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METALLIC GLASSES - SOME CURRENT ISSUES

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Résumé. - On discute quatre aspects du comportement des verres métalliques en tenant compte des dernières observations et théories:

- 1) La capacité de former les verres parmi diverses alliages.
- 2) La structure et l'ordre à courte distance.
- 3) La nature du volume libre.
- 4) La relaxation thermique, réversible ou irréversible.

Car le concept de l'Ordre à courte distance est un aspect commun, on passe en revue l'histoire de ce concept en relation avec les alliages cristallins, pour en tirer des leçons. On souligne l'importance de la variation de cet ordre en fonction de la température.

Abstract. - Four aspects of the behaviour of metallic glasses are analysed in the light of recent results and theories:

- 1) Glass-forming ability of different alloys.
- 2) Structure and short-range order.
- 3) The nature of free volume.
- 4) Thermal relaxation, reversible or irreversible.

The concept of chemical short-range order runs as a common thread through these various issues, and some space is devoted to a historical resume of the study of SRO in crystalline solid solutions, in order to draw some instructive parallels. The special importance of establishing how SRO in glasses varies as a function of temperature is emphasised.

1. Introduction. - Research on metallic glasses has become big business. In 1980, for instance, over 1000 papers were published on rapidly quenched alloys and over 90% of these were concerned with metallic glasses. The breakeven year as between glasses and rapidly quenched crystalline alloys had been 1974, when papers on rapid quenching totalled only 123 (1), whereas in 1981, the Fourth International Conference on Rapidly Quenched Alloys, alone, included 336 papers on metallic glasses. It is thus no longer realistic to attempt a general survey of recent developments in this field, be they fundamental or applied: one would need to be at the same time a polymath and a monomaniac. Accordingly, in this short survey I propose to focus on a few scientific (as opposed to technological) topics, within the larger field of metallic glasses, which are in a state of especially rapid development, on which, in consequence, ideas are in a state of flux. Since the precursor to an important advance in any branch of science is generally a newfound recognition of the depth of one's ignorance, this survey could without much hyperbole be termed an outline of ignorance.

2. Glass-Forming Ability. - In the 1960's, everybody knew that glasses are easily made only if they approximate to the composition $Mg_{20}M_{80}$,

where M is a transition or noble metal and m a metalloid. Now that many metal-metal glasses are known, things are recognised to be more complicated and much effort has gone into attempts to find universal criteria that can distinguish those alloy compositions that can be made glassy by rapid quenching, at up to 10^8 K/s, and those that cannot.

The proper test for glass-forming ability (GFA) is the critical quenching rate, R_c , which will just allow the cooling liquid to miss the nose of the C-curve that relates the start of crystallisation to temperature; the lower R_c , the higher the GFA. In the literature, R_c is always treated rather simplistically as a single rate, whereas in fact dT/dt itself varies during the cooling process; but this subtlety is a matter for future attention. Many authors tacitly treat the stability of a glass, as measured by its crystallisation temperature, T_x , under standard conditions, as equivalent to GFA, in the sense that if one increases, so must the other. This tacit hypothesis has not been critically examined and is probably only very roughly valid.

The simplest structural criterion for a high GFA/stability is in terms of atomic/ionic radii. In the 1960's, model experiments on the mixing of two-dimensional rafts, either of soap bubbles (which mimic potentials between metal ions) or of hard spheres, both indicated that a size difference approaching 15% was necessary for ready "glass" formation. This is a simple matter of kinetic hindrance - a limitation on diffusion kinetics in the liquid. Latterly, this simple criterion has been made more realistic by the postulation of "glass-forming maps", in which one axis defines the atomic radius ratio of the elemental components and the other some measure of bond strength in the liquid (which again, by implication, is a measure of the difficulty of atomic transport). Giessen (2) for this purpose uses a quantity, ΔH_M , the maximum value of the heat of mixing for a series of mixtures between two specified metals, itself calculated from electronegativities and electron concentrations by a well-tested procedure (3). Sommer (4) independently introduced glass formation diagrams of the same type, but he used $\Delta \bar{H}_S$ (or $\Delta \bar{H}_V$), the mean vaporization enthalpy of the components. These diagrams were applied by both authors to a large variety of binary mixtures. Both Giessen and Sommer found that the atomic radius ratio was preponderant but that a strong interatomic bond could serve to relax the radius criterion, which is normally that r_x/r_y must depart from unity by at least 10%. Both bond strength and radius ratio determine the kinetics of atomic transport and thus of crystallisation, and the magnitude of ΔH_M is also linked with the free energy change that drives crystallisation.

