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Résumé. — La structure des alliages amorphes de terres rares avec des métaux de transition est étudiée en se basant sur la disposition aléatoire compacte de sphères atomiques.

Ce modèle semble expliquer plusieurs caractéristiques trouvées dans les mesures expérimentales sur le TbFe₂ amorphe et en particulier semble justifier le récent modèle proposé pour expliquer les propriétés magnétiques des matériaux.

Abstract. — The structure of amorphous rare-earth transition-metal compounds is discussed on the basis of the random packing of atomic spheres. This model is shown to account for several features of the experimental data on amorphous $TbFe_2$, and, in particular, is shown to provide a justification for a recent model of the magnetic properties of such materials.

1. **Introduction.** — Recent experiments by Rhyne *et al.* [1] show that the intermetallic compound $TbFe_2$ has strong magnetic properties even when prepared by sputtering [2] in a non-crystalline state. Measurements of the sputtered material show that the saturation magnetization is reduced from 4.7 μ_B/atom in the crystalline cubic Laves phase material [3] to 2.8 μ_B/atom, and that the Curie temperature is reduced from 720 K [3] to 388 K. Analysis of the elastic neutron scattering data shows no trace of structure characteristic of the crystalline material.

In a recent publication the present authors [4] proposed a model which seems to account for the magnetic properties of the sputtered material. We suggested that other rare-earth transition-metal compounds will exhibit similar properties when prepared in the non-crystalline state. Our model depends upon the assumption that the non-crystalline state of rare-earth transition-metal compounds has a topologically disordered or « amorphous » structure, of the type given by the random close packing (RCP) of atomic spheres. This structure has been shown by Cargill [5] to be consistent with experimental radial distribution functions (RDF's) for all « amorphous » metallic systems so far studied. In the present paper we discuss the RCP model in more detail and show that it is consistent with the assumptions of the model for the magnetic properties [4]. Some further discussion is then given of the possibility of induced-moment systems in the amorphous state.

2. **The Random Close Packing model.** — Previous studies of the RCP model with spheres of two different

sizes have been based in an empirical way on the ball-bearing packings of Finney [6] or the computer simulations of Bennett [7] which are both concerned with spheres of one size. We have followed Bennett's technique but have generalized it to RCP's with spheres of two different sizes with a relative concentration of 2 : 1. The ratio of radii for the spheres is taken as $\sqrt{2} : \sqrt{3}$ which is the ideal ratio for the constituent atoms in the ideal close-packed cubic Laves phase structure [8]. The RDF for the larger (terbium) atoms resulting from a calculation with 1 700 atoms is shown in figure 1, where it is compared with the RDF obtained by Rhyne [9] from the neutron diffraction data for $TbFe_2$.

At first sight agreement is disappointing, since even the first peak, at 3.24 Å, does not agree well with data. Agreement is not improved by mixing in
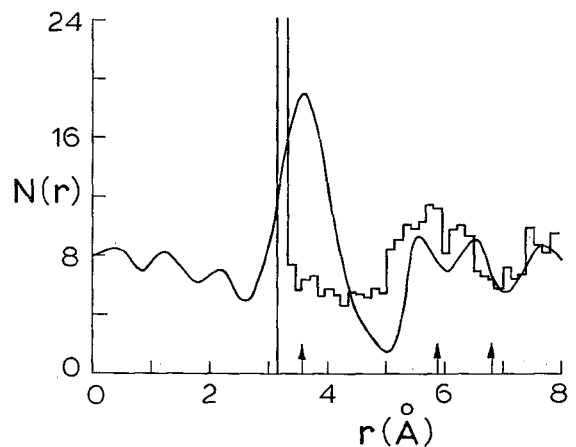

FIG. 1. — Comparison of the Tb-Tb pair correlation function with neutron scattering results of Rhyne *et al.* [9]. The arrows mark the positions of the first few peaks in the crystalline cubic Laves phase.

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the RDF for the smaller (iron) atoms, nor by including the terbium-iron or iron-terbium distribution functions. However, the split second peak seems to correspond with the second and third peaks of the data, and our third peak is also in good agreement with the data. Attempts to relate positions of peaks to geometrical configurations are displayed in figure 2 peaks. Although configurations C and F appear

