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Tunneling states in metallic glasses: Model structures for $Ni_{80}P_{20}$ and $Cu_{33}Zr_{67}$

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A computer model based on the analogy between local environments in the crystalline and amorphous states is presented and used to generate and relax structures which simulate two typical metallic glasses, namely $Ni_{80}P_{20}$ and $Cu_{33}Zr_{67}$. It is found that this model gives a physically realistic picture of the systems examined; in particular, the short-range order is properly described, yielding good agreement between calculated and measured coordination numbers. The structures are then analyzed in terms of single-atom tunneling taking place between two metastable minimum-energy positions. The probability of occurrence of these "two-level systems" is shown to be strongly correlated with the degree of relaxation and thus with the density. Moreover, they are seen to be associated with voids in the structure, which disappear upon relaxation. It is therefore proposed that the relaxation procedure is analogous to the physical process of annealing metallic glasses below their glass transition temperatures. Hence, it is concluded that a reduction of the various low-temperature anomalies in these materials should result from the annealing process.

I. INTRODUCTION

As reviewed in a recent article,[1] the anomalous low-temperature properties of metallic glasses find a natural explanation in terms of so-called two-level systems (TLS's), first introduced by Anderson *et al.*[2] and Phillips[3] to describe the corresponding properties of insulating glasses. Such systems form a simple representation of the tunneling motion of atoms or groups of atoms between two (or more) possible positions of local equilibrium, so that the "two levels" are the lowest levels of an equivalent anharmonic oscillator.

The success of the TLS model has been that it is sufficiently general to be applicable to a wide variety of materials. On the other hand, the generality of the model means that it does not specify the microscopic nature of the TLS's and so it cannot provide a first-principles procedure for calculating low-temperature properties of glasses. To complement it, there have been several attempts to identify potential TLS's in insulating glasses; some of these are referred to in the review article by Hunklinger and Arnold,[4] but none of them have been particularly successful. The difficulty is to identify the atoms or groups of atoms which can tunnel; the details of the tunneling motion remain obscure.

A more productive approach was pioneered by Smith[5] who used a computer model of the structure of a tetrahedrally bonded glass to identify TLS's. In this model, the Monte Carlo dynamics were necessarily limited to the motion of individual atoms and therefore, *a priori,* the tunneling motion was performed by small adjustments to the bonds attached to particular atoms. Despite this simplifying feature, the densities of the TLS's were of the correct order of magnitude to describe the low-temperature data suggesting, perhaps, that single-atom tunneling is a good approximation to the real situation.

A corresponding calculation was carried out by Banville and Harris[6] for a simple model of a monoatomic metallic glass in which the atoms interacted via a simple Lennard-Jones 6-12 potential. Using a conjugate gradient algorithm[7] for the motion of single atoms, their structure was relaxed so as to lower its potential energy and then searched to identify those atoms capable of tunneling motion. It was found that the possibility of tunneling was linked to the existence of voids in the structure and, correspondingly, that by eliminating the voids, relaxation of the structure reduced the number of TLS's relevant to low-temperature properties.

The present article is a development of this work. Rather than using an unrealistic model of a monoatomic glass, it develops realistic structural models of a typical metal-metalloid glass (Ni-P) and a typical metal-metal glass (Cu-Zr). Next, the two models are analyzed both before and after relaxation, to identify atoms capable of tunneling. An attempt is then made to relate to experimental data.

Thus we describe, in Sec. II, the model we have used to simulate the structures of $Ni_{80}P_{20}$ and $Cu_{33}Zr_{67}$, which takes into account the role played by short-range order in these materials. The results obtained with this model are then presented and compared with experimental data: radial distribution functions (RDF's), density, and coordination numbers. In Sec. III, the structures are searched for tunneling states; again, our analysis displays the link between TLS's and voids in the structures and allows us to draw a parallel between the relaxation procedure and the physical process of annealing. In Sec. IV, we give some general discussion and present some tentative conclusions.

II. STRUCTURE

A. General aspects of the model

The amorphous structures in the present calculation were computer-simulated using a generalization to binary systems of Bennett's dense random packing of hard spheres (DRPHS) global algorithm.[8] Although the method has been used with some success by other authors,[9–12] there are still unresolved problems, in particular with the description of short-range order (SRO), for which no model has yet given a realistic picture. In our work we have attempted to provide a satisfactory solution to these problems.