Sommer and his collaborators (4 - 7) have taken the thermodynamic-cum-kinetic analysis of GFA further than this. Briefly, they have established systematically that (as might be expected) small free energy differences between the liquid and the equilibrium crystal for a supercooled melt favours glass formation (6); but the matter is complicated by the tendency of melts to form short-range order or, more exactly, clusters of an ideal local composition; Sommer uses the general term associations. The ideal composition and frequency of these associations can be determined from measurements of thermodynamic and various physical properties (6). If such chemically ordered clusters are present in the melt and have a different composition from the stable crystalline forms, then the nucleation of the latter is chemically hindered. Thus the systems Mg - Ca, Mg - Sr and Mg - Ba behave quite differently: glasses form readily over a wide composition range in the first, over a narrower range in the second and not at all in the third. Thermodynamic measurements indicate clusters of composition MgCa in the Mg - Ca melts, but Mg₂Ba in the Mg - Ba melts. Since in all three systems there is a Laves phase of composition A₂B, it follows that nucleation in the Mg - Ba system is easy in view of

the presence of clusters of suitable composition, whereas nucleation in Mg - Ca is hindered. In Mg - Sr, there are also Mg_2Sr clusters, but a smaller volume fraction. Sommer's model presupposes a variable degree of microcompositional heterogeneity which goes further than the conventional picture of "short-range order".

The distinction can be made clearer by discussing the thoroughly studied Cu - Ti system in more detail. The degree of chemical SRO in Cu - Ti alloys has been measured directly both by diffraction methods (8) and by EXAFS (9) and both approaches agree in showing very strong maximum order at a composition Cu_2Ti . Glasses can be made over a wide composition range. Sakata et al. (8), in an important paper, have shown that the crystallisation temperature, T_x , is highest close to the Cu_2Ti composition, and the normalised crystallisation temperature, T_x/T_m (where T_m is the equilibrium melting temperature of the crystallized glass) accurately mimics the variation of the SRO parameter as a function of composition. This is a result of great theoretical interest.

Sommer et al. (7) have made thermodynamic measurements of a series of Cu - Ti melts and conclude that, for a range of melt compositions, associations having the composition Cu_3Ti_2 (not Cu_2Ti) are present in the melt, in variable volume fractions. Since the stable crystalline species are CuTi and CuTi_2 , plainly the presence of the associates hinders crystal nucleation. Sommer et al. (7) discuss the slight mismatch between the neutron diffraction and the thermodynamic data and propose a way of reconciling the two. Nevertheless, it is not at present clear just what the structural relation is between an association model (which implies heterogeneity on a fine scale) and conventional chemical short-range order, which implies homogeneity.

However this difficulty is resolved, it is already clear that SRO plays an important role in determining GFA of metallic melts and the related thermal stability of the resulting glasses.

The Sommer-Giessen approach, relating high GFA with a small free energy change on crystallisation combined with kinetic hindrance through atomic size mismatch and through the formation of associations is somewhat related to an alternative model based on atomic volumes. Yavari and coworkers (10) have recently established an impressive correlation between GFA and ΔV , the change in volume on fusion. A volume change close to zero, or even a contraction, on fusion is found to favour glass formation. Yavari's ideas can be summarised in terms of the idea that an expansion on fusion implies the injection of free volume into the liquid, a decrease of its viscosity and hence an enhanced ability of crystalline nuclei to grow even at substantial undercoolings.

