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A critique of the roles of TSRO and CSRO in metallic glasses by application of the activation energy spectrum model to dilatometric data

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Dilatometric data is analysed in terms of the activation energy spectrum (AES) model for metallic glasses. Particular importance is placed on E_0 plots. Comparison with a theory which draws a sharp distinction between the kinetics of topological and chemical short range order changes, shows that the AES model provides a more complete analysis of the time–temperature behaviour.

1. Introduction

Metallic glasses exhibit marked changes in many physical properties during annealing at elevated temperatures below those sufficient to introduce crystallization. The study of these changes is central to an understanding of the relationship between atomic structure and physical properties. Of particular importance is a study of the contraction in length observed on isothermal annealing of metallic glasses. This length contraction reflects an increase in density of the material. Owing to the non-periodic structure it is not possible to define a lattice parameter, but an increase in density does reflect a decrease in the average nearest neighbour spacing. Many physical properties (e.g. ferromagnetic Curie temperature) are understood to be primarily determined by the distance between nearest neighbour atoms, and thus changes in nearest neighbour spacing have a significant effect. The ability to quantify the consequences of any thermal treatment on a physical property is a necessary prerequisite of useful applications of these materials.

Van den Beukel *et al.* [1] have recently presented an analysis of dilatometric data in terms of a model [2] and its extension based on the concepts of topological and chemical short range order (TSRO and CSRO respectively). They ascribe TSRO to a description of the topological positions of the atoms, and thus interatomic distances are described in terms of TSRO. They regard TSRO changes as being irreversible with changes of temperature; that is, the TSRO always changes in a sense which increases the density of the material. In CSRO the chemical identities of the atoms are taken into account. The degree of CSRO is temperature-dependent, and thus CSRO changes are reversible with changes of temperature. In their model the kinetics of TSRO changes are governed by a single activation energy [2], whilst in the proposed extension [1] the kinetics of CSRO changes are governed by a spectrum of activation energies according to the activation energy spectrum (AES) model of Gibbs *et al.* [3]. Using the revised model van den Beukel *et al.* [1] were able to obtain a quantitative fit to parts of their dilatometric data on $Fe_{40}Ni_{40}B_{20}$. The parts which do not fit with the calculated TSRO changes they ascribed to CSRO changes. If CSRO changes are reversible with temperature, the magnitude of the reversible length change on changing the temperature should be readily

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observed experimentally. Van den Beukel *et al.* [1] do state that they have observed reversible length changes but do not quantify the effect. Other workers [4] have found that the reversible component is at most 1% of the total length change on annealing, much less than the magnitude required by van den Beukel *et al.* [1].

Cahn *et al.* [4] have discussed how changes in TSRO and CSRO may cause a change in length. Gibbs [5] discussed how, in general, it is not possible to have a change in CSRO without an accompanying change in TSRO. The strict division into two categories by van den Beukel *et al.* [1, 2] seems to lack a fundamental basis. A model must be developed which recognizes the role of nearest neighbour spacing, number and identity of nearest neighbours in one formalism.

The activation energy spectrum (AES) model proposed by Gibbs *et al.* [3] is based on the work of Primak [6] and has been successfully applied in the quantitative analysis of diffraction data [7], Curie temperature data [8, 9], Young's modulus data [5, 10] and data on isothermal creep [11]. The AES model has been analysed for the validity of various approximations and applied to dilatometric data by Sinning *et al.* [12]. Gibbs [5] has discussed how the parameters of the AES model may be related to TSRO and CSRO. In this paper the AES model is quantitatively applied to dilatometric data on the metallic glasses $Fe_{40}Ni_{40}B_{20}$, $Cu_{66}Ti_{34}$ and $Ni_{64}Zr_{36}$. The recently introduced concept of E_0 plots is found to be important in the analysis [5, 8, 9]. The data of van den Beukel *et al.* [1] are re-examined, and it is demonstrated that the AES formalism is sufficient to discuss dilatometric data over a wide time–temperature range, thus embracing the concepts of TSRO and CSRO.

2. Theoretical background

The AES model described the change in a measured property, ΔP, on annealing in the following way.

$$\Delta P = \int_0^\infty \overline{c(E)}\,[Q(E) - q_s(E, T)]\,\theta(E, T, t)\,\mathrm{d}E \tag{1}$$

$Q(E)\,\mathrm{d}E$ is the total number of thermally activated atomic rearrangements in the energy range E to $E + \mathrm{d}E$. $q_s(E, T)\,\mathrm{d}E$ is the equilibrium number of such atomic rearrangements over the same energy range. $\theta(E, T, t)$, called the characteristic annealing function after [6], to a good approximation, can be replaced by a step function at an energy $E = E_0$ where

$$E_0 = kT \ln(\nu_0 t) \tag{2}$$

k is Boltzmann's constant, T is the temperature, t is time and ν_0 is attack frequency. $\overline{c(E)}$ is the coupling parameter between the thermal activation of an atomic rearrangement in the energy range E to $E + \mathrm{d}E$ and the macroscopically measured change in physical property. The relationship of $\overline{c(E)}$ to TSRO and CSRO has been discussed elsewhere [5]. This parameterization was introduced in detail in [3].

