

## Electronic structure and sign reversal of the Hall coefficient in amorphous CuZr alloys

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We present calculated densities of states (DOS) for  $\text{Cu}_x\text{Zr}_{1-x}$  amorphous alloys across the compositional range. We find that for  $x < 80$  at. % Cu there is no ordering and the Fermi level  $E_F$  is dominated by the Zr 4*d* subband, while above 80 at. % Cu the local order increases and the DOS at  $E_F$  abruptly decreases and is dominated by the *s* states. These changes in the DOS and the fact that the energy derivative of the self-energy changes its sign (implying a change of sign of the Fermi velocity) gives further insight into the experimentally observed sign reversal of the Hall coefficient which occurs for  $80 \leq x \leq 85$  at. % Cu.

Recent advancement in calculations of electronic structure of disordered systems enable one to elucidate many fine features of the density of states (DOS) as a function of the composition of an alloy system<sup>1-7</sup> and consequently bring new insight into behavior of the transport coefficients.<sup>7-9</sup> On the other hand, the sign reversal of the Hall coefficient,  $R_H$ , from "metallic" (negative) to "anomalous" (positive) has been experimentally observed in numerous liquid or glassy alloys.<sup>10-16</sup> Several theoretical explanations have been put forward to account for this effect<sup>17-22</sup> as, for example, the *s-d* hybridization effect<sup>6,19-21</sup> or strong skew scattering of band electrons.<sup>23</sup> The Hall effect gives information about the dynamical properties of electrons and is also closely related to the electronic structure of an alloy. It is this latter aspect to which we address ourselves in this Rapid Communication.

We have studied the concentration dependence of electronic structure in disordered transition-metal alloys  $\text{Cu}_x\text{TM}_{1-x}$  ( $\text{TM} = \text{Ti, Zr, Hf}$ ) as well as some other metal-metal glasses in which the sign reversal of the Hall coefficient has been observed.<sup>8,9,11-14</sup> In this Rapid Communication we present the results on  $\text{Cu}_x\text{Zr}_{1-x}$  alloys and show that there are several important changes in electronic structure of this alloy between 80–85 at. % Cu. In the middle of the glass-forming range ( $\sim 20$ –75 at. % Cu) the Fermi level,  $E_F$ , is situated at Zr 4*d* subband and there is practically no ordering in disordered alloys. At high Cu concentrations ( $x \geq 80$  at. %)  $E_F$  shifts to the very edge of Zr 4*d* resonance so that the *s* states dominate the electron transport; the local chemical ordering increases and  $N(E_F)$  gets dramatically reduced. Moreover, we observe the change of sign of the energy derivative of the self-energy which is directly associated with the sign reversal of the Hall coefficient.

To simulate  $\text{Cu}_x\text{Zr}_{1-x}$  disordered alloys we have used the Bethe lattice in which every atom is situated in a fcc environment. Using a standard tight-binding Hamiltonian including *s-d* hybridization we calculated configurational entropy in the pair approximation with two independent parameters: concentration,  $x$ , and short-range order param-

eter,  $\sigma$ . The details of our calculations as well as the justification for our choice of parameters (that are presented in Table I) are discussed at length elsewhere.<sup>5</sup> The values taken for the widths of the *s* band,  $W_s^{\text{Cu}}$  and  $W_s^{\text{Zr}}$ , were evaluated from Harrison's expression<sup>4</sup> and those for the *d* band,  $W_d^{\text{Cu}}$  and  $W_d^{\text{Zr}}$ , from Ref. 24;  $E_s^{\text{Cu}}$ ,  $E_d^{\text{Cu}}$ ,  $E_s^{\text{Zr}}$ , and  $E_d^{\text{Zr}}$ , the atomic site energies, were taken from tables of Ref. 25, and they were recalculated for transition-metal atom with  $d_s^{n+1}$  configuration.<sup>26</sup> The last four parameters in Table I, e.g.,  $U_{dd}$ ,  $U_{ss}$ ,  $U_{sd}$ , and  $V$  represent the Coulomb interaction between electrons of different bands (*s* or *d*) and ion-ion interaction correspondingly; they have been used in the auto-coherent charge-transfer model developed by Brouers, Holzley, and Franz<sup>3</sup> to calculate the charge transfer in our alloys. In that model the intersite interaction is limited to the nearest-neighbor atoms. Previous studies<sup>1</sup> have shown that this approximation, when applied to disordered systems, gives a very realistic description of electronic structure of liquid or amorphous alloys.<sup>7</sup>