Our model is based on the analogy between local environments in crystalline and amorphous phases. Recent measurements of iron hyperfine field distributions in amorphous Fe-B alloys[13,14] have shown the presence of a strongly correlated local order which can be described, in a-$Fe_{75}B_{25}$, by a transposition of the chemical SRO found in the Fe_3B intermetallic compounds. Moreover, a-$Fe_{75}B_{25}$ transforms into Fe_3B upon crystallization[15] while a-$Cu_{33}Zr_{67}$ crystallizes into body-centered tetragonal $CuZr_2$ by a polymorphous transformation.[16] In light of these results, it seemed natural to describe the short-range aspects of the glassy structure as corresponding to a locally distorted quasicrystalline state, and this therefore lead us to a realistic choice of interatomic potentials, which were such that the desired SRO was properly reproduced; this choice will be fully discussed later. In practice, the SRO could be conveniently quantified by coordination numbers.

Once the structure and realistic potentials had been obtained, we proceeded with the structural relaxation, which is known to improve the agreement with the experimentally determined RDF's.[17–19] The relaxation was performed using a conjugate gradient method[7] (also used for the detection of TLS's), in which each atom of the cluster was given a small displacement proportional to and in the direction of the total force exerted on it by its neighbors; this procedure was repeated until the energy underwent sufficiently small variations from one step to another. In order to save on computer time, summations were truncated so as to include only those atoms lying within a sphere of radius r_t around a given site. Instabilities which might have resulted from this truncation were avoided by adding corrective terms, as suggested by Boudreaux and Gregor,[20] to insure that the potential and its derivative vanished at r_t. The potentials were chosen to be of the pairwise Lennard-Jones type, and hence were of the form

$$\phi_{ij}^{t}(r)=4\epsilon_{ij}[(\sigma_{ij}/r)^{12}-(\sigma_{ij}/r)^{6}]+a_{ij}+b_{ij}r/\sigma_{ij} ,$$

where the subscripts i and j refer to the atomic species.

The structures were analyzed by calculating RDF's, coordination numbers, and density. The RDF's were evaluated by computing all of the interatomic distances for the atoms lying within a sphere of given radius from the center; statistics were improved by weighting each interatomic distance with the inverse of the probability of finding that distance in a finite sphere.[21] The total RDF was then obtained as a weighted sum of the individual contributions.[22] Finally, coordination numbers were computed directly from the RDF's by calculating the areas under their first peak up to the first minimum.

B. Specific aspects of the model

In our first calculation, we chose to simulate a $Ni_{80}P_{20}$ alloy as a typical example of a transition-metal–metalloid (T-M) glass. In the crystalline state, such alloys have been systematically studied by Rundqvist[23] (phosphides) and Aronsson[24] (borides and silicides). In particular, in those alloys containing less than 33 at. % metalloid (corresponding more or less to the glass-forming range), they observe a complete absence of *M*-*M* close contacts; the structures can be conveniently described as assemblies of coordination polyhedra (tetrakaidecahedra) where the *M* atoms, which are nonconnected (i.e., isolated) occupy the centers of the triangular prismatic holes and are surrounded by 9 *T* atoms at the corners of the polyhedron. Moreover, it was shown[23] that these structures could be very satisfactorily represented by a model based only on geometrical packing of "hard-sphere" atoms. Although this model does not give any indication concerning the nature of the chemical bond, it does lead to the observation (see Aronsson[24]) that the interaction may be of greater importance for the cohesion of these alloys than was first believed.

Gaskell[25] has recognized the relevance of the crystalline state for modeling the amorphous structure of such alloys by noting the remarkable persistence of the coordination polyhedra in the crystalline phase. A well-defined coordination being an almost universal feature of glassy metals, he concludes that these polyhedra should also represent the dominant motif in the amorphous state of such alloys. The amorphous structure can therefore be modeled in analogy with the crystalline state, by assuming that the local environment is solely dictated by geometrical considerations, so that there are no directional effects. This assumption justifies our use of two-body potentials and does not support Jansen *et al.*'s suggestion of many-body forces.[26] However, we have found the geometrical model[23] too restrictive to account for observed interatomic distances in *a*-*T*-*M* alloys, showing, as could be expected, that the hard-sphere model is unrealistic. Thus, the amorphous structure should be characterized by interatomic distances instead of sphere diameters or the packing fraction which are arbitrarily defined.

Since the structure is fully determined by the potentials through the relaxation process, the local environment is dictated by the relative strengths of the potentials' attractive tails and, therefore, the *M*-*M* interaction requires special consideration. Since, as we have seen, the *M* atoms occupy holes in the metallic matrix and since they can never be in close contact, the equilibrium distance for this interaction is not defined. It should not, therefore, be specified *a priori* but rather should be a function of the other interactions. In other words, the attractive part of the *M*-*M* potential should be weak with respect to the others (ideally, we could use a zero strength potential). In any case, the results should be insensitive to the choice of $\phi^t_{M\text{-}M}$, provided that it is weak.