These ideas are closely related to but independent of those advanced slightly earlier by Ramachandrarao (11). He applied a theoretical model developed over 20 years ago by Varley to an estimation of the variation, with composition, of the molar volume of liquid binary mixtures of metals, and showed that in those systems where glasses could be formed by quenching, the glass-forming range of compositions invariably includes the composition of minimum molar volume. A negative deviation of actual molar volume from the ideal (interpolated) molar volume, of 15% or more, seems to be required for glass formation. Because of the ambiguity attached to the size of metalloid atoms in melts and glasses (12), this approach is valid only for metal-metal glasses. Presumably, those liquid mixtures with particularly small molar volumes are also those for which the solid-liquid transformation is associated with a minimum volume expansion, so that Ramachandrarao's and Yavari's criteria may well be equivalent.

There is a whole battery of empirical attempts to relate freezing-point depression in eutectic systems to GFA; the best known is Donald and Davies's (13) criterion based on the difference between the actual equilibrium melting temperature and the weighted mean of the melting temperatures of the constituent elements. (This criterion has the distinction that it has predictive value). Recently, Massalski (14) has developed this approach by relating the equilibrium melting temperatures across a phase diagram to those lower temperatures, T_0 , at which a liquid tends to freeze without segregation to form a homogeneous crystalline solid. If the onset of freezing during fast cooling can be delayed to below this temperature, the formation of a homogeneous, "unpartitioned" glass is thermodynamically favoured. This approach by Massalski represents a preliminary attempt to extrapolate arguments used to interpret massive phase transformations to the problems of GFA.

A number of older approaches to GFA have been relatively neglected of late. Nagel and Tauc's famous electronic criterion for GFA (15, 16) has not been much developed. An issue which is currently in suspended animation is the problem of "Polk stuffing" (17). The question here is whether a metal-metalloid glass, of the type of $\text{Fe}_{80}\text{B}_{20}$ or $\text{Pd}_{80}\text{Si}_{20}$, is particularly stable because the holes of the Bernal dense random packing structure are stabilised by being "stuffed" by metalloid atoms only slightly too large for them. This simplistic model has repeatedly been condemned for being outdated, but it is not quite clear why this is thought to be the case and no serious analysis of the model has appeared for a long time. What is clear is that the properties and fine structure of $\text{M}_{1-x}\text{M}_2^x$ glass series varies to a surprising extent as x is varied (for instance, Warlimont, private communication, has documented such variations for Fe-B glasses, as indeed have a number of other investigators). The reasons for such variations are as yet speculative.

There have been essentially no attempts to achieve a unified theory of GFA for metallic, oxide and polymeric glasses. For instance, Goodman's (18) model relating GFA to a tendency to polymorphism in the corresponding crystalline phases, developed for oxide systems, has not been applied to metallic systems. Occasionally, a paper is published which attempts to identify unifying features of the glass transformation (19) or of relaxation mechanisms (20), but such attempts have not extended to analyses of which factors predispose to glass formation in the first place.

In connection with Massalski's attempts to relate GFA to the form of the phase diagram, it is to be noted that one is not restricted to ultrafast quenching from the melt. In favourable cases (up to now, this has meant low-melting systems) glasses can also be made by slow cooling finely dispersed microdrops of molten alloy, relying on the Turnbull-Cech principle of preventing heterogeneous nucleation by compartmentalising the liquid. When this is done, the thermal characteristics of the alloy (glass transition temperatures, temperatures of crystallisation on reheating) can be measured during slow temperature change. This type of experiment has been most clearly presented with regard to Te-Cu alloys (21): if ways could be found of extending this technique to higher-melting alloys (e.g. by use of a molten-salt dispersing medium), the technique could be widely applied to GFA studies.

2. Structure and Short-Range Order. - In what has been said above concerning short-range order and the concept of local associations it emerged that there is a measure of disagreement whether the structure of a metallic glass subject to SRO is to be regarded in homogeneous or heterogeneous terms. This dichotomy has of late become

increasingly pronounced, especially in view of the structural heterogeneity evident in high-resolution electron microscopy of both oxide and metallic glasses (22, 23); there is evidence for the existence of regions of higher structural order separated by regions of less order. Since we shall be returning below to a consideration of the role of SRO in relaxation, it is worth pointing out here that the homogeneous/heterogeneous dispute has also been rife in the analysis of (chemical) SRO in crystalline solid solutions; it appears to be a particularly difficult problem to resolve. It is worth devoting a few lines to this dispute, since it carries lessons for the student of glasses.