In Fig. 1 we present our results on total DOS for different concentrations ( $0.20 \leq x \leq 0.75$ ) of  $\text{Cu}_x\text{Zr}_{1-x}$ . All curves were obtained for  $\sigma = 0.0$  which corresponds to a completely disordered system. We note that our calculated DOS at  $E_F$  are in accordance with experimental measurements of Ref. 27. We also note that the form of the total or partial DOS, the position of the Fermi level,  $E_F$ , and  $N(E_F)$  are very similar to those obtained recently by Ching, Sang, and Jasual.<sup>2</sup> They also studied a model structure of  $\text{Cu}_x\text{Zr}_{1-x}$  glasses and used a first-principles orthogonalized linear combination of atomic orbitals in their calculations (for details, see Ref. 2). Furthermore, the position of the *d*-band maximum of Cu with respect to the Fermi level (see  $x = 0.33$  and  $x = 0.66$  in Fig. 1) is fully in accordance with experimental ultraviolet-photoemission-spectroscopy measurements of Oelhafen, Hauser, and Güntherodt.<sup>28</sup> Moreover, our analysis indicates that the charge transfer is almost negligible in the whole range of concentrations (0.06 in  $\text{Cu}_{25}\text{Zr}_{75}$  and 0.11 in  $\text{Cu}_{75}\text{Zr}_{25}$ ) and it is always from Zr to Cu.

TABLE I. Model parameters of our calculation (in eV).

$W_s^{\text{Cu}}$	$W_d^{\text{Cu}}$	$E_s^{\text{Cu}}$	$E_d^{\text{Cu}}$	$W_s^{\text{Zr}}$	$W_d^{\text{Zr}}$	$E_s^{\text{Zr}}$	$E_d^{\text{Zr}}$	$U_{dd}$	$U_{ss}$	$U_{sd}$	$V$
17.62	3.06	-0.62	-2.54	11.64	8.60	1.63	2.54	1.6	0.5	0.75	0.25

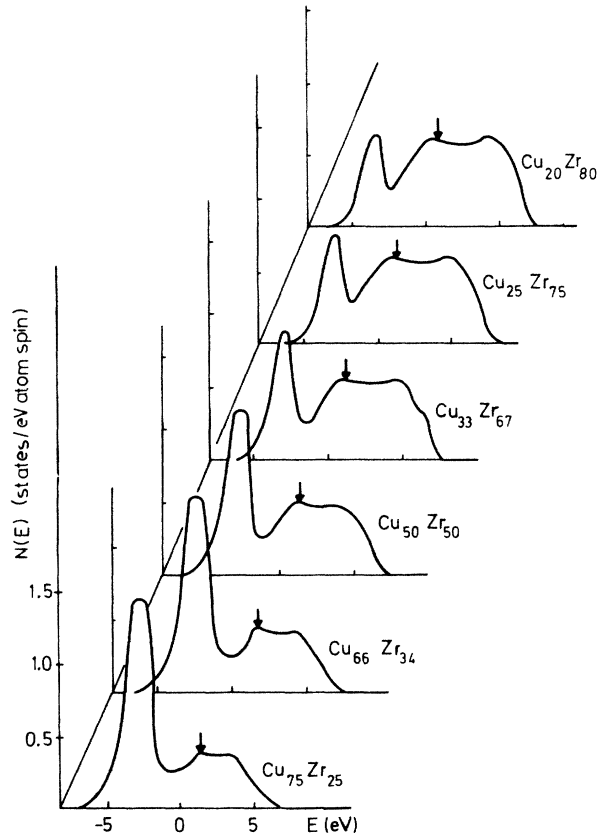


FIG. 1. Calculated total density of states (DOS) for different concentrations,  $x$  ( $0.25 < x < 0.75$ ) of  $\text{Cu}_x\text{Zr}_{1-x}$  amorphous alloys.

Turning now to the very edge of the glass-forming range, e.g., the Cu-rich end, we present in Fig. 2 partial DOS (and total DOS as an inset) of  $\text{Cu}_{75}\text{Zr}_{25}$  amorphous alloy. We point out that  $E_F$  is still situated at Zr  $4d$  subband as in the rest of the alloying range rich in Zr. At this concentration, the hybridization between  $s$  and  $d$  band is of importance. However, if we now increase the concentration of Cu of our model alloy by only  $\sim 10\%$  we observe several important changes in the electronic structure (see Fig. 3 as compared to Fig. 2):

(i) The position of the Fermi level,  $E_F$  has been shifted to the very edge of Zr  $4d$  resonance, so it is the  $s$  states that will dominate the transport properties (see inset and note that the partial DOS have to be multiplied by concentration in order to obtain relevant “total” contributions of  $s$  or  $d$  states, respectively).

(ii) The local-order parameter increased to its minimal value:  $\sigma = -0.17$  at 85% as compared with  $\sigma \sim 0.0$  at 75% Cu and the rest of glass-forming range.

