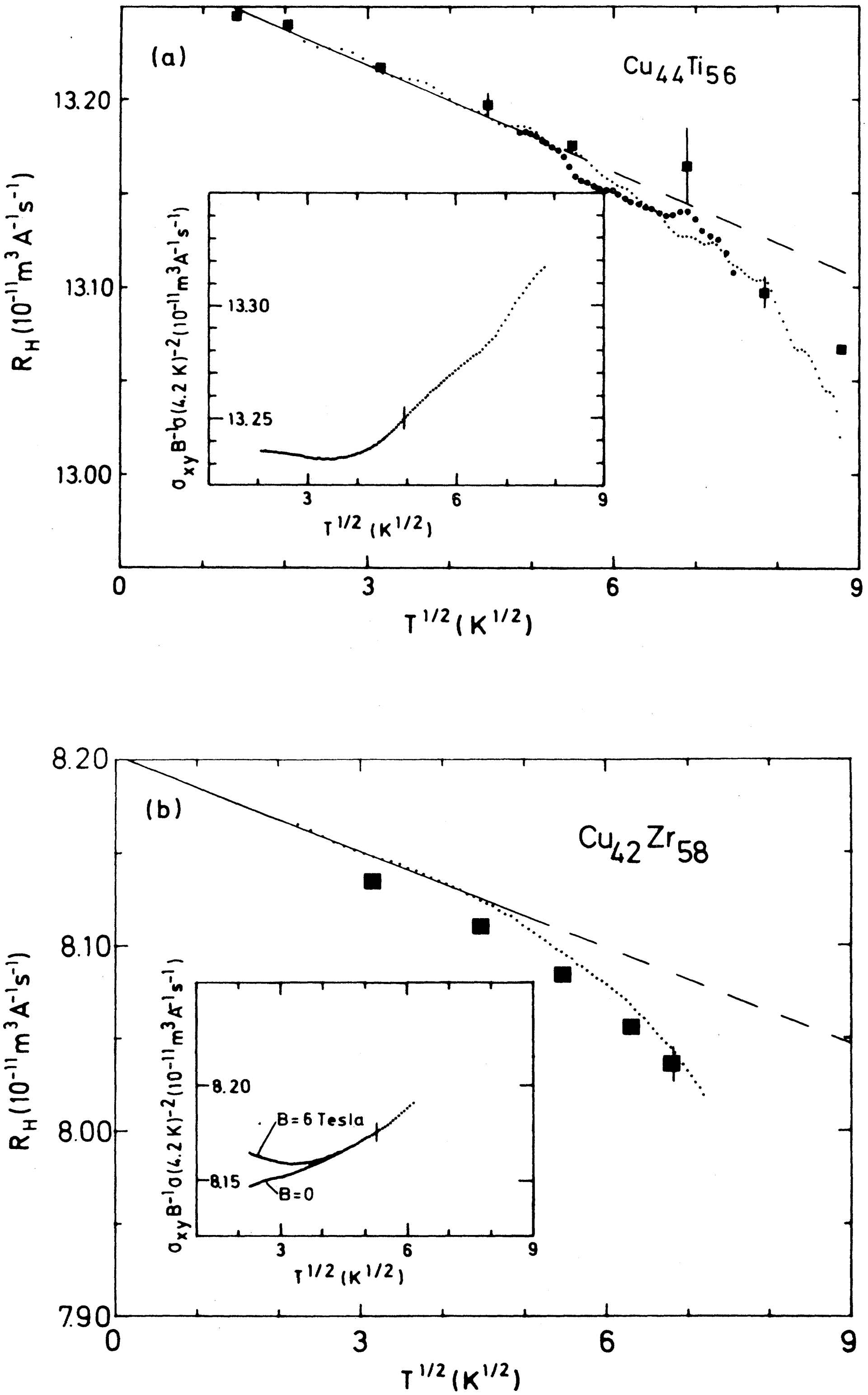

FIG. 3. Hall coefficient R_H as a function of the square root of the temperature for amorphous $Cu_{44}Ti_{56}$, $Cu_{42}Zr_{58}$, and $Cu_{28}Zr_{72}$. ■ denote results from the magnetic field dependence of the Hall resistivity at constant temperature. The other data were taken by varying the temperature at constant magnetic field (· · · ·, 6 T; ●●●●, 3 T). The $T^{1/2}$ dependence is indicated by straight lines. Insets show the normalized transverse conductivity σ_{xy} obtained from R_H and the conductivity at zero field. The conductivity $\sigma(4.2)$ at 4.2 K is about $5 \times 10^5\ \Omega^{-1}\,m^{-1}$.