Reversibility in the sense of change of a physical property with changes in temperature has been quantitatively analysed by considering that $q_s(E, T)$ has a temperature dependence, and that $q_s(E, T_2) > q_s(E, T_1)$ for $T_2 > T_1$ [3, 5, 8].

If $\theta(E, T, t)$ is replaced by a step function at $E = E_0$ Equations 1 and 2 combine to give

$$\Delta P = \int_0^{E_0} \overline{c(E)}\,q(E, T)\,\mathrm{d}E \tag{3}$$

where

$$q(E, T)\,\mathrm{d}E = [Q(E) - q_s(E, T)]\,\mathrm{d}E \tag{4}$$

It has been shown [3, 8, 12] that if $\overline{c(E)}q(E, T)$ is constant over a particular energy range sampled in an isothermal annealing experiment then

$$\Delta P = \overline{c(E)}q(E, T)kT \ln(\nu_0 t) \tag{5}$$

The property change varies linearly with the logarithm of the isothermal annealing time, a case observed experimentally under restricted conditions [11, 12].

If $q(E, T)$ is not a function of temperature, i.e. $q(E, T) = q(E)$, Equation 3 gives that a plot of ΔP against E_0 should follow a single curve, irrespective of the isothermal annealing temperature. The concept of E_0 is initially introduced for the step-function approximation to $\theta(E, T, t)$. This approximation must be dropped for quantitative analysis [8, 11, 12]. However, in plotting ΔP against E_0 the full functional form of $\theta(E, T, t)$ is still being considered as E_0 marks the position of $\theta(E, T, t)$ with time and temperature, and $\theta(E, T, t)$ has a profile that is only weakly temperature dependent for the range of temperatures considered experimentally [3, 6].

A "master" curve of ΔP against E_0 should be obtained for dilatometry data, where it is believed that the reversible part of the length change is negligible compared to the overall length change on isothermal annealing [4, 11] and hence $q_s(E, T)$ will have a negligible experimentally determined temperature-dependence.

If $q_s(E, T)$ has a temperature-dependence which can be resolved experimentally, i.e. the sense of a property change is altered on changing the temperature, then for a given value of E_0 in Equation 3, the value of ΔP will decrease as $q(E, T)$ decreases due to the increase of $q_s(E, T)$ with temperature. Such cases have been examined and found to be consistent with this approach [5].

3. Experimental procedure

The dilatometric measurements have been performed in a French commercial dilatometer (ADAMEL LK 02) which has the major advantage of allowing extremely high heating and cooling rates (up to $300 \mathrm{K} \sec^{-1}$) by means of radiation focused on to the specimen by elliptical mirrors (a so-called "image furnace") [13]. With such high heating rates it is in principle possible to follow length changes during structural relaxation of metallic glasses from zero time in a truly isothermal experiment, i.e. without any detectable relaxation during heating up. Most other dilatometers require a settling time of the order of minutes before a stable temperature is achieved [1, 16].

The experimental techniques of applying this instrument to metallic glasses have already been described and discussed in detail [14]. Due to the requirements of the instrument, wire-tied sandwiches of about 20 foils, 12 mm long were used.

To correct for instrumental artefacts, a reference curve was subtracted from each isothermal measurement. This reference curve was obtained in a second identical run after the specimen had been heat-treated further at a higher temperature to complete relaxation. With this correction method the instrument gives very reliable results on metallic glasses in the range of short to intermediate times, whereas the stability for long times ($> 10^4$ sec) is less [11, 14, 15].

Most of the experiments have been performed on specimens cut from a 15 mm wide ribbon of $Fe_{40}Ni_{40}B_{20}$ (Vitrovac 0040). Measurements have been taken both along the ribbon length and across the ribbon width, and the original data has been published elsewhere [4, 11]. In addition a few measurements were also made on the metal–metal glasses $Cu_{66}Ti_{34}$ and $Ni_{64}Zr_{36}$.

4. Results

Fig. 1 shows the isothermal length changes of as-quenched $Fe_{40}Ni_{40}B_{20}$ both in the longitudinal and transverse directions (data from [4, 11]), plotted as a function of E_0. As estimated from measurements on pre-annealed samples [11], a value of $\nu_0 = 10^{11} \sec^{-1}$ has been taken. This E_0 plot is again a clear demonstration of the anisotropy of length changes during structural relaxation in $Fe_{40}Ni_{40}B_{20}$ [4, 11]. For each measuring direction, however, the different isothermal curves do indeed fit to a master curve as proposed above, within the experimental error and the scatter between specimens.