A long-range ordered crystalline solid solution such as Cu_3Au is never quite perfectly ordered; the Bragg-Williams order parameter, S , is always somewhat less than unity. There has been dispute over whether the "wrong" atoms are randomly dispersed (homogeneous) or clustered in minute groups (heterogeneous). As the mean antiphase domain size becomes smaller, there is a continuous transition from long-range to short-range order, and the dispute in due course becomes one about the nature of short-range order. In the literature of this topic, two kinds of heterogeneity are discussed: compositional heterogeneity (often referred to as "clustering"), and variations from point to point of the statistical extent to which A atoms have B atoms as their nearest neighbours (the classical meaning of "SRO"). The mean "static" (as opposed to thermal) displacement of atoms from their lattice sites is a further variable; this reduces as SRO strengthens. The two forms of heterogeneity seem to be closely linked. The experimental diffraction methods, which have become very sophisticated, are discussed by Chen et al. (24) and by Georgopoulos and Cohen (25); clustering effects are discussed by de Fontaine (26). The most thoroughly studied special case is that of the copper-rich Cu - Al alloys: calorimetric (27), diffraction (28 - 31), micrographic (31a) and resistometric (32, 33) studies have gradually produced a unified picture. Some thirty very variegated publications on SRO in Cu - Al alloys and the main conclusions from them have recently been reviewed (33).

The degree of SRO (in Cu - 13 to 16 at.% Al) is a function of temperature: in equilibrium, SRO increases as the temperature falls. But equilibrium is established very slowly at the lower temperatures. If alloy samples are quenched from different temperatures T_q , the degree of SRO is high for $T_q = 500 - 900^\circ\text{C}$, low for $T_q = 550^\circ\text{C}$ or below. If however the alloy is quenched from a high T_q (650°C) and then held at a temperature in the range $150 - 300^\circ\text{C}$, high degrees of SRO are rapidly attained (29, 32). This behaviour is kinetically determined: only if the alloy is quenched from a high T_q so that a high vacancy concentration is quenched in can the alloy then order rapidly and approach equilibrium at low temperatures. - The short-range order is spatially heterogeneous. TEM (31a) shows that islands of appreciable SRO are surrounded by regions without it; all the evidence suggests that the more ordered regions are of somewhat different composition, and the early calorimetric data (27) suggest that these regions are trying to achieve the status of a localised Cu_3Al superlattice.

The point of this little historical excursion into the nature of crystalline SRO is that there are lessons to be learned for application to metallic glasses. As we have seen, the role of SRO in melts on glass-forming ability is now clear, and as we shall see, its role in glasses in determining their relaxation behaviour is equally clear. However, up to now the study of chemical SRO in metallic glasses by diffraction has repeated an error made by the physicists, such as Warren and Averbach, who undertook the study of SRO in crystalline alloys during the period 1950 - 65: with the sole exception of a few of those who studied Cu - Al alloys (29, 31, 32), all others treated SRO as a function of alloy composition but not of temperature. The same has been true of most of the direct measurement of SRO in

metallic glasses, such as those published in the Proceedings of the 1981 Sendai Conference. Sakata et al. (8), working with Cu - Ti glasses have however begun to study the effect of annealing temperature and have already established that SRO is greater in a glass than in the melt from which it is made (i.e., SRO is greater at T_g than at a temperature well above T_g) and considerably greater in the glass at 700K than at 1173 K. Scott (34) has just published an important indirect study of the variation of SRO with annealing temperature: he used isothermal calorimetry to show very clearly that SRO in the glass $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ varies reversibly as the temperature is cycled. Since the boron atoms are known to avoid each other always, the SRO in question mainly affects the relative positions of the Fe and Ni atoms. This kind of investigation now urgently needs to be done in a systematic way for a number of two-metal glasses such as Cu - Ti, Ni - Ti, Ni - Nb which are specially subject to SRO (Cowlam, private communication). Preferably, calorimetric and diffraction studies should be combined to find how SRO varies reversibly with annealing temperature and how changes in SRO affect specific heat. (The diffraction measurements could be expressed in terms of an improved SRO parameter, as proposed by Cargill and Spaepen (35)). This kind of knowledge could then be properly correlated with reversible relaxation behaviour (see below). Recent experiments and theories by Radelaar and his colleagues (61, 71) mark an excellent start in this direction.