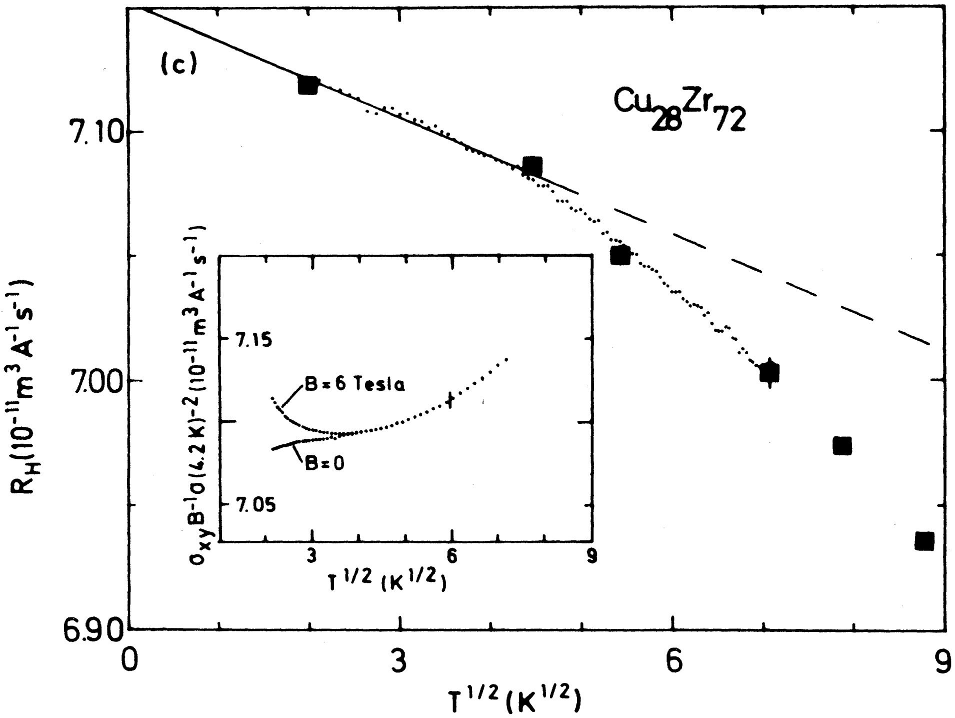

FIG. 3. (*Continued*).

both systems R_H is positive in the transition-metal-rich region and depends only weakly on concentration. R_H becomes less positive with increasing Cu concentration and changes sign at about 80 at. % Cu. In order to discuss a possible relation of the sign of the Hall coefficient with the density of states, we will consider experimental values for $N(\epsilon)$. Measurements of this quantity by the ultraviolet-photoemission-spectroscopy (UPS) method have been published by Oelhafen *et al.*[26] According to them $N(\epsilon)$ of the transition-metal alloys is dominated by the d bands with maxima at the Fermi energy ε_F. The spectra for the alloys are not merely a superposition of those of the metals, but exhibit a characteristic splitting into two maxima. It follows from the concentration dependence that the peak at higher binding energy is due to the Cu $3d$ states, whereas the peak at the Fermi energy ε_F is due to Zr $4d$ and Ti $3d$ states, respectively. For $\varepsilon \lesssim \varepsilon_F$, $N(\varepsilon)$ is increasing with energy, i.e., $dN/d\varepsilon > 0$. Recent bremsstrahlung isochromat spectra by Dutzi *et al.*[27] show that $dN/d\varepsilon \gtrsim 0$ also for $\varepsilon > \varepsilon_F$ in $Cu_{60}Ti_{40}$ and $Cu_{30}Ti_{70}$. $N(\varepsilon_F)$ can be determined independently from the electronic part of the specific heat. Measurements by Samwer and v. Loehneysen[28] as well as Moody and Ng[29] show that $N(\varepsilon_F)$ is decreasing roughly linearly with increasing Cu concentration. Hence, there is no change of sign in $dN/d\varepsilon$ at 70–80 at. % Cu.

Over a wide concentration range the CuZr and the CuTi glasses show a positive sign of the Hall coefficient. Because of the isotropic amorphous structure the "Fermi surface" should have spherical symmetry. It has been proposed[12] that the sign of the Hall constant in some metallic glasses and amorphous iron arises from the slope in the dispersion relation[16] at the Fermi surface. This idea is based on an earlier work by Jan[30] derived from the Boltzmann equation. If a dispersion relation $\varepsilon(k)$ can be defined, the sign of the Hall effect should be given by the sign of the group velocity at the Fermi energy $v_F = \hbar^{-1} \partial\varepsilon/\partial k|_{k_F}$:

$$R_H = \gamma/ne \ , \tag{3}$$

where n is the charge carrier concentration and

$$\gamma = \frac{\partial\varepsilon}{\partial k} \Big/ \left| \frac{\partial\varepsilon}{\partial k} \right| \ . \tag{4}$$

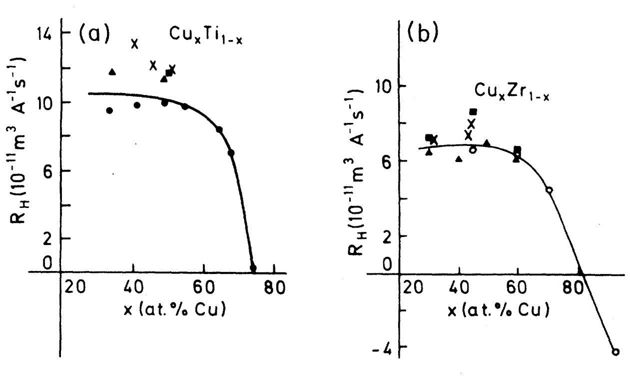

FIG. 4. (a) Hall coefficient R_H as a function of the Cu concentration for amorphous Cu_xTi_{100-x}. Shown are results of this work (×) and data of other authors (●, Ref. 22; ■, Ref. 23; ▲, Ref. 24; ○, Ref. 25). The solid line is a guide for the eye. (b) The same data for Cu_xZr_{100-x}.

III. A MODEL INCLUDING FINITE-LEVEL-WIDTH EFFECTS FOR THE HALL EFFECT

Numerical results show that the spectral function has broad peaks and that it is very similar for liquid and amorphous alloys.[16,17] However, it is not obvious that an effective dispersion, e.g., by the locus of the maxima, can still be defined. Due to the finite width of the spectral function details of the zero-order dispersion average out. Therefore, we propose a very schematic model for amorphous transition metals, which takes the finite lifetime of the electronic states into account.

Although this model can by no means cover the situation in a generic amorphous transition alloy, it is able to explain certain experimental features, such as the correlation between the temperature dependences of the conductivity σ_{xx} and the Hall constant R_H. This model also shows that a possible sign change of R_H is not necessarily related with a sign change in $dN/d\varepsilon$ if finite-level-width effects are taken into account. The effect of level broadening is examined in a two-band model with one-band Hamiltonians for a wide s and a narrow d band. Both are coupled by a hybridization interaction. Disorder is included by using spectral functions with finite widths. The diagonal and nondiagonal elements of the conductivity tensor are evaluated in the presence of a magnetic field applying the Kubo formalism. The free-electron result is recovered in the quasiparticle limit, i.e., with vanishing level broadening.