An unrelaxed cluster simulating $Ni_{80}P_{20}$ was generated as detailed earlier except that, following Sadoc *et al.*,[9] a structural constraint prohibiting the existence of *P*-*P* near-neighbor pairs was introduced. The parameters used in our calculations are listed in Table I(a). The equilibrium distances d_{ij} were chosen to reproduce the experimental data[22] (except for $d_{P\text{-}P}$ which is discussed below), but the relative strengths of the potentials' attractive tails are difficult to determine. According to Gilman,[27] who studied the structure of ferrous eutectic liquids, there is evidence in the glasses derived from these liquids that the *T* atoms strongly interact with the *M* atoms. This hypothesis is also

TABLE I. Equilibrium distances, relative potential strengths, and truncated Lennard-Jones potentials parameters for the structures studied. (a) $Ni_{80}P_{20}$; unit of distance l_0 is $d_{\text{Ni-Ni}} = 2.55$ Å and energies are measured in units of $E_0 = \epsilon^0_{\text{Ni-P}}$. (b) $Cu_{33}Zr_{67}$; unit of distance l_0 is $d_{\text{Cu-Zr}} = 2.71$ Å and energies are measured in units of $E_0 = \epsilon^0_{\text{Cu-Zr}}$. Actual values of E_0 are discussed in Sec. III.

	(a) $Ni_{80}P_{20}$				(b) $Cu_{33}Zr_{67}$				
	Ni-Ni	Ni-P	P-P (1)	P-P (2)	Cu-Cu (1)	Cu-Cu (2)	Cu-Zr	Zr-Zr (1)	Zr-Zr (2)
$d(l_0)$	1.0	0.867	1.35	1.45	0.937	0.937	1.0	1.151	1.151
$\epsilon^0(E_0)$	0.5	1.0	10^{-3}	10^{-6}	1.0	0.5	1.0	1.0	0.5
$\sigma(l_0)$	0.883	0.770	1.133	1.184	0.830	0.830	0.883	1.002	1.002
$\epsilon(E_0)$	0.938	1.334	0.041	0.001	1.153	0.776	1.876	3.982	1.991
$a(E_0)$	1.007	0.659	0.141	0.004	1.180	0.590	2.013	8.277	4.139
$b(E_0)$	−0.505	−0.289	−0.088	−0.003	−0.557	−0.279	−1.009	−4.668	−2.334

supported by the persistence of the coordination polyhedron in the crystalline compounds, as described above. Thus, we chose (somewhat arbitrarily) the T-M interaction to be twice as strong as the T-T one. As for the M-M interaction, it was stressed earlier that it should have no significant effect on the structure as long as it is much weaker than the other two. To verify this hypothesis, two relaxation calculations were performed, in which the relative strength of $\phi^t_{P\text{-}P}$ and the equilibrium distance $d_{P\text{-}P}$ were varied. In Table I(a), the ϵ^0_{ij}'s designate the relative strengths of the potentials while the other quantities define the truncated Lennard-Jones potentials.

In our second calculation, a metal-metal amorphous alloy, namely $Cu_{33}Zr_{67}$, was modeled. This particular alloy was chosen because it is being extensively studied in this laboratory and because its crystallization process is fairly simple;[16] it transforms, upon annealing, into c-$CuZr_2$, a body-centered tetragonal system.[28] The modeling of this structure is based on the same principles as that of $Ni_{80}P_{20}$; no directional effects are present and the structure is fully determined by the relative strengths of the potentials. The SRO, however, is very different here: first, no tendency to avoid nearest-neighbor contact is observed[29] which, in principle, makes the structure much simpler to model; second, the coordination numbers vary more or less linearly with composition,[30,31] are almost independent of the species under consideration, and are of the order of 12, suggesting a similarity with the fcc coordination.[29,32,33] These features may actually be viewed as an absence of SRO, i.e., to a first approximation, the alloy consists of a random mixture of its constituent elements. Hence, it may be regarded as an ideal amorphous structure, indicating that it could well be satisfactorily represented by the binary DRPHS model as originally formulated.[34] However, to a second approximation, experimental evidence seems to support the existence of a preferred Zr-Cu interaction. In particular, in the similar Zr-T alloys (T = Fe, Co, Ni, and Pd), the contribution of the Zr-T partial RDF to the first peak of the total RDF is sharper than that of the other two partial RDF's.[29,35] Moreover, the equilibrium distance $d_{\text{Zr-Cu}}$ is less than the sum of Goldschmidt radii,[31] while these radii represent fairly well $d_{\text{Cu-Cu}}$ and $d_{\text{Zr-Zr}}$. Finally, thermodynamic data show a negative heat of mixing[36,37] which again is attributed to the preferred atomic bonding of unlike atom pairs. However, it seems, in contrast with the situation in T-M glasses, that no interaction is strong enough to prohibit any constituent elements from close contacts.