In spite of some indications (51) there has been no direct evidence as yet of the kind of kinetic hindrance cited above for crystalline Cu - Al alloys, in the sense that a glass quenched from just below T_g might order faster at lower temperatures than if it had been slow-cooled to those temperatures. Such effects may well prove to exist, since it is well established that free volume, which determines diffusion rates, varies substantially with temperature. In some glasses diffusion rates are much slower than in their crystalline counterparts, so that establishment of equilibrium SRO might be very slow. Thus, for instance, the remarkable fact has very recently been established that diffusion of gold in a Ni - Nb glass is 5 - 6 orders of magnitude slower than in the same material after crystallisation (J.D. Wiley et al. (36); Wiley, private communication). This striking observation is being applied to the production of metallised contacts on integrated circuits, which must be very stable against interdiffusion of metal and semiconductor.

3. Nature of Free Volume, Glass Transition and Diffusion in Metallic Glasses.

- The experimental study of diffusion in metallic glasses has developed at great speed in the past few years, and this has been linked with increased speculation about the nature of free volume, which in turn is closely related to the glass transition. In the space available here, there is room only for a summary of recent ideas.

The most striking development is the publication of Cohen and Grest's model of the glass transition (1973, 38). The basic ideas of this theory, which have been worked out in considerable quantitative detail, involve the existence of a specified distribution of structural cells of different volumes; mobility presupposes a minimum cell volume, and cells exceeding this are said to be liquid-like. The glass transition is determined by a solution of the percolation problem in a population of liquid-like cells contained in rigid, non-diffusing solid-like cells.

This model is one which presupposes a continuously variable range of free volume in the liquid/glass structure (a continuously distributed free volume model, CDFV), as opposed to a hole model in which free volume exists in vacancy-like units. Cantor and Ramachandrarao (39) have recently published another form of free volume

theory, by applying configurational entropy calculations to the problem of the relative numbers of different kinds of Bernal polyhedra in a Bernal DRP structure. They analysed for the first time how these relative numbers should vary with temperature (which implies changes in free volume since different kinds of polyhedra have different volumes per atom); good accord was achieved between theory and measured specific heats and other physical quantities. This important new model is also a CDFV version .

Egami et al. (40) have worked out some implications of another CDFV model, based on the idea that a metallic glass contains regions of hydrostatic tension and others which are locally compressed, so that the aggregate free volume in the former regions can be much greater than is usually estimated from the macroscopic density. Kiritani and Hamada (41) have advanced a closely related model, incorporating what they call "latent vacancies".

Others have proposed hole models. Ramachandrarao himself, with coworkers (42, 42) developed ideas first advanced by polymer physicists into a self-consistent free volume model for metallic glasses which can explain a number of experimental facts such as the variation of viscosity with temperature, and also the relative stability of different glasses (linked closely with the energy of formation of a hole); the size of the hole can also be estimated from this theory. Buschow (44) independently produced a similar theory relating thermal stability to an estimated hole formation energy. (There is now so much activity in this sector of theory that people have repeatedly published similar models in ignorance of each other).

The balance of credibility between CDFV and hole models is as yet uncertain (45). There are also beginning to appear detailed structural theories of line defects (not dislocations) in metallic glasses (Rivier, 46; Venkataraman, private communication), but how and indeed whether they are related to free volume, diffusion and T_g is as yet unclear.