For simplicity, let us start with a one-band model. The first approximation to the conductivity tensor σ, neglecting vertex corrections, will be

$$\sigma_{xx}=(e^2/4\pi\hbar)V^{-1}\sum_{\mathbf{k}}\varepsilon'(k)^2 \times\int d\varepsilon\left[-\frac{\partial n(\varepsilon)}{\partial\varepsilon}\right]A^2_{\mathrm{av}}(\mathbf{k},\varepsilon)\ , \tag{5}$$

and

$$\sigma_{xy}=(e^2/6\pi\hbar)(eB)V^{-1} \times\sum_{\mathbf{k}}\frac{\varepsilon'(k)^3}{k}\int d\varepsilon\, n_F(\varepsilon)A_{\mathrm{av}}(\mathbf{k},\varepsilon) \times\frac{\partial^2}{\partial\varepsilon^2}[\mathrm{Re}G^{\mathrm{ret}}_{\mathrm{av}}(\mathbf{k},\varepsilon)]\ . \tag{6}$$

Here, $n_F(\varepsilon)$ denotes the Fermi-Dirac distribution function, e the electronic charge, B the magnetic field, $\hbar$ Planck's constant divided by 2π, and V the volume of the system. $A_{\mathrm{av}}(\mathbf{k},\varepsilon)$ describes the electronic spectral function, averaged over the atomic configuration, and $G^{\mathrm{ret}}_{\mathrm{av}}$ is the retarded electronic Green's function. These equations show how the special electronic structure, contained in A_{av} and $G^{\mathrm{ret}}_{\mathrm{av}}$, enter the transport properties.

For simplicity, we choose a special electronic spectral function, containing a level broadening Γ:

$$A_{\mathrm{av}}(\mathbf{k},\varepsilon)=\left.\frac{2\Gamma}{(\varepsilon-\xi)^2+\Gamma^2}\right|_{\xi=\varepsilon(k)}\ . \tag{7}$$

The Fermi-Dirac distribution function $n_F(\varepsilon)$ is approximated by the step function, i.e.,

$$n_F(\varepsilon)=\Theta(\varepsilon_F-\varepsilon)\ , \tag{8}$$

since we can assume $\Gamma\gg k_BT$, where k_B denotes the Boltzmann constant.

From these assumptions we get

$$\sigma_{xx}=\left.\frac{e^2}{12\pi\hbar V}\int d\xi\, g_1(\xi)A^2_{\mathrm{av}}(\xi,\varepsilon)\right|_{\varepsilon=\varepsilon_F/\hbar} \tag{9}$$

and

$$\sigma_{xy}=-\frac{e^2}{12\pi\hbar V}\frac{eB}{2\Gamma}\int d\xi\, g_2(\xi)\left[1-\frac{4\Gamma}{3}A_{\mathrm{av}}(\xi,\varepsilon)\right] \left.\times A^2_{\mathrm{av}}(\xi,\varepsilon)\right|_{\varepsilon=\varepsilon_F/\hbar} \tag{10}$$

as well as for the density of states:

$$N(\varepsilon)=V^{-1}\int d\xi\, g_0(\xi)A_{\mathrm{av}}(\xi,\varepsilon)\ , \tag{11}$$

where

$$\begin{aligned} g_0(\xi)&=\sum_{\mathbf{k}}\delta(\varepsilon(k)-\xi)\ ,\\ g_1(\xi)&=\sum_{\mathbf{k}}\varepsilon'(k)^2\delta(\varepsilon(k)-\xi)\ ,\\ g_2(\xi)&=\sum_{\mathbf{k}}\frac{\varepsilon'(k)^3}{k}\delta(\varepsilon(k)-\xi)\ . \end{aligned} \tag{12}$$

The usual electronic quasiparticle limit is recovered for $\Gamma\to 0$.

Next, we generalize these results to a two-band model, where a coupling (hybridization) between the bands is included. In order to model a transition metal we assume a wide s band and a narrow d band. Since only the situation at the Fermi level ε_F will be important, the other d band at higher binding energies will play no role. The Hamiltonian is

$$H=H^s+H^d+H^{s-d}\ , \tag{13}$$

where H^s and H^d are one-band Hamiltonians. The hybridization interaction $H^{s\text{-}d}$ couples the bands. For the moment we disregard all interactions in the single-band parts. The Hamiltonian then reads

$$H=\sum_{\mathbf{k}}\varepsilon_s(k)|s\mathbf{k}\rangle\langle\mathbf{k}s|+\sum_{\mathbf{k}}\varepsilon_d(k)|d\mathbf{k}\rangle\langle\mathbf{k}d| +\tfrac{1}{2}\left[\sum_{\mathbf{k},\mathbf{k}'}|sk\rangle V^{s-d}_{\mathbf{k}\mathbf{k}'}\langle\mathbf{k}'d|+\mathrm{c.c.}\right]\ . \tag{13a}$$

Here c.c. means the complex conjugate. Separating the k-diagonal term we have

$$\sum_{\mathbf{k}}[\varepsilon_s(k)|s\mathbf{k}\rangle\langle\mathbf{k}s|+\varepsilon_d(k)|d\mathbf{k}\rangle\langle\mathbf{k}d| +\tfrac{1}{2}(V^{s-d}_{\mathbf{k}\mathbf{k}}|s\mathbf{k}\rangle\langle\mathbf{k}d|+\mathrm{c.c.})]\ . \tag{13b}$$

We diagonalize H and obtain new bands $\varepsilon_+(k)$ and $\varepsilon_-(k)$,

$$H=\sum_{\mathbf{k}}[\varepsilon_+(k)|+\mathbf{k}\rangle\langle+\mathbf{k}|+\varepsilon_-(k)|-\mathbf{k}\rangle\langle-\mathbf{k}|] \tag{14a}$$

with

$$\varepsilon_\pm^2=\tfrac{1}{2}(\varepsilon_s^2+\varepsilon_d^2+\tfrac{1}{2}V_H)$$
$$\pm\tfrac{1}{2}[(\varepsilon_s^2-\varepsilon_d^2)^2+V_H^2(\varepsilon_s+\varepsilon_d)^2]^{1/2}\ . \tag{14b}$$

V_H denotes the constant-hybridization matrix element. The remaining nondiagonal k contributions can be included in the scattering terms, which give the finite-level broadening. Equations (9)–(11), suitably modified for two bands, can now be evaluated alternatively with the unhybridized or hybridized states $\varepsilon_s(k),\varepsilon_d(k)$ and $\varepsilon_+(k),\varepsilon_-(k)$, respectively.