An amorphous structure was therefore constructed using our generalized version of Bennett's algorithm[8] without constraint; the parameters used are listed in Table I(b). The equilibrium distances were again chosen to reproduce the experimental data; two sets of measurements for Cu_xZr_{100-x} alloys are available: extended x-ray absorption fine structure (EXAFS) measurements[31] and x-ray diffraction experiments.[29] In the case of EXAFS, it is found that the equilibrium distances $d_{\text{Cu-Zr}}$ and $d_{\text{Zr-Zr}}$ increase with increasing x, while they decrease in the case of x-ray diffraction. Taking into account the experimental errors, we simply assumed that the distances were essentially constant with x and used the average values in our calculations. Concerning the relative interaction strengths ϵ^0_{ij}'s, two calculations were again carried out. For the reasons detailed above, we assumed, in a first approximation, that all three interactions were of the same strength and, in a second approximation, we chose the Zr-Cu interaction to be arbitrarily twice as strong as the other two.

C. Results and discussion

For each substance ($Ni_{80}P_{20}$ and $Cu_{33}Zr_{67}$) a cluster containing 1000 atoms was generated and relaxed until the relative changes in energy became sufficiently small. (In practice, 600 steps were employed.) It must be pointed out that no minimum of energy was ever obtained. We attributed this to either incomplete convergence towards a real minimum of energy (a numerical problem) or to the absence of any metastable energy configuration (perhaps representing a real aspect of the glassy state). At present, we have no means of distinguishing between those two alternatives.

In $Ni_{80}P_{20}$, no differences were found between the two relaxation calculations, confirming the relative unimportance of $\phi^t_{P\text{-}P}$. RDF's were calculated for both the unrelaxed and relaxed structures and are displayed in Fig. 1, along with the experimentally determined one; Table II(a) lists the exact values (within error) of the relative positions of the peaks. The second peak of the RDF exhibits an interesting feature of our calculation. It is well known that the DRPHS model does not properly account for the split second peak in metallic glasses in giving the wrong weighting for the two subpeaks. As shown in Fig. 1(a), the same prob-

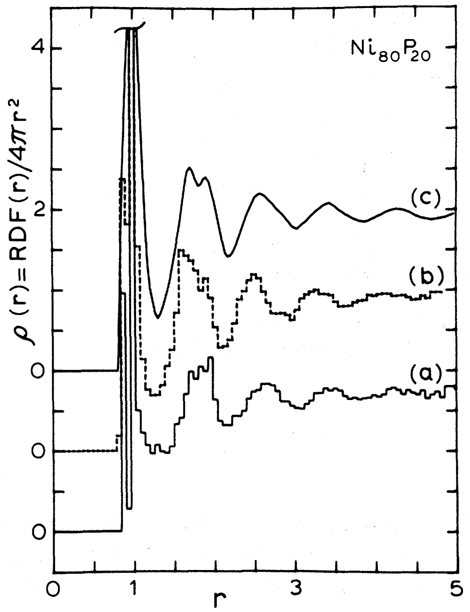

FIG. 1. Comparison between calculated and experimentally obtained pair distribution functions $\rho(r)$ [$=\mathrm{RDF}(r)/4\pi r^2$] for $Ni_{80}P_{20}$: (a) unrelaxed, (b) relaxed, and (c) experimental (Ref. 22); zeroes are displaced.

lem occurs here, in the unrelaxed structure; however, Fig. 1(b) shows that the relaxation process has restored the proper weighting, bringing further support to our choice of potentials. Finally, it is worth noting that the details of the RDF's are enhanced by the relaxation; this point will be discussed below.

The density was evaluated to increase from 7.43 to 8.24 g/cm^3 during the relaxation process; the latter value compares favorably with the experimental[22] value of 8.00 g/cm^3.

As we have pointed out earlier, the SRO can be quantitatively described by the coordination numbers, which should be properly accounted for by any realistic model. Determining which atoms are to be considered as nearest neighbors is, however, not a simple problem, in contrast with the situation in a crystalline material. For the purpose of this calculation, it is necessary to define a nearest-neighbor distance for each pair of atomic species r_{ij}^{nn} within which all atoms j will be counted as nearest neighbors of a given atom i. The effect of varying these distances on the partial coordination numbers n_{ij} was examined and more or less linear variations were observed. To be consistent with the usual procedure,[22] r_{ij}^{nn} was set equal to the first minimum following the first peak of the corresponding RDF in the relaxed state. Partial and total coordination numbers as well as nearest-neighbor distances are listed in Table III along with experimental data.