The dilatometric data of van den Beukel *et al.* [1] are re-plotted in Fig. 1. These data have been corrected for the length change during the period before the measurement started [16], and 20 min has been added to the times of van den Beukel *et al.* [1] for the calculation of E_0. This is discussed below. The curves of these data, although obtained from much narrower ribbons

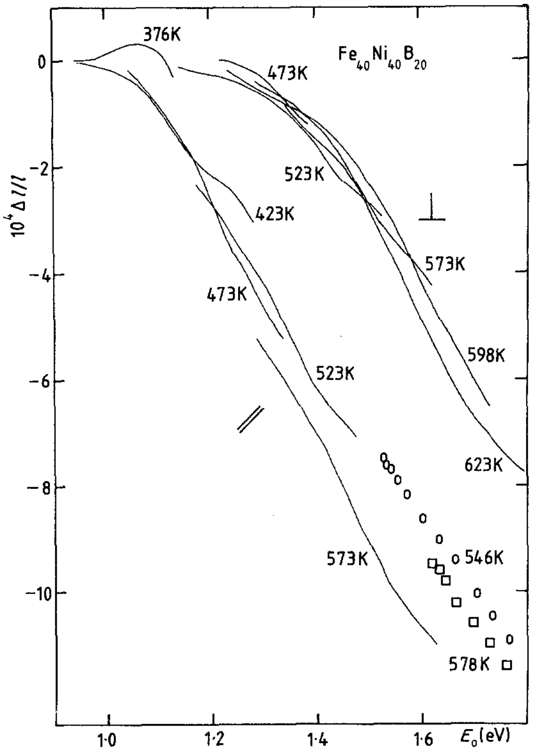

Figure 1 Isothermal length changes of as-quenched $Fe_{40}Ni_{40}B_{20}$ at different temperatures, plotted as a function of $E_0 = kT \ln \nu_0 t (\nu_0 = 10^{11} \sec^{-1})$. Solid lines: data from [4] and Sinning *et al.* [11] measured along the ribbon length (∥) and across the ribbon width (⊥). Symbols: data from van den Beukel *et al.* [1].

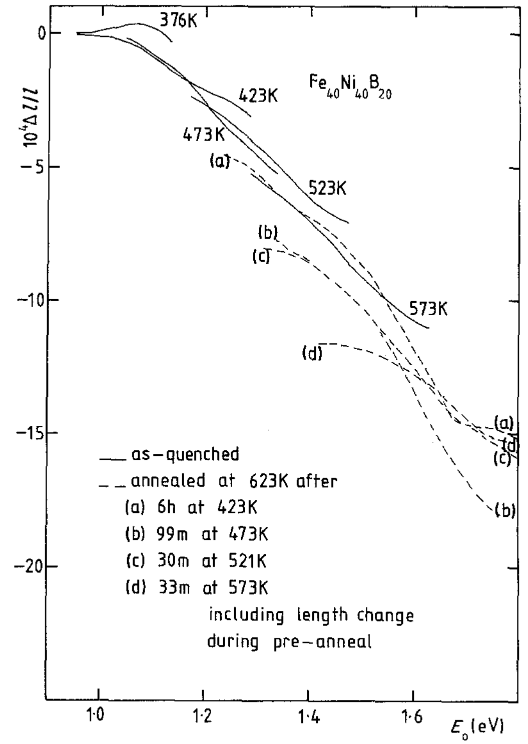

Figure 2 Isothermal length changes of $Fe_{40}Ni_{40}B_{20}$ along the ribbon length (from Sinning *et al.* [11]), plotted as in Fig. 1. Solid lines: as-quenched samples. Dashed lines: pre-annealed samples.

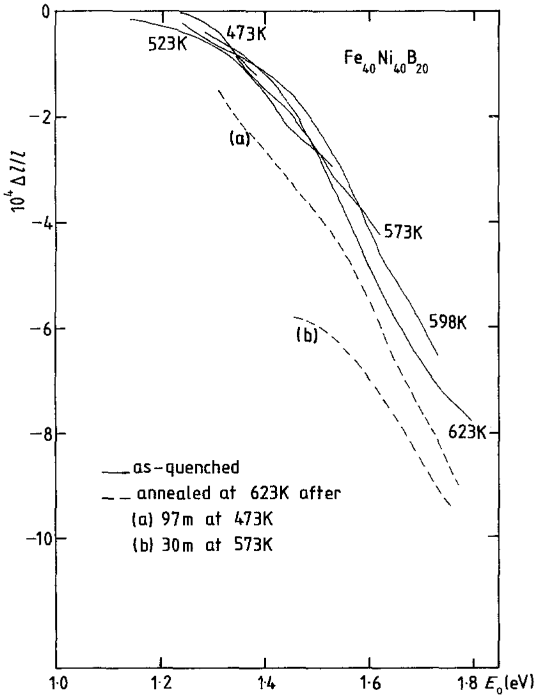

Figure 3 As Fig. 2, but for data across the ribbon width.

of $Fe_{40}Ni_{40}B_{20}$, show the same slope and may be fitted to the longitudinal master curve.