The unhybridized bands $\varepsilon_s(k)$ and $\varepsilon_d(k)$ are given by the tight-binding-type expressions appropriate for amorphous systems:

$$\begin{aligned}\varepsilon_s(k)&\sim 1-\frac{\sin ak}{ak}\ ,\\ \varepsilon_d(k)&\sim\varepsilon_0+\frac{\Delta d}{2}\cos\tfrac{2}{3}ak\ .\end{aligned} \tag{15}$$

In the following, all energies are measured in units of the s-band width Δ_s, i.e., $\Delta_s=1$. The momentum is measured in arbitrary units and a cutoff at $k=1$ is introduced. The hybridization interaction V_H is of the order of the d-band width Δ_d. The main features of our results do not depend drastically on the cutoff, because the crossing of the bands is far away from the band edge. We choose a d band of negative slope to assure the possibility of a positive Hall constant. This model provides a tool simple enough to gain insight into the influence of the finite level width. Representing the d electrons by a single band is not a serious limitation, because usually only one hybridizes with the s band. For the unhybridized bands we assume a constant broadening Γ_s and Γ_d for the s and d band, respectively. For the hybridized bands a linear combination of Γ_s and Γ_d is used so that at the band edges the broadening is of s or d type. The d band is weighted by a factor of 3 relative to the s band. This corresponds to six d electrons and two s electrons. For hybridized states we assume equal population. All of these specifications do not change the qualitative features. In Fig. 5 both the Hall constant and the density of states (DOS) are shown for $V_H\approx\Delta_d$, $\Gamma_s=\Delta_s/10$, and $\Gamma_d=\Delta_d/10$, which might be a realistic set of parameters for an amorphous metal. The positive peak resembles very closely what one would expect from an S-shaped dispersion as proposed by Weir *et al.*[16] In an extension of that work Morgan *et al.*[31] and Nguyen-Manh *et al.*[32] find that an S-shaped dispersion curve of the electrons and s-d hybridization both lead to a negative slope in the density of states. However, an S-shaped dispersion is only obtained for a certain strength of the hybridization. The positive Hall coefficient is then explained as being caused by the negative slope in the density of states. As is evident from Fig. 5, we do not get such a clear-cut correlation. An S-shaped dispersion is not seen also, since $g_2(\xi)$ containing $\varepsilon'(k)^3$ can be shown by numerical calculations to be always positive. In fact, the pronounced structure seen in Fig. 5 can be attributed only to the finite width of the spectral function according to Eqs. (10) and (7). Hence, we encounter the situation where the weighting factor in Eq. (10) determines the sign of σ_{xy}. This is a surprising outcome, which was not realized before.

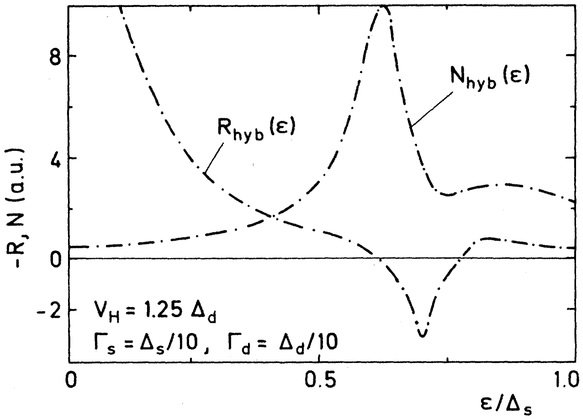

FIG. 5. The negative of the Hall constant and the DOS for hybridized bands calculated with Eqs. (7)–(12) and (14) as a function of energy. $\Gamma_{s'}$, s-band broadening; $\Gamma_{d'}$, d-band broadening. $\Delta_s=1.0$, $\Delta_d=0.2$, and $V_H=0.05$.

The Hall constant becomes positive if the Fermi energy is located in the d band. At its edges it gets negative again. This is a behavior previously attributed to an S-shaped deformation of the s band, due to hybridization. We do not observe a direct correlation of the DOS and the sign of the Hall constant (Fig. 5). The general shift of pronounced structures in the DOS and Hall constant is explained by the fact that the DOS is essentially proportional to $\varepsilon'(k)^{-1}$ [Eqs. (11) and (12)] and the Hall constant to $\varepsilon'(k)^3$ [Eqs. (10) and (12)]. This gives for the DOS a pronounced peak at the bottom of the d band and for the Hall constant a dip located somewhere in the middle of the d band.

Although the positive sign of R_H can be attributed to the finite width of the spectral function, a quantitative analysis cannot be made using the simple approach outlined above.[33] A different approximation would be a direct evaluation of the spectral function for an amorphous alloy, extending calculations for a one-component amorphous system by Morgan *et al.*[16] and Bose *et al.*[17] Taking into account the electron-phonon interaction in the spectral function seems to be of some importance since this gives a temperature-dependent contribution.[34] Alternative explanations have been put forward by Movaghar[35] and by Hoshino.[36] However, since they either are not in agreement with experiment or rely on the existence of electrons and holes, we will not discuss them here.