A similar calculation was attempted by Boudreaux *et al.*;[12] and although they did, to some extent, vary r_{ij}^{nn}, they chose in an apparently *ad hoc* manner to fix the nearest-neighbor distances as the "sphere-touching" distances plus 10%. (Actually, the range of values examined—5 to 13 % more than the sphere-touching distances—is much too low in comparison with values typically observed—25 to 30 %). In the light of our model, it is clear that this procedure is meaningless in the case of *M-M* near-neighbor pairs since we actually want to show that these atoms can never touch, so that the expression sphere-touching does not apply.

TABLE II. Comparison between the relative positions of the peaks of the calculated and experimentally determined RDF's; r_{nm} designates the mth subpeak of the nth peak. (a) $Ni_{80}P_{20}$; the first peak is not split while the second has two subpeaks (see Fig. 1). (b) $Cu_{33}Zr_{67}$; the first two peaks are not split as such, but exhibit distinct shoulders (see Fig. 2).

	r_{12}/r_{11}	r_{21}/r_{11}	r_{22}/r_{11}	r_{23}/r_{11}	r_{31}/r_{11}
(a) $Ni_{80}P_{20}$					
Unrelaxed		1.70±0.05	1.95±0.05		2.65±0.1
Relaxed		1.65±0.05	1.90±0.05		2.50±0.05
Experimental[a]		1.73	1.91		2.5
(b) $Cu_{33}Zr_{67}$					
Unrelaxed	1.15±0.05	1.75±0.05	2.00±0.05		2.9±0.1
Relaxed	1.15±0.05	1.65±0.1	1.85±0.05	2.1±0.1	2.7±0.1
Experimental[b]	1.15±0.05	1.7±0.1	1.9±0.1	2.1±0.1	2.6±0.1

[a] See Ref. 22.

[b] See Ref. 29.

TABLE III. Nearest-neighbor distances and partial coordination numbers in $Ni_{80}P_{20}$, along with experimental data ($n_i=\sum_j n_{ij}$). Estimated error on all coordination numbers: ± 0.5.

	$n_{\text{Ni-Ni}}$	$n_{\text{Ni-P}}$	$n_{\text{P-Ni}}$	$n_{\text{P-P}}$	n_{Ni}	n_{P}
r^{nn}	1.30	1.10	1.10	$<1.2^{a}$		
Unrelaxed	10.6	2.1	8.2	0	12.7	8.2
Relaxed	11.1	2.3	9.0	0	13.4	9.0
Experimental	$\sim 10.5^{b}$	$\sim 2.2^{b}$	$\sim 8.1^{c}$	$<<1^{d}$	13.0^{e}	$\sim 8.1^{f}$

[a] No first-neighbor peak was found in $\rho_{\text{P-P}}$ and $n_{\text{P-P}}\simeq 0$ for all $r_{\text{P-P}}\leq 1.2$.

[b] Average of values obtained for $Fe_{75}B_{25}$ (Ref. 50) and $Fe_{75}P_{25}$ (Refs. 50 and 51).

[c] Average of values obtained for $Fe_{75}B_{25}$ (Ref. 50), $Fe_{75}P_{25}$ (Ref. 50 and 51), and Pd-Ge (Ref. 52).

[d] Estimated values for Pd-Ge (Ref. 52).

[e] Average of values (Refs. 22, 53, and 54) obtained for Ni_xP_{100-x}, $74\leq x\leq 85$.

[f] $n_{\text{P}}=n_{\text{P-Ni}}+n_{\text{P-P}}\simeq n_{\text{P-Ni}}$; see d.

A very similar analysis was performed on our model structure for $Cu_{33}Zr_{67}$. It was found that the first relaxation calculation (with all interatomic potentials equal) could not, after 200 iterations, properly account for the experimentally observed RDF; the contribution of Zr-Zr pairs to the first peak was clearly overestimated and thus, this approach was abandoned. The second calculation, in which the Zr-Cu interaction is preferred, did, however, give a reasonable description of the RDF; the relaxation procedure restored the proper weighting of the subpeaks of the first peak, as it did for the second peak of $Ni_{80}P_{20}$. This is illustrated in Fig. 2, where we have also plotted the experimentally obtained RDF for comparison; Table II(b) lists the exact positions of the peaks. Another interesting feature of our RDF is, as exhibited in Fig. 2, the almost complete lack of structure after the second near-neighbor peak (the fifth peak was resolved in $Ni_{80}P_{20}$); we believe that this reflects the lack of SRO in these materials.