(iii) The total DOS is abruptly reduced: 0.22-states/eV atom spin at 85% as compared with 0.40-states/eV atom spin at 75% Cu.

We now turn to the sign reversal of the Hall coefficient. The sign reversal of the Hall conductivity as a function of concentration can be interpreted by a skew-scattering model for  $3d$  transition-metal alloys<sup>29</sup> like  $\text{Ni}_x\text{Fe}_{1-x}$ , for example. However, we believe that model does not give a correct physical picture in paramagnetic glassy alloys like  $\text{Cu}_x\text{Zr}_{1-x}$  or Zr-rich  $\text{Ni}_x\text{Zr}_{1-x}$ . In those alloys  $E_F$  is always found on

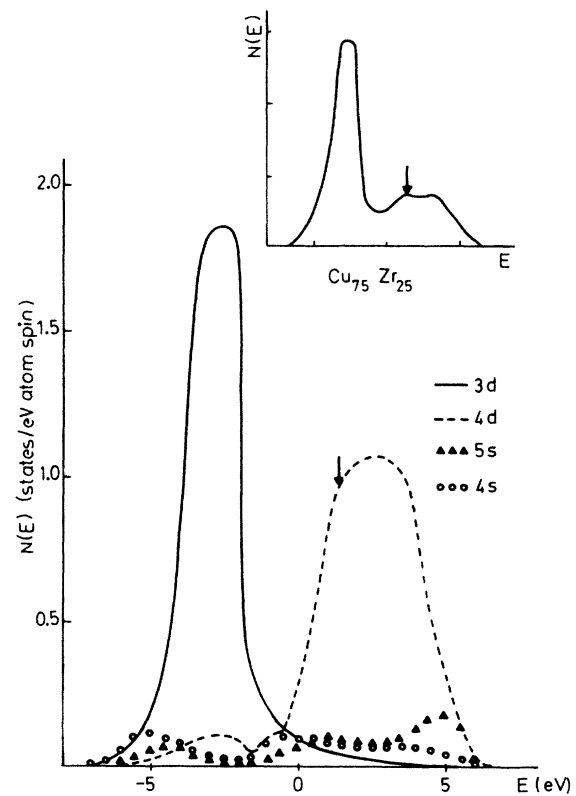


FIG. 2. Partial DOS and total DOS (in the inset) of  $\text{Cu}_{75}\text{Zr}_{25}$  amorphous alloy.

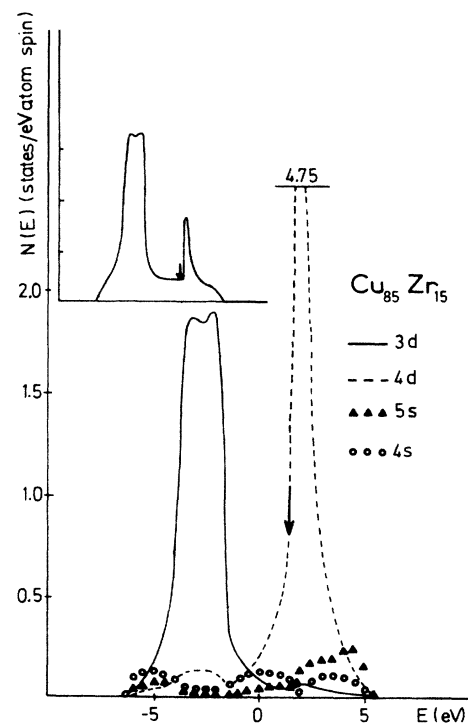


FIG. 3. Partial DOS and total DOS (in the inset) for amorphous  $\text{Cu}_{85}\text{Zr}_{15}$ .

TABLE II. Variation of sign of  $T$  and thus of  $R_H$ , across the compositional range.

$x$	0.85	0.75	0.66	0.50	0.33	0.25	0.20
$T$	3.452	-0.722	-0.865	-0.961	-1.047	-0.971	-1.062

the top of the  $4d$  band of Zr that is half filled and there is no spontaneous magnetic moment as is required by the skew-scattering model of Ref. 29. On the other hand, Morgan and co-workers have suggested that if group velocity is defined by the slope of the  $E$ - $k$  dispersion relation, then the negative value in the middle of the  $d$  band provides an explanation for positive Hall coefficients.<sup>19,21</sup> These ideas were considered somewhat controversial and Bose, Ballentine, and Hammerberg gave a different interpretation of the calculated spectral function.<sup>22</sup> However, in a recent paper, Howson and Morgan<sup>20</sup> put their ideas on a much firmer footing by taking into account the strong "damping."<sup>20</sup> It is not our intention here to discuss the complex intricacies of the theory of positive Hall coefficient in disordered medium. Rather we should explore indirect consequences of our calculations of electronic structure for the Hall coefficient by assuming that (i) the sign of the Hall coefficient depends on the sign of the Fermi velocity, and (ii) the sign of the Fermi velocity is that of the expression,

$$T = 1 - \sigma_{sd}^2 \frac{\partial}{\partial E} [\text{Re}G_d(z)]_{E=E_F} \quad (1)$$