In Fig. 6 the Hall coefficient is plotted as a function of the resistivity for some metallic glasses. There is no correlation between an anomalous sign and a high resistivity. In the metallic regime, positive Hall coefficients have only been observed in glasses with transition metals. On the other hand, R_H is negative in high-resistivity alloys like CaAl.[37,38] These findings suggest that d elec-

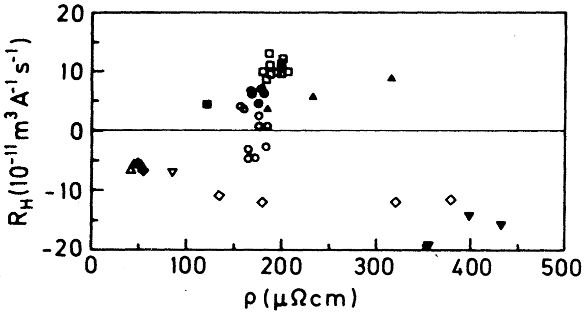

FIG. 6. The Hall coefficient R_H as a function of the resistivity ρ for some amorphous alloys ∇, PdSi (Ref. 47); ■, LaGa; ▲, LaAl (Ref. 48); ◇, CaAl; ▼, CaAl (Ref. 37); ◆, MgCu (Ref. 49); △, MgZn; ●, CuZr; ○, NiZr; □, CuTi. When no reference is indicated, the data are taken from Ref. 11.

trons are relevant for the sign of R_H, but ρ is influenced by both d electrons and disorder. In this sense we have neglected all two-particle correlations for the sign of the Hall coefficient and emphasized the aspect of short-range order by calculating the defect-averaged one-particle correlation functions.

IV. THE TEMPERATURE DEPENDENCE OF THE HALL COEFFICIENT

A. Preliminary remarks

The sign of the Hall coefficient in amorphous transition-metal alloys has been discussed with the energy dependence of the density of states and finite-level-width effects. A finite lifetime of the electronic states means that the density of states is modified by the nonvanishing imaginary part of the self-energy Σ. This quantity is temperature dependent in the presence of the electron-phonon interaction and can cause a weakly temperature-dependent Hall constant. Another contribution is due to the temperature dependence of the Fermi energy. The influence of the self-energy can be described by a broadening of the spectral function and will be discussed.

Prange and Kadanoff[39] have shown that many-body effects due to the electron-phonon interaction cancel in the dc conductivity as calculated with the Boltzmann equation. The same applies for the electronic part of the thermal conductivity and the galvanomagnetic transport coefficients. Experimentally, no corrections due to renormalization (e.g., for the effective mass) could be observed in the temperature dependence of R_H for amorphous Bi, Pb, and Ga films.[40] On the other hand, the density of states changes between 4 and 30 K by a certain percentage due to the renormalization.[40] Thus, deviations from such a behavior would be consistent with corrections not contained in the Boltzmann equation, for instance due to disorder or electron-electron interaction.

As shown in Figs. 2 and 3 there is a non-negligible temperature dependence of the Hall effect, independent of the preparation method. Thermal expansion would result in a positive temperature coefficient $R_H^{-1}dR_H/dT$ of R_H. The temperature coefficient observed, however, has the opposite sign. We exclude magnetic effects, since the magnetic field dependence of the Hall resistivity is linear and no peculiarities could be detected in the thermopower.[41] The results of the annealing experiment performed on $Cu_{41}Ti_{59}$ and the temperature dependence of the resistance rule out spurious effects due to crystallization. We have discussed possible systematic errors to the temperature dependence in detail in Ref. 14.

In a study of Hall effect of noncrystalline ZrCu films, von Minnigerode and Boettjer[42] find that the quantity R_H of unannealed Zr-rich films depends only weakly on temperature. Within the limited accuracy of their experiments the variation of R_H with temperature is always linear between 4 and 280 K. Both the values of R_H and its temperature coefficient, $R_H^{-1}dR_H/dT$, change with heat treatment performed 50 K below the crystallization temperature. We do not observe such a significant change of the temperature dependence with annealing. However, our heat treatment was done at much lower temperature ($T_A \approx 468$ K). In isothermal annealing experiments[43] we found that 50 K below the crystallization temperature ($T_x \approx 700$ K) is too high a temperature to exclude crystallization effects.

B. Thermal broadening of the spectral function

As has been shown in Sec. III, the sign of the Hall coefficient can be explained with d states in the DOS and a finite spread of the spectral function due to strong scattering. Such a spread depends on temperature in general, i.e., it is due to the electron-phonon contribution to the self-energy Σ. To explain the experimental results the absolute magnitude of R_H has to decrease with increasing temperature, if the imaginary part of Σ exhibits a positive temperature coefficient. The relative variation of the Hall constant is a factor of 3–5 larger than that of the conductivity, at least for temperatures above 30 K (see Figs. 2 and 3). We would like to discuss this regime first.

For a binary alloy with substitutional disorder, Chen, Weisz, and Sher[34] performed calculations in the coherent potential approximation (CPA) taking into account an electron-phonon coupling but neglecting vertex corrections. The temperature dependence of Σ results in a temperature-dependent DOS and conductivity. The details of the alloy are of some importance. Depending on concentration, strength of the scattering potential, and the position of the Fermi energy the authors obtain positive or negative temperature coefficients for the conductivity. Now, we can schematically account for the effect of a temperature-dependent self-energy Σ produced by an increasing width of the spectral function. We neglect a temperature dependence in the position of the Fermi energy. The DOS, conductivity, and the Hall constant calculated with Eqs. (9)–(11) for various widths of the spectral function are plotted in Fig. 7. The variation of about 10% in the width corresponds to the values of Chen, Weisz, and Sher.[34] With increasing Γ, i.e., increasing temperature, the DOS is increasing at the center and decreasing at the band edges. Depending on the position of the Fermi energy, σ_{xx} is increasing or decreasing with Γ.