A   3.24 Å   3.6 Å

B   5.9 Å   6.2 Å

C   6.5 Å   7.2 Å

D   5.25 Å   5.65 Å

E   5.4 Å   5.9 Å
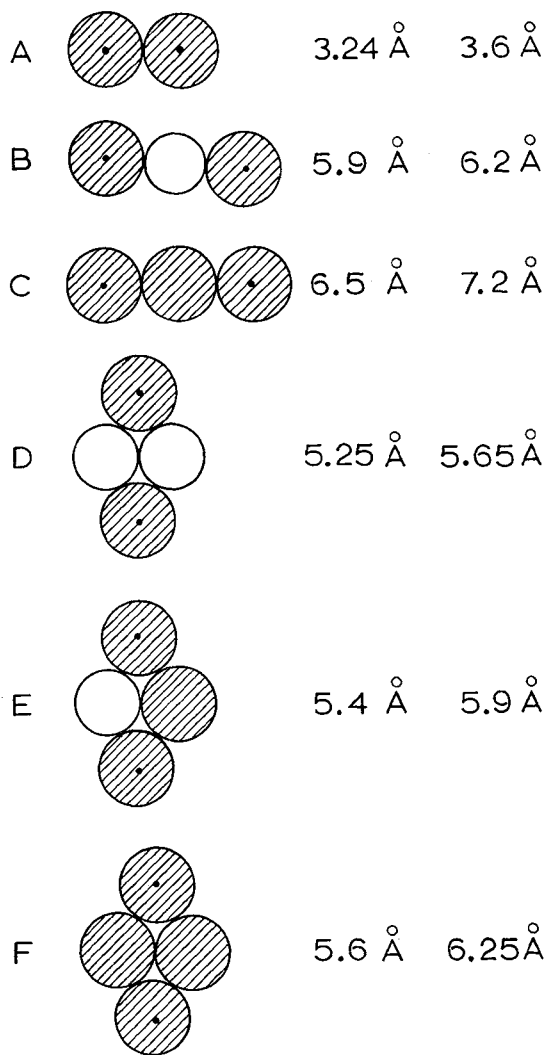
F   5.6 Å   6.25 Å

FIG. 2. — Some simple planar geometrical configurations which occur in random close packing of spheres. Shaded atoms correspond to Tb, unshaded to Fe. The numbers next to the configuration give the distance between the marked Tb centers first using $r_{Fe} = 1.32$ Å, $r_{Te} = 1.62$ Å and secondly $r_{Fe} = 1.32$ Å, $r_{Tb} = 1.8$ Å. The latter are the numbers obtained from the crystalline phase.

to correspond to the data, their statistical weights must be very low, and the correspondence must be coincidental. On the other hand, neither does the data show any correspondence to the crystalline next nearest-neighbour distances which are marked in figure 1 by arrows. Since the ratio of radii for Fe and Tb atoms is not quite the ideal one used on our calcu-

lation, the agreement which we obtain is remarkably good. Further discussion of the computer-simulated RCP structure will be given elsewhere [11], and, although the simulation is not entirely satisfactory, use of it to discuss structural aspects of the magnetic properties does seem to be appropriate.

3. Magnetic anisotropy. — The magnetic properties of the amorphous rare-earth transition-metal compounds depend, we believe, upon the nature of the crystal fields acting on the rare-earth atoms. Such crystal fields are responsible for the huge magneto-crystalline anisotropy and magnetostriction observed in the crystalline materials [12]. Calculations by Dariel et al. [13] show that in the crystalline rare-earth iron Laves compounds the crystal fields are well represented by a point charge model where the rare-earth atom sites in the cubic environment of its 12 iron nearest neighbours. We propose that, in the amorphous material, the crystal fields still exist, although, of course, they no longer have cubic symmetry.

Using our computer simulated RCP structure and the point charge model we have investigated the variation of the magnitude and orientation of the crystal field at different rare-earth sites. Although the point charge model is unlikely to be completely appropriate, we believe that its success in the crystalline materials justifies its use in the amorphous case. In any case, we are not interested primarily in absolute values, but in trends for which the point charge model is quite adequate.

We evaluate the expression

$$\Phi_i^{(l)} = Ve_i^{(l)}(\theta, \varphi) = e^2 < r^n > \sum_j \frac{Z_j}{|R_j - R_i|^{l+1}} \times$$

$$\times \sum_{m=-l}^{l} Y_m^l(\theta_j, \varphi_j) Y_m^l(\theta, \varphi)$$

for each of 467 rare-earth sites, but allowing n to take only even values. Harmonics of odd parity can cause no crystal field splitting because of time-reversal invariance [14]. Because there is no longer any cubic symmetry the most important terms are those of second order ($l = 2$), while the fourth order terms (dominant in cubic symmetry) are approximately equal to their value in the Laves phase.