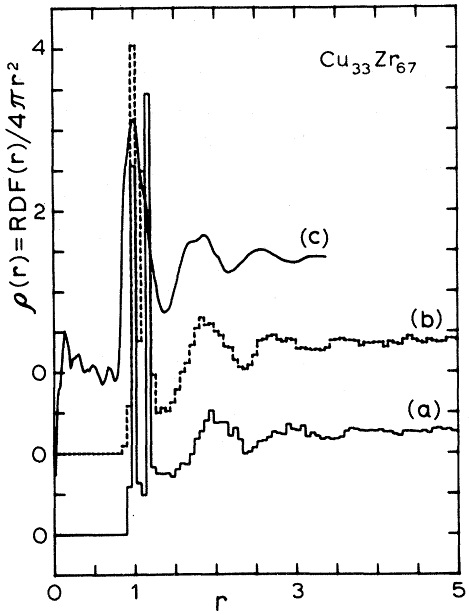

FIG. 2. Comparison between calculated and experimentally obtained pair distribution functions $\rho(r)$ for $Cu_{33}Zr_{67}$: (a) unrelaxed, (b) relaxed, and (c) experimental (Ref. 29) (for $Cu_{35}Zr_{65}$); zeroes are displaced. In the model structure Cu-Zr and Zr-Zr contribution to the first peak are resolvable (Cu-Cu contribution is very small), while in the experimentally determined RDF, only a shoulder is observed.

The density was again evaluated and increased, upon relaxation, from 5.83 to 6.32 g/cm^3, thus reaching a value which compares fairly well with the experimental value of 6.7 ± 0.2 g/cm^3 (obtained by linear extrapolation[29,32]). Finally, the SRO was also examined through a detailed study of coordination numbers. The results are listed in Table IV along with experimental data.

Given the relatively small size of the structures considered, we may expect errors due to statistical fluctuations to be of the order of a few per cent. For example, we have obtained a fairly good agreement between measured and calculated densities. Now, the density is inversely proportional to $\bar{r}^3$ (where $\bar{r}$ is the cluster radius[38]); hence, a variation of 3% in the density means a variation of only about 1% in $\bar{r}$, i.e., largely within the statistical error. It is also interesting to note that the calculated density for $Ni_{80}P_{20}$ is greater than the measured one, while the situation is reversed for $Cu_{33}Zr_{67}$; the observed variations may thus be viewed as a measure of the effect of statistical fluctuations.

As we have seen, through the analysis of local environments, the SRO is also well represented by

TABLE IV. Nearest-neighbor distances and partial coordination numbers in $Cu_{33}Zr_{67}$, along with experimental data (Ref. 29) (for $Cu_{35}Zr_{65}$). Estimated error on all coordination numbers: ±1.0.

	$n_{\text{Cu-Cu}}$	$n_{\text{Cu-Zr}}$	$n_{\text{Zr-Cu}}$	$n_{\text{Zr-Zr}}$	n_{Cu}	n_{Zr}
r^{nn}	1.14	1.20	1.20	1.40		
Unrelaxed	3.3	5.7	4.8	7.2	9.0	12.0
Relaxed	3.6	6.3	5.2	7.7	9.9	12.9
Experimental	4.6	7.4	4.0	7.8	12.0	11.8

our model. The relaxation restores the proper order of the subpeaks of first- and second-neighbor shells, bringing further evidence for the existence of preferred interactions. The difference in SRO's in the two systems is reflected through the corresponding RDF's; the lack of structure after the second peak in $Cu_{33}Zr_{67}$ exhibits, in contrast with $Ni_{80}P_{20}$, the lack of SRO in this material. As pointed out by Chen and Waseda,[29] the difference in the two structures may also be partly due to the weaker atomic interactions in the metal-metal system, as evidenced by the relatively low melting point of the intermetallic phases.

III. TUNNELING STATES

A. The model

As pointed out in the introduction, Smith[5] was the first to obtain a correct order-of-magnitude estimate of the density of states relevant to low-temperature anomalous properties. More recently, Banville and Harris[6] examined a monatomic DRPHS structure and found a direct correlation between the probability of tunneling and the existence of voids in the structure. Such voids are eliminated by the relaxation procedure. However, although their results are qualitatively correct, it is well known that such a DRPHS structure cannot give a realistic picture of the amorphous state and, as shown in Sec. II, chemical constraints play a dominant role in determining the structure, particularly in the case of T-M glasses. It therefore seemed desirable to carry out those TLS calculations again, but now using physically realistic models. Thus, in what follows, the unrelaxed and relaxed structures obtained in Sec. II are analyzed to identify potential candidates for tunneling.