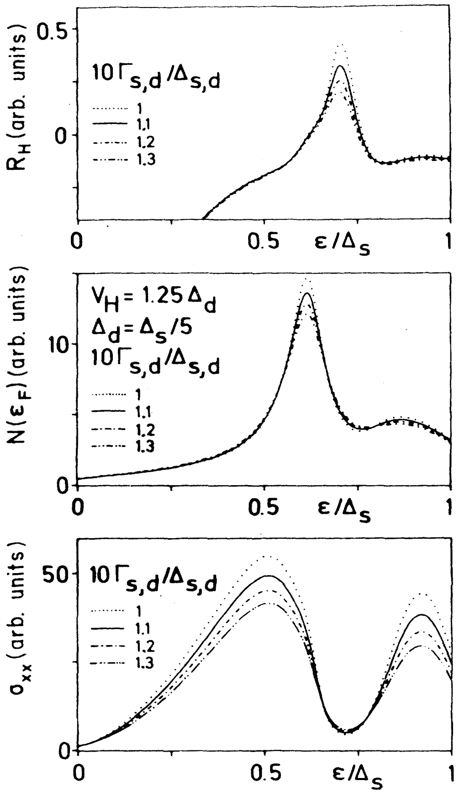

FIG. 7. Hall coefficient R_H, density of states $N(\varepsilon_F)$, and longitudinal conductivity σ_{xx} calculated with the model presented in Sec. III. Δ_s and Δ_d denote the s- and d-band width, respectively. V_H is the hybridization energy. The broadening Γ is assumed to be proportional to the temperature.

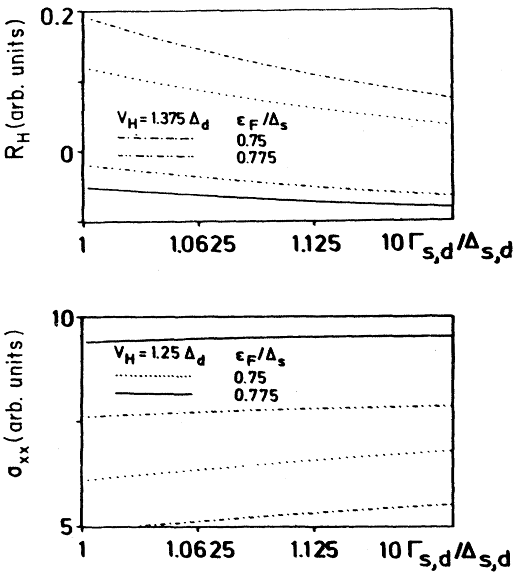

FIG. 8. Hall coefficient R_H, and longitudinal conductivity σ_{xx} as a function of the width Γ of the spectral function (see text). For other specifications, see Fig. 7.

The Hall coefficient is decreasing with T in the energy range where the sign is positive. $N(\varepsilon_F)$, σ_{xx}, and R_H are shown in Fig. 8 as a function of $\Gamma \sim T$ for fixed energy. ε_F was chosen in the range where $R_H > 0$. The temperature dependence is rather sensitive to the position of ε_F. The resulting temperature coefficient of the conductivity is positive and thus consistent with the experimental data. Hence, we can explain simultaneously the positive sign and the T dependence of R_H as well as the T dependence of the conductivity with the same model.

C. Electron-electron interaction effects at low temperatures

The Coulomb anomaly, i.e., modifications of the electronic Fermi liquid by impurities, was observed in two-dimensional disordered systems[21] after theoretical predictions.[20] Such anomalies have been detected in the conductivity and the Hall effect only at temperatures below about 30 K. Perturbation theories give the relative change of the Hall constant in a weakly disordered system as a function of temperature. They ignore the absolute value and the sign of R_H.

The result of Alt'shuler *et al.*[20,44] for the fractional change of $R_H(T)$ is

$$\frac{\delta R_H(T)}{R_H(0)} = 1.3\frac{e^2}{2\pi^2\hbar}\rho(0)\left(\tfrac{4}{3} - \tfrac{3}{2}\widetilde{F}\right)\left[\frac{k_B T}{2\hbar D}\right]^{1/2} = \frac{R_H(0) - R_H(T)}{R_H(0)}\,, \tag{16}$$

where $\widetilde{F}$ is a screening parameter[44] and D denotes the electronic diffusion constant. The other symbols have the usual meaning. In Table I the parameters determined from the experimental results ($T < 25$ K) are summarized, assuming

$$R_H(T) = R_H(0) + \Delta R_H T^{1/2}\,. \tag{17}$$

Here, R_H is defined by Eqs. (1) and (2). This interpretation relies on the fact that trivial phonon effects, as discussed in Sec. IV A, have been frozen out in the temperature range considered. With the help of the conductivity the quantity $\widetilde{F}$ was found to lie between 0 and 1.[9] The electronic diffusivity D was estimated from the resistivity ρ and the bare density of states $N(\varepsilon_F)$ by using the Einstein relation,

$$D = [e^2\rho(0)N(\varepsilon_F)]^{-1}\,. \tag{18}$$

$\widetilde{F}$ deduced in this way is consistent with the magnetic field dependence and the temperature dependence of the conductivity at low temperatures.[9] According to Alt'shuler *et al.* the effect of electron-electron interaction should be given by

$$\frac{\delta R_H(T)}{R_H(0)} = -2\frac{\delta\sigma_{xx}(T)}{\sigma_{xx}(0)}\,. \tag{19}$$

TABLE I. Parameters determined from a comparison of Eqs. (18) and (19) to the temperature dependence of the Hall coefficient below 25 K. The electronic diffusion constant D was estimated from the conductivity and the density of states as described in the text [Eq. (18)]. The quantity ΔR_H is defined to be $\delta R_H = \Delta R_H T^{1/2} = R_H(T) - R_H(0)$.