Experimental studies of diffusion in metallic glasses have suddenly burgeoned in the past three years, as methods were established to measure the very shallow diffusion profiles (less than 1 μm), imposed by the need to avoid any crystallisation during the diffusion anneal. The extensive work recently published is surveyed in detail in a forthcoming review (47). Special mention should be made of the first observation (48) of a concentration dependence of D (relating to hydrogen in a Pd-Cu-Si glass), accompanied by a structural interpretation (49) of this observation, in terms of a reducing tightness of solute-solvent binding as the most favourable sites are occupied first, so that D increases with H concentration. - The theoretical interpretation of diffusion in metallic glasses is in a highly unsatisfactory state: an initial approach exists for interstitial-type diffusion (49, 50) but none at all for diffusion of large atoms. This comes high on any list of current unresolved issues. On the experimental front, the chief disputed issue concerns the effect of thermal relaxation on diffusivities in metallic glasses: published results up to now have been contradictory, but it may be (47) that the contradictions are more apparent than real. This dispute will be further complicated by the recent claim (51) that the atomic mobility in a metallic glass can be partly reversible with temperature! Another topic requiring further experimentation is the diffusion of carbon, a small atom, and its kinetic relation to the diffusion of boron (larger) and hydrogen (smaller). The only extant measurement, by an elegant but indirect method (52) shows that carbon diffuses substantially faster than boron in a Fe-B-Si-C glass, but slower than hydrogen.

Few systematic studies have been undertaken of the relative diffusion rates of a component or impurity atom in a metallic glass and the same material after it has crystallised. The above-mentioned (36)

dramatic contrast between these two quantities in the case of gold diffusing in a Ni-Nb glass - ita has been suggested that the very fast diffusion in the crystallised alloy is due to migration along the boundaries of the very small grains - suggests that a systematic study of this kind for several glasses should be of practical as well as fundamental interest.

4. Thermal Relaxation of Metallic Glasses. - This topic has attracted rapidly increasing attention in the past few years, and as facts accumulate, so do uncertainties about the proper structural interpretation of what has been observed. It is a particularly intriguing subject at its present stage.

Four excellent, very recent treatments of thermal relaxation characteristics are by Greer and Spaepen (53), Scott and Kursumović (54), Balanzat et al (55) and Chambron and Chamberod (51, 56). These concentrate, respectively, on changes in magnetic Curie temperature, elastic modulus, electrical resistivity and induced magnetic anisotropy. The relaxation of the coercive field has also been studied very recently (Kronmüller, private communication; Gibbs and Evetts, private communication). The essential facts are these: All properties change both irreversibly and reversibly; the latter component is characterised by values of the property which are specific to the annealing temperature and revert to these values - after a period for equilibration - whatever the preceding annealing temperature. Irreversible changes are much slower at a given temperature than the corresponding reversible change. The kinetics of both types of recovery depend somewhat on the previous thermal history, and particularly on the temperature from which the glass was last quenched. Relaxation kinetics, generally so in the case of irreversible and sometimes in the case of reversible relaxation, follow a logt law.

For those properties and annealing times which lead to predominantly reversible changes, plots of property change from the initial state in the as-prepared glass show standard characteristics. Thus, if ΔT_C (where T_C is the magnetic Curie temperature) is plotted against annealing temperature, T_a , for constant annealing time, then ΔT_C vs T_a always shows a maximum for a particular value of T_a . Recent studies by Mizoguchi et al. (57) have shown clearly that this peak is reduced to lower temperatures for longer isochronal annealing periods. Similar peaks have been established for resistivity (55) and uniaxial anisotropy (56). It is clear that, above the peak, the property is already in equilibrium at the annealing temperature after an anneal for the standardised time. Whereas in equilibrium the property would continue to rise with decreasing temperature, in fact it cannot do so below the peak because there is not enough time at these lower temperatures to attain equilibrium.

A particularly interesting question which has not previously been considered in general terms is the ratio between the magnitudes of reversible and irreversible changes (let us call it the R/I ratio). This ratio of course depends on the property in question, the temperature, the annealing time and the composition of the glass, but the different properties can at any rate be put in a sequence. So far as the available evidence goes, R/I quite generally decreases in the following order: Curie temperature, elastic modulus (both quite similar); uniaxial magnetic anisotropy; coercive field; electrical resistivity; change in length (or density). With the first two, the irreversible component is often quite slight, and for the Curie temperature has only recently been observed (58).