As in the earlier work,[6] the TLS's were modeled by single atoms having access to two (or more) positions of local equilibrium, separated by energy barriers V and with energy differences ΔE between the two minima.[2] The rationale for looking at single-atom tunneling was that it is the simplest hypothesis consistent with the existence of TLS's. Other situations—tunneling by groups of atoms—were not thereby ruled out. In order to explain experimental data, one must postulate that there is a finite probability of finding both V and ΔE close to zero. Moreover, the levels which contribute to the specific heat must be separated by barriers small enough to allow tunneling to take place ($V \leq V_{\max}$), but large enough to prevent resonant tunneling from occurring.

The environment of a limited number of atoms in the center of the models before and after relaxation was examined for possible identification of tunneling states. To do this, the local environment of pairs of atoms in the structures was analyzed in detail using the procedure first suggested by Banville;[6] we assumed that those atoms which are the only common neighbor to a given pair of atoms are the most likely to give rise to tunneling states. Once those atoms have been identified, we then searched for alternate metastable minimum energy positions for the single atom in the force field of its neighbors (as defined in Sec. II); when successful, the relevant TLS parameters[2] were tabulated. Cooperative rearrangements of neighbors around the single atom undergoing tunneling were ignored, since these were not found to be significant in any interesting cases.[6,39]

B. Results and discussion

Figure 3 shows the probability distribution of TLS parameters ΔE and V (defined in the inset) for $Ni_{80}P_{20}$ before and after relaxation; results for $Cu_{33}Zr_{67}$ are very similar and need not be reproduced here. It should be stressed that statistics are rather poor so that the results are to be considered as qualitative only.

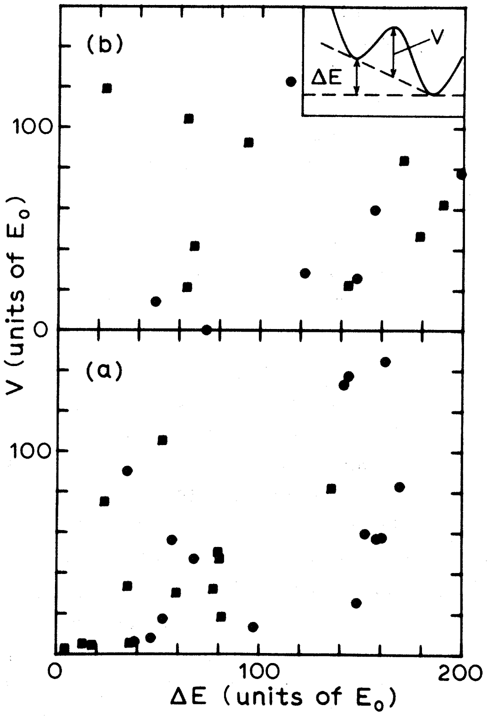

FIG. 3. Probability distribution of TLS's for the central 250 atoms of model structure for $Ni_{80}P_{20}$: (a) before relaxation and (b) after relaxation. The horizontal axis corresponds to the energy difference ΔE and the vertical one to the energy barrier V between the two wells, as indicated in the inset; energies are measured in units of E_0 (see text). Circles denote Ni tunneling states while squares denote P tunneling states. Probability distributions for $Cu_{33}Zr_{67}$ are similar and therefore need not be reproduced; in that case, Cu atoms are seen to have a greater probability of tunneling.

A rough estimate of the density of states $n(0)$ relevant to specific heat[2] can be attempted. The energy parameter can be evaluated by comparing the activation energy for the diffusion of a T atom of the $3d$ series in a bcc lattice (about 0.5 to 5.0 eV) with the corresponding values calculated with our potentials (about $50E_0$); this indicates that E_0 is in the range 0.01 to 0.1 eV. the parameter $V_{\max}$ introduced earlier is only very weakly dependent on the value of the zero-point energy, and thus on E_0, and was typically found to be of the order of 0.05 eV for Ni tunneling atoms (mass of 60 a.u.) and 0.1 eV for P tunneling atoms (mass of 30 a.u.). The density of states $n(0)$ can be obtained by extrapolating the probability distribution $n(\Delta E)\,|_{V\leq V_{\max}}$ to $\Delta E=0$. Assuming $E_0=0.01$ eV, a value we believe to be reasonable, we obtain, to within an order of magnitude, $n(0)=0.04$ states eV^{-1} atom^{-1} for the unrelaxed cluster; this quantity decreases with increasing E_0 and is reduced by two orders of magnitude when E_0 reaches 0.1 eV. Given the large error due to statistical fluctuations, our result is in qualitative agreement with the experimental value (quoted by Black[1]) of 0.05 states eV^{-1} atom^{-1}. Results for $Cu_{33}Zr_{67}$ are very similar.