We take values of the neighbouring point charges Z_j to be 2 on an iron atom and 3 on a terbium atom, and cut off the sum over neighbouring atoms at $|R_i - R_j| = 3.62$ Å which is slightly greater than the distance between two of the (larger) terbium atoms in close contact. Using values for $< r^2 >$ and $< r^4 >$ quoted and Freeman et Watson [15] we obtain average values for $\Phi^{(2)}$ and $\Phi^{(4)}$ which are 4.03×10^{-1} eV/atom and 3.23×10^{-2} eV/atom, and find that the mean-square deviation from these averages is surprisingly small — only 2 %. Thus the ratio $V^{(4)}/V^{(2)}$ is about 0.08. Thus, to a good approximation, as assumed

previously [4], the fourth order terms can be neglected in a model calculation of the magnetic properties, and the second order terms taken to have constant magnitude.

The orientations of the « local easy axes », as given by the minima of the functions $V_i^{(2)}$ at different sites i, are found to be isotropically distributed within the limitations of the calculation and show no correlation between nearby sites [11]. This confirms another assumption of our previous work [4].

4. Bulk magnetic properties.

— The RCP model thus provides a justification for the model Hamiltonian used in our earlier publication [4] which was written, for the case of a spin J_i at a position i, as

$$\mathcal{H} = - DJ_{z_i}^2 - \mathfrak{J} \sum_{i \neq j} J_i . J_j ,$$

with D an anisotropy constant and $\mathfrak{J}$ a Heisenberg nearest neighbour coupling constant. The operator J_{z_i} is defined with respect to the *local* easy axis $\hat{z}_i$ which is the direction defined by the local crystal field $V_i^{(2)}$. The introduction of a molecular field along a unique $\hat{z}$ axis permits the calculation of temperature-dependent magnetization $M(T)$ and Curie temperature T_c as a function of D and $\mathfrak{J}$ [4]. Some specimen results are shown in figure 3.

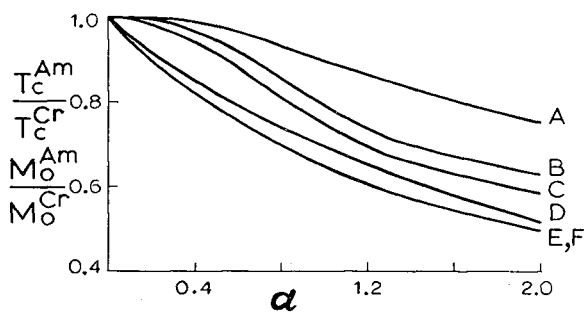

FIG. 3. — Ratio of zero temperature amorphous and crystalline magnetizations, M^{Am}/M^{Cr}, as a function of $\alpha = D/v\mathfrak{J}$, where v is the coordination number of the structure. Curve A, $J = 1$; B, $J = 2$; C, $J = 3$. Also plotted is the ratio of critical temperatures Tc^{Am}/Tc^{Cr}. Curve D, $J = 1$; E, $J = 2$; F, $J = 3$. Reproduced from Harris et al. [4].

In this figure, as in our earlier paper, the characteristics of the amorphous material are compared with a fictitious crystalline material with second order (i. e. uniaxial) anisotropy. However, since the average magnitude of $V^{(2)}$ in the amorphous material is greater than the magnitude of $V^{(4)}$ in the real crystalline material, the anisotropy energy in the amorphous material will also be correspondingly higher. Thus the reductions in magnetization and critical temperature may be even larger than was indicated by the simple model [4].

5. Possible induced moment systems.

— The treatment of an amorphous induced moment system (the singlet-singlet model) given in our previous paper [4] depends on a local symmetry that is higher than uniaxial even in the amorphous material. Thus in this respect it is incorrect. However, a uniaxial field can provide an environment for which a singlet-doublet model is appropriate. Preliminary calculations indicate that in this case the magnetization and Curie temperature are again reduced by substantial amounts, and full details will be published at a later time (ZOBIN, D. and ZUCKERMANN, M. J., to be published).

The existence of induced moment systems in the amorphous state depends very strongly on the relative magnitudes of $V_i^{(2)}$ and $V_i^{(4)}$ at each site i. If $V_i^{(2)}$ is not dominant at the majority of sites, then the detailed predictions of the model will be seriously incorrect. We suggest, therefore, that measurements of a compound such as $PrCo_2$ in the amorphous state will be a strong test of our theory.

6. Conclusion.

— We have shown that the RCP model for the structure of an amorphous material is consistent with the model previously proposed for the magnetism of such materials. It seems that this model [4] is closer to being realistic than was previously supposed, and so it will be interesting to check its predictions by a series of systematic experiments on other amorphous rare-earth transition-metal compounds.

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