Egami (59) was the first to propose a distinction between topological (TSRO) and chemical (CSRO) short-range order; the former

refers to geometrical packing, and is said to increase when packing becomes denser, while the second has its usual meaning, familiar as we have seen from crystalline alloys, and refers only to the probability of finding chemically unlike nearest neighbours (relative to the probability for a random arrangement of atomic species). Egami proposed that reversible changes, which are rapid, involve only changes in CSRO, and such changes involve movements of atoms only over distances of the order of interatomic separations; whereas irreversible changes of properties involve changes of TSRO and concomitant changes of density, and such changes involve long-range diffusion of atoms. Egami has gone some way towards confirming his ideas (which remain extremely controversial) by his recent very exact experiments on changes in x-ray diffraction patterns of glasses on irreversible relaxation (60), but it is true that neither he nor anyone else has demonstrated reversible changes in x-ray diffraction patterns, though Radelaar and his collaborators (61) are making progress towards this important objective. It is agreed by many that changes in TSRO necessarily involve some changes in CSRO, and vice versa. Yet the distinction is conceptually clear and operationally useful, and it is in principle possible to distinguish between them by combining diffraction and density measurements. This is the main reason why I regard measurements of changes, both irreversible and reversible, in density (or length) as being particularly valuable in affording insight into changes in order during relaxation; it is a pity that this kind of measurement has been so neglected hitherto.

It appears to be widely agreed among magneticians that the magnetic Curie temperature is especially sensitive to nearest neighbour identity (and to a lesser extent, nearest neighbour separation), and this would account for the high R/I ratio for this property. Elastic modulus is known to be sensitive to chemical (long-range) order in crystalline alloys (62) and it is thus not surprising that the same is true for metallic glasses. However, the matter has not been examined theoretically. Induced uniaxial magnetic anisotropy is known (from Néel's decisive experiments many years ago on crystalline solid solutions) to be directly due to an anisotropic arrangement of the frequency of A - B atom pairs parallel and normal to the direction of the magnetic induction vector applied during the anneal. The fact that this property does not behave in a wholly reversible manner (as the induction vector is rotated between successive anneals) implies that irreversible structural changes reduce the number of atom pairs which are available for free reorientation, but why this should be so has not been analysed.

Resistivity is much more a collective property, especially sensitive to electronic band structure, and therefore to interatomic distances and TSRO generally (this is quite clear from the success of the standard Ziman theory of resistivity of liquids and glasses); thus one expects irreversible changes to predominate, as is indeed found. The French work (55) shows a fairly substantial reversible component in $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ (and the reversible component is especially large (55) in $\text{Cu}_{50}\text{Ti}_{50}$, which as we have seen has very substantial CSRO), but Kelton and Spaepen (63) find only a small reversible component in resistivity changes in Pd - Si glasses while Cost and Stanley (64) find no reversible component at all in $\text{Fe}_{80}\text{B}_{20}$. This last fact is intriguing, because the peak magnitude of reversible Curie temperature changes are much smaller in $\text{Fe}_{80}\text{B}_{20}$ than in a glass like $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_{20}$ (65); only the latter kind of glass can have changes in CSRO between metal atoms. It seems then that changes in CSRO involving only metal-metalloid atom pairs (as opposed to metal-metal pairs) can produce some, reversible, changes in Curie temperature (and also in induced anisotropy) but has negligible effect on electrical resistivity, and therefore glasses like $\text{Fe}_{80}\text{B}_{20}$ have no measurable reversible changes in resistivity.

Nothing specific has been said yet about density changes - or length changes, which are equivalent in an isotropic material. These are very difficult to measure accurately. With the most elaborate precautions, density of metallic glass specimens can only be measured to about 0.05% precision, and this is only marginally sufficient for measurements of irreversible changes (Pratten, Scott and Cahn, to be published) and insufficient to observe reversible changes. Length changes are thus a better quantity to measure. Irreversible length changes have been measured by Kursumović et al. (66), Dietz and Hüller (67) and recently by Sinning, Cizeron and Cahn (to be published). The last two groups used precision isothermal dilatometry, a technique full of pitfalls. Sinning, Cizeron and Cahn have tentative observations of what appear to be small reversible components of length change in $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ glass, but this component is less than 0.01 % and the R/I ratio is small. Efforts are under way to confirm these preliminary results. Such reversible changes should indeed be found if CSRO is responsible, since higher CSRO implies more efficient packing of atoms and therefore a slight contraction. One possibility of confirming a link between changes in CSRO and length changes in glasses is to use irradiation to enhance atomic mobility so that equilibrium CSRO can be attained at low temperatures where under normal circumstances it is never attained (this has repeatedly been successfully done with crystalline alloys); in that case, large changes in CSRO might lead to readily measurable length changes. Some dilatometric results recently obtained by Cahn et al. (68) have been interpreted as due to an increase in CSRO, but to carry conviction they need to be complemented by diffraction studies, which are not easy when a material is highly radioactive! - Difficult though the problem is in experimental terms, reversible length changes should be sought in a number of different glasses.