Alloy	$R_H(0)$ $[10^{-11}\ \text{m}^3(\text{A s})^{-1}]$	ΔR_H $[10^{-13}\ \text{K}^{-1/2}\text{m}^3(\text{A s})^{-1}]$	$\rho(0)$ $(10^{-6}\ \Omega\,\text{m})$	D $(10^{-5}\ \text{m}^2\text{s}^{-1})$	$\tilde{F}$
$\text{Cu}_{44}\text{Ti}_{56}$	13.28	−1.91	1.94	3.1	0.22
$\text{Cu}_{42}\text{Zr}_{58}$	8.2	−1.72	1.72	1.0	0.26
$\text{Cu}_{28}\text{Zr}_{72}$	7.15	−1.56	1.61	1.3	≈0.09

Therefore, as far as this contribution is concerned, due to Eq. (1) σ_{xy} must be constant in the T range, where the $T^{1/2}$ behavior is observed. It can be seen in Fig. 3 (insets) that this prediction is verified for the nonsuperconducting samples. The situation is more complicated for the CuZr glasses. Here, superconducting fluctuations interfere. Quenching them with a magnetic field introduces additional contributions from magnetoresistivity. However, it is clear from Fig. 3 that the curves labeled 0 and 6 T are not inconsistent with the anticipated behavior: $\sigma_{xy} = \text{const}$. For a certain field $0 < B < 6$ T superconducting fluctuation effects and magnetoconductivity effects may cancel to give a horizontal line.

We may test the predictions made by Eq. (19) for the very precise data obtained in the case $\text{Cu}_{44}\text{Ti}_{56}$. From Table I we obtain $-\Delta R_H / R_H(0) = 1.44 \times 10^{-3}$ $\text{K}^{-1/2}$. Using for the Coulomb correction to the conductivity $\delta\sigma_{xx}(T) = aT^{1/2}$, the prefactor 343 $\Omega^{-1}\text{m}^{-1}\text{K}^{-1/2}$, and $\sigma(0) = 5.2 \times 10^5\ \Omega^{-1}\text{m}^{-1}$ (Refs. 7 and 9), we obtain $a/\sigma(0) = 0.66 \times 10^{-3}\ \text{K}^{-1/2}$, and thus $[\delta R_H / R_H(0)]/[\delta\sigma_{xx}/\sigma(0)] = -2.19$. On the other hand, assuming the validity of Eq. (19), we get, with $a = 472$ and 309 $\Omega^{-1}\text{m}^{-1}\text{K}^{-1/2}$ (Refs. 7 and 9), $\sigma(0) = 5.1 \times 10^5\ \Omega^{-1}\text{m}^{-1}$, as well as $a/\sigma(0) = 0.93$ and $0.61 \times 10^{-3}\ \text{K}^{-1/2}$, the results $-\Delta R_H / R_H(0) = 1.86$ and $1.22 \times 10^{-3}\ \text{K}^{-1/2}$ for $\text{Cu}_{41}\text{Ti}_{59}$ and $\text{Cu}_{50}\text{Ti}_{50}$, respectively. Corresponding lines with slopes of −2.67 and $-1.65 \times 10^{-13}\ \text{m}^3(\text{A s})^{-1}\text{K}^{-1/2}$ are indicated in Fig. 2. The agreement is quite good for temperatures $T < 25$ K. However, at higher temperatures we observe an additional temperature dependence which is different from the one predicted by the interaction effect (see discussion in Sec. IV B).

The present analysis invalidates an earlier interpretation given by Gallagher *et al.*[25] These authors argue that the electron-electron interaction should lead to a significant temperature dependence of R_H even above 200 K. In our opinion such a contribution, which, in addition, is unable to account for the sign of R_H in general, is only detectable at low temperatures. It is in this regime that the phase coherence time of the electronic wave function is sufficiently long to allow for significant quantum corrections. Very recently, additional support was reported for contributions due to electron-electron interaction effects in quasi-two-dimensional[45] and thin-film[46] CuTi samples and in amorphous Ag-Cu-Ge alloys.[50] The overall temperature dependence of the resistivity, which seems to be larger in the thin-film samples[46]—also showing higher resistivities—is yet to be explored in more detail.

V. CONCLUSIONS

We have presented precise Hall-effect measurements on the transition-metal glasses $\text{Cu}_x\text{Ti}_{100-x}$ and $\text{Cu}_x\text{Zr}_{100-x}$. In the transition-metal-rich concentration range the Hall coefficient R_H exhibits a positive sign and R_H is weakly decreasing with increasing temperature. To discuss theoretically finite-width effects in the electron spectral function, we neglected vertex corrections altogether and replaced the exact configuration-dependent propagators by averaged ones. Therefore, it was possible to express the elements of the conductivity tensor through the electrons spectral function. For free electrons the Hall coefficient in the limit of zero width is $R_H = (en)^{-1}$ where n is the electronic density. We studied the Hall constant for arbitrary width Γ in a two-band model. An amorphous transition metal was modeled assuming a flat d band at the Fermi surface and a wide s band. Hybridization between the bands was taken into account. As a main result for the hybridized bands we derive a positive Hall constant attributed to the finite width of the electron's spectral function.

Within this model thermal disorder can lead to the observed overall temperature dependence in the transport properties discussed. In addition, at low temperatures ($T < 25$ K) a $T^{1/2}$ law is consistent with additional perturbative corrections due to electron-electron interaction. This effect is related to the quantum corrections to the conductivity. The origin of the positive sign of R_H in metallic glass with d electrons can be understood by studying only a one-particle property, namely the electric spectral function. Here, broadening by static and thermal disorder and hybridization of s and d electrons proves to be important.

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[1] *Proceedings of the International Conference on Localization, Interaction, and Transport Phenomena in Impure Metals,* Vol. 61 of *Springer Series in Solid-State Sciences,* edited by B. Kramer, G. Bergmann, and V. Brynseraede (Springer-Verlag, Berlin, 1985).

[2] See supplement to Ref. 1, edited by L. Schweitzer and B. Kramer (Physikalisch-Technische Bundesanstadt, Braunschweig, 1984).