To gain further insight into the structural aspects of TLS's they were thoroughly examined from a configurational point of view, either by computer plotting the nearby equipotential contours or by examining sections of their local environments. It was found that all TLS's are associated with voids in the structure, similar to vacancies in crystalline materials, and that these voids are scarcely large enough to accommodate an extra atom; this can be seen in Fig. 4, which displays a sectional view of the local environment of a typical TLS. This conclusion is in full accord with our preliminary results.[6]

Two further qualitative results deserve mention. First, the TLS probability density decreases drastically during the relaxation process (see Fig. 3), suggesting that the number of voids also decreases; again, this is in accord with our previous analysis.[6] Second is a new feature of our binary structures; it is the smaller atoms (P or Cu) which contribute most to the TLS probability density at low energies; such a result might be expected on geometrical grounds, and it is encouraging to see it emerge from the simulation.

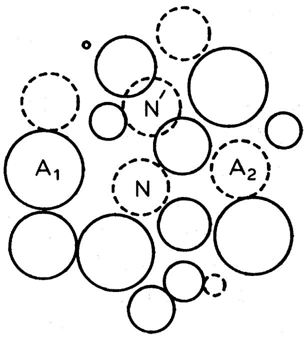

FIG. 4. Configurational analysis of a typical TLS; sectional view of its local environment. A_1 and A_2 designate the atomic pair to which N is the only common near neighbor while N' represents the alternate minimum energy position, towards which N could tunnel. Notice that N' corresponds to a void scarcely large enough to accomodate an extra atom of the same size as N. Full circles represent Ni atoms, while dotted ones represent P atoms; smaller circles represent atoms with centers above or below the plane of the diagram, defined by the centers of A_1, A_2, and N'.

IV. GENERAL DISCUSSION

One of the most significant features of the calculations reported in Sec. III is the decrease of the TLS probability density upon relaxation, as shown in Fig. 3. This effect could be regarded as an artifact of the relaxation procedure; however, as was argued in our previous work,[6] there is considerable evidence for an analogy between the relaxation process and the physical process of annealing metallic glasses below their glass transition temperatures. Some of this evidence is reviewed below.

In the first place, although the relaxation procedure qualitatively improves agreement between modeled and experimentally determined RDF's, it also enhances the details visible in the model calculation; this was established in Sec. II. Correspondingly, Egami[40] has shown, by energy-dispersive x-ray diffraction (EDXD) measurements, that the short-time annealing of a $Fe_{40}Ni_{40}P_{14}B_6$ glass leads to a similar enhancement of details. He suggests, indeed, that the effect of such annealing is to transform the structure towards a more stable inconsistent with our results.

Secondly, there is evidence in the literature that the density of the glasses themselves increases during annealing in a manner corresponding qualitatively at least to the density changes observed in our relaxation. The large total changes ($\sim 10\%$) that we observe are much larger than those seen experimentally. They are due in part to the unrealistic nature of our unrelaxed structures; however, the trend towards higher densities persists throughout the calculation. We are aware of only one documented example of experimental measurements,[41] where the observed changes were of order 2%; such a small value illustrates the difficulty of monitoring the density changes, and perhaps explains the absence of more published data. Nevertheless, the effect has been observed by other workers.[42]

Thirdly, along the same lines, there is evidence from self-diffusion measurements[43] that the effect of annealing is to remove voids from the structure. It is commonly believed that the existence of voids provides the mechanism for the almost liquidlike diffusion constants[44] in metallic glasses. Thus, the large drop (by two orders of magnitude) in the diffusion constants after annealing[43] is indicative of fewer voids remaining. In our simulation, the existence of voids is monitored by the number of observed TLS's; clearly, the number decreases during the relaxation process.

Finally, there is direct evidence in the literature that annealing reduces the number of TLS's, in accord with the relaxation results. In our previous article[6] we quoted the thermal conductivity data of Matey and Anderson,[45] now corroborated by Herlach *et al.*;[46] more recently, there have been specific-heat measurements[41] showing a factor of 2 decrease in the anomalous linear specific heat after annealing. There is as yet no data indicating the decrease in the controversial logarithmic resistivity anomaly with annealing, although reductions in the overall resistivity on annealing have been shown to be of order 1%.[47] Also still to be performed are the corresponding ultrasonic experiments.

More controversial is the observation[48] that the superconducting transition temperatures of metallic glasses drop after annealing. This suggests either significant changes in the phonon spectrum or else a coupling between TLS's and electrons which can enhance or even produce superconductivity. Some theoretical work already exists in this area;[49] our own investigations are in progress.

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