In Figs. 2 and 3 measurements at 623 K on pre-annealed samples [11] have been added to the data of Fig. 1, plotting the sum of the measured length change and the total contraction during pre-annealing. Again the data are consistent with a master curve.

The isothermal length changes of the two metal–metal glasses $Ni_{64}Zr_{36}$ and $Cu_{66}Ti_{34}$, measured successively at two different temperatures each, are plotted in Figs. 4 and 5. As the data on these glasses are not sufficient to determine reliable values of the frequency factor ν_0 experimentally, we have established the corresponding E_0 plots on the basis of two different values of ν_0 in Figs. 6 and 7a, b, respectively. It is seen that the value of ν_0 does not have a strong influence on the relative positions of the isothermal curves as a function of E_0, so that the method of E_0 plots is rather insensitive to the particular value of ν_0 chosen. The trend in these data is still in favour of a master curve.

5. Discussion

Cahn *et al.* [4] and Sinning *et al.* [11] describe in detail how the data used for Figs. 1 and 7 have been obtained. The method of comparison of data with a fully relaxed specimen (one in which there is no further contraction with time detected) ensures that at a given temperature the data are capable of displaying a component from the temperature dependence of $q_s(E, T)$ on an E_0 plot if it can be resolved. The sample and reference runs are for the same time at the same temperature, thus resulting in the same value of E_0 at the end of both runs. Hence, from Equation 3 above, ΔP (in this case $\Delta l/l$) will depend on $q(E, T)$ which decreases if $q_s(E, T)$ increases with temperature.

The initial rise $\Delta l/l$, i.e. a measured expansion, at the lowest temperatures, they tentatively ascribe to the removal of the CSRO obtained at room temperature during the long storage at room temperature. Storage for one year at room temperature will reduce $Q(E)$ to $q_s(E, T_r)$ (T_r is room temperature) for all $E < 1.076\,eV$. The initial anneal will cause $Q(E)$ to increase from $q_s(E, T_r)$ to $q_s(E, T)$ $(T > T_r)$ for all $E < 1.076\,eV$. The period at room temperature between the high temperature anneal to fully relax the specimen and the reference run is insufficient to create the degree of order initially attained at room

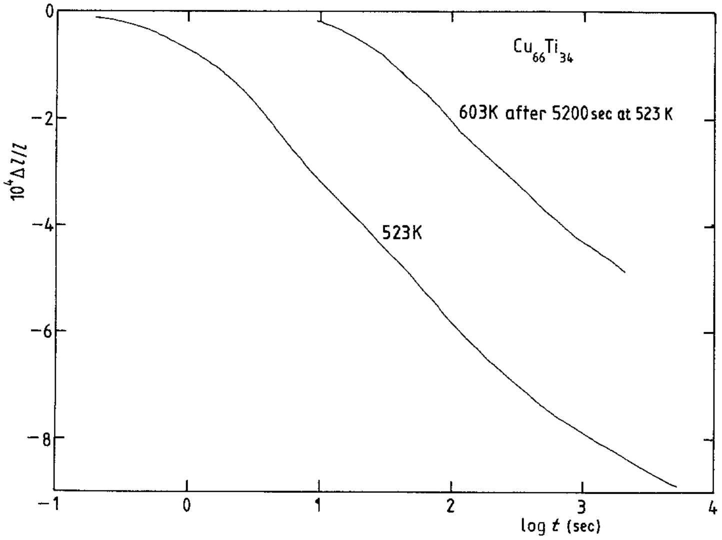

Figure 4 Isothermal length changes of $Cu_{66}Ti_{34}$ taken successively at 523 K and then at 603 K on one sample.

temperature. For example, 10 min at 293 K will decrease $Q(E)$ from $q_s(E, T_2)$, where T_2 is the high temperature used for stabilizing the specimen, to $q_s(E, T_r)$ for all $E < 0.802$ eV. Thus the total number of atomic rearrangements leading to an increase in $Q(E)$ for $E < 1.076$ eV is less after the stabilizing anneal, and the corresponding expansion is less. Thus the difference between the two runs which is plotted in Figs. 1 to 7 is a net expansion. No effect of this should be observed for data resulting from sampling the spectrum at energies above 1.076 eV. However, if this truly is the cause of the measured expansion it is at first sight surprsing that the data at 423 and 473 K in Fig. 1 do not show a similar initial expansion for $E < 1.076$ eV. It is worth noting that in what follows we demonstrate that the magnitude of the