This expression follows from our work on the  $s$ - $d$  hybridization effect in disordered system.<sup>6</sup>  $\sigma_{sd}^2$  in the second moment of the  $s$ - $d$  hybridization Hamiltonian on an  $s$  orbital and  $\text{Re}G_d(z)$  is the real part of the Green's function of the  $d$  band.<sup>6</sup> Here we take that  $G_d(z)|_{E_F} \approx G_d^{Zr}(z)|_{E_F}$ . This simplification follows from our results on partial DOS at  $E_F$  presented in Figs. 1-3 as well as from experimental studies of Ref. 28. As can be seen from Table II the sign of  $T$  and, consequently, of the Hall coefficient  $R_H$  changes at 85 at. % Cu; hence, we can distinguish two situations: (a) For  $x < 0.85$ , the sign of the Hall coefficient is positive as observed experimentally. We note from Fig. 4(a), the sign of energy derivative of the self-energy [second half of the expression (1)] is also positive; (b) for  $x > 0.85$ ,  $R_H$  and energy derivative of the self-energy are negative [see Fig. 4(b)].

These results show that with the assumption that the Fermi velocity represents the link between energy derivative of the self-energy and the sign of the Hall coefficient, one can obtain good agreement with the change of sign observed experimentally.<sup>11-13</sup> Moreover, this analysis can be extended

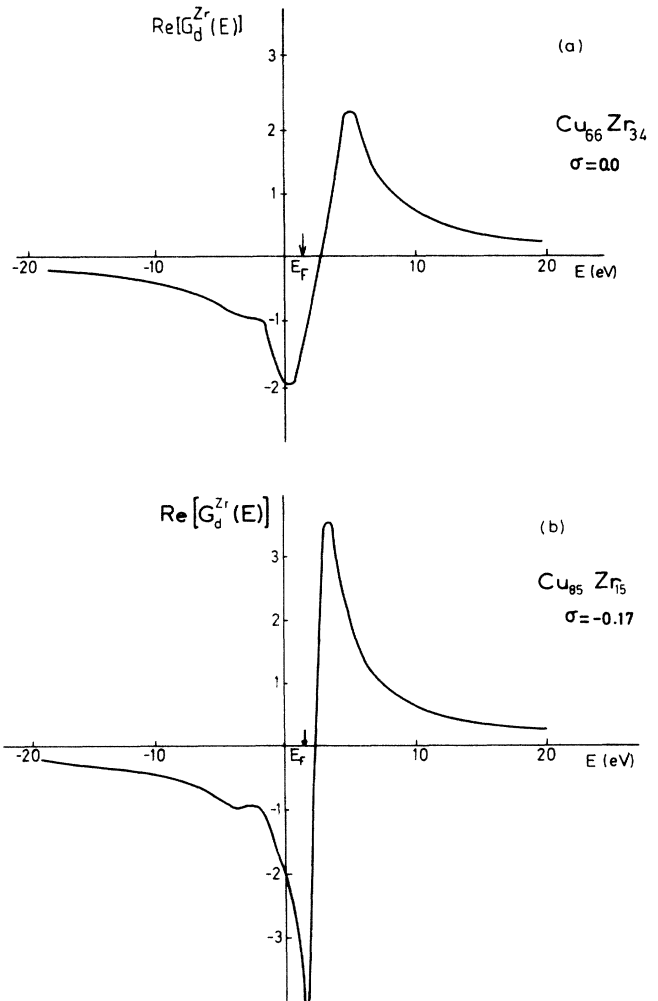


FIG. 4. Real part of the Green's function of Zr  $d$  band as a function of energy for (a)  $\text{Cu}_{66}\text{Zr}_{34}$  amorphous alloy and (b)  $\text{Cu}_{85}\text{Zr}_{15}$  amorphous alloy.

to  $\text{Cu}_x\text{Ti}_{1-x}$  and  $\text{Cu}_x\text{Hf}_{1-x}$  alloy systems<sup>9,13</sup> where again we obtain good agreement with the experimental measurements.<sup>9</sup> These results encourage us to extend our studies to the problem of the magnitude of  $R_H$ . This work is now in progress and will be presented in the near future.<sup>30</sup>

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