The kinetics of relaxation, both reversible and irreversible, have been increasingly studied. Generally, irreversible densification leads to a slowing down of subsequent changes (this includes superimposed reversible changes also (55)), but the observations of Chambron and Chamberod (51) that kinetics can change reversibly as a glass is quenched successively from different high temperatures and after each quench, annealed at a fixed lower temperature, has created a new mystery, because it implies that kinetics themselves are to some extent reversible. This mystery is further compounded by some intriguing measurements due to Hilzinger and Warlimont (69), of kinetics of relaxation of magnetostriction and induced anisotropy, which indicate the existence of two quite distinct kinds of kinetics, according to the quenching and annealing temperatures used.

Superimposed on these new experimental complications concerning relaxation kinetics is a conflict of opinion on the question whether relaxation, reversible or irreversible, is governed by one, two or a whole spectrum of activation energies. Gibbs et al (70) marshal an impressive range of evidence in favour of the existence of a spectrum of activation energies, whereas van den Beukel and Radelaar (71) marshal equally impressive evidence from their quantitative kinetic analysis of microcalorimetric measurements of relaxation (in this connection, see also the recent work of Duddek et al.⁽⁷²⁾ on microcalorimetry of relaxation), that a reasonably good though not perfect accord with observed relaxation kinetics of both kinds can be obtained by assuming only a single activation energy. Battle must now be joined between these two irreconcilable approaches.

There is one type of experiment which makes it unambiguously clear that at least two relaxation times must govern reversible kinetics, which implies at least two different activation energies and two physically distinct contributory processes. This is the crossover experiment, which has now been done for Curie temperature (73) and elastic modulus (54) in metallic glasses and also for

refractive index in an oxide glass (74). For details, the reader must refer to the original papers: in outline, the sample is annealed at a temperature T_1 till reversible equilibrium is reached, then at T_3 for a time t' when the property, not yet in equilibrium at T_3 , has reached a level L known to be characteristic of equilibrium at an intermediate temperature T_2 ($T_1 > T_2 > T_3$); from this moment the sample is held at T_2 . It has been found in all the experiments that the property goes through further changes before returning to and remaining at the value L . If there were only a single relaxation time, this would be impossible, and the sample, when brought to temperature T_2 , would not change further; there must therefore be either two relaxation times, or a spectrum.

In conclusion, the crossover experiment takes us back to Section 2 and SRO in crystalline alloys. We have seen that CSRO is prime candidate for the central process in reversible relaxation in metallic glasses, and that related property changes, as a function of relaxation temperature, reach a peak value (below which equilibrium cannot be attained in the available time). This is just what is found in crystalline alloys also (e.g. 32). Trieb and Veith (75) have done a crossover experiment on crystalline 16 at.% Cu - Al alloy, using very precise resistivity experiments. They found results similar to those obtained on glasses, and they postulated that the two relaxation times were associated with a change in CSRO and a microsegregation process. This interpretation (which is hotly contested!) is very similar to that advanced by Sommer et al. (4-7) for glasses - his "association" model. It may well prove that this model, implying both segregation and changes in CSRO, will serve to interpret some of the anomalies in reversible relaxation behaviour in metallic glasses. In any case, it is important that students of metallic glasses learn from the experience of crystallographers 20 years ago, and make proper studies of CSRO in metallic glasses as function both of annealing temperature and of composition. Without this, the understanding of relaxation, which is of both fundamental and practical concern, will hardly make much progress.

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