[3] P. A. Lee and T. V. Ramakrishnan, Rev. Mod. Phys. **57**, 287 (1985).

[4] *Amorphous and Liquid Materials,* edited by E. Lüscher, G. Fritsch, and G. Jacucci (Nijhoff, Dordrecht, 1986).

[5] *Liquid and Amorphous Metals,* edited by E. Lüscher, F. Hensel, and W. Gläser (Oldenbourg, München, 1987), Vols. 1 and 2.

[6] For a recent review of electron localization and interaction effects in amorphous alloys, see R. W. Cochrane and other papers in Ref. 5.

[7] A. Schulte and G. Fritsch, J. Phys. F **16**, L55 (1986).

[8] A. Schulte, Solid State Commun. **60**, 99 (1986).

[9] A. Schulte, G. Fritsch, and E. Lüscher (unpublished).

[10] A. Schulte, A. Roithmayer, G. Fritsch, and E. Lüscher, in Ref. 4.

[11] D. G. Naugle, J. Phys. Chem. Solids **45**, 367 (1984).

[12] B. L. Gallagher, D. Greig, M. A. Howson, and A. A. M. Croxon, J. Phys. F **13**, 119 (1983).

[13] R. W. Cochrane, J. Destry, and M. Trudeau, Phys. Rev. B **27**, 5955 (1983).

[14] A. Schulte, A. Eckert, G. Fritsch, and E. Lüscher, J. Phys. F **14**, 1877 (1984).

[15] For a review, see G. Bergmann, Phys. Rep. **107**, 1 (1984).

[16] G. F. Weir, M. A. Howson, B. L. Gallagher, and G. J. Morgan, Philos. Mag. B **47**, 163 (1983); G. J. Morgan and G. F. Weir, *ibid.* B **47**, 177 (1983).

[17] S. K. Bose, L. E. Ballentine, and J. E. Hammerberg, J. Phys. F **13**, 2089 (1983).

[18] H.-J. Güntherodt *et al.*, *Physics of Transition Metals 1980,* Institute of Physics Conference Series No. 55 (Institute of Physics, London, 1981), Chap. 13, p. 619.

[19] A. Fleischmann, Diplomarbeit, Technische Universität München, 1985.

[20] B. L. Alt'shuler, D. Khmelnitzki, A. I. Larkin, and P. A. Lee, Phys. Rev. B **22**, 5142 (1980).

[21] G. Bergmann, Solid State Commun. **49**, 775 (1984); M. J. Uren, R. A. Davies, and M. Pepper, J. Phys. C **13**, 1985 (1980).

[22] M. A. Howson, D. Greig, B. L. Gallagher, and G. J. Morgan, J. Non-Cryst. Solids **61&62**, 1261 (1984).

[23] H.-J. Güntherodt *et al.*, J. Phys. (Paris) Colloq. **41**, C8-381 (1980).

[24] A. Tschumi, T. Laubscher, R. Jeker, E. Schüper, H.-U. Künzi, and H.-J. Güntherodt, J. Non-Cryst. Solids **61&62**, 1091 (1984).

[25] B. L. Gallagher, D. Greig, and M. A. Howson, J. Phys. F **14**, L225 (1984).

[26] P. Oelhafen, in *Glassy Metals II,* edited by H.-J. Güntherodt and H. Beck (Springer, Berlin, 1983), p. 283.

[27] W. Dutzi (private communication).

[28] K. Samwer and H. v. Loehneysen, Phys. Rev. B **26**, 107 (1982).

[29] D. E. Moody and T. K. Ng, Physica B+C **126B**, 371 (1984).

[30] J. P. Jan, Am. J. Phys. **30**, 497 (1962).

[31] G. J. Morgan, M. A. Howson, and D. Nguyen-Mahn, in Ref. 5, Vol. 2, p. 777.

[32] D. Nguyen-Manh, D. Mayon, G. J. Morgan, and A. Pasturel, J. Phys. F **17**, 999 (1987).

[33] L. M. Roth and V. A. Singh, Phys. Rev. B **25**, 2522 (1982).

[34] A. B. Chen, G. Weisz, and A. Sher, Phys. Rev. B **5**, 2897 (1972).

[35] B. Movaghar, in *Physics of Disordered Materials,* edited by D. Adler, H. Fritzsche, and S. R. Ovshinsky (Plenum, New York, 1985).

[36] K. Hoshino, J. Phys. C **10**, 2147 (1977).

[37] U. Mizutani and T. Matsuda, J. Phys. F **13**, 2115 (1983).

[38] A. Roithmayer, Diplomarbeit, Technische Universität München, 1985.

[39] R. E. Prange and L. P. Kadanoff, Phys. Rev. **134**, 566 (1964).

[40] G. Bergmann, Solid State Commun. **16**, 919 (1975).

[41] G. Fritsch, W. Dyckhoff, W. Pollich, W. Zottmann, and E. Lüscher, Z. Phys. B **59**, 27 (1985).

[42] G. v. Minnigerode and H. G. Böttjer, Z. Phys. B **60**, 351 (1985).

[43] J. Wohlfahrt, Diplomarbeit, Technische Universität München, 1985.

[44] B. L. Alt'shuler and A. G. Aronov, Solid State Commun. **46**, 429 (1983).

[45] C. Shearwood, M. A. Howson, D. Greig, and M. Simpson, in Ref. 5, Vol. 2, p. 771.

[46] J. S. Drewery and R. H. Friend, J. Phys. F **17**, 1739 (1987).

[47] A. Schulte, dissertation, Technische Universität München, 1985.

[48] C. L. Tsai and F. C. Lu, J. Appl. Phys. **55**, 1145 (1984).

[49] U. Mizutani, J. Hashizume, and T. Matsuda, J. Phys. Soc. Jpn. **55**, 3188 (1986).

[50] I. Sokamoto, K. Yonemitsu, K. Sato, and U. Mizutani, J. Phys. F **18**, 2009 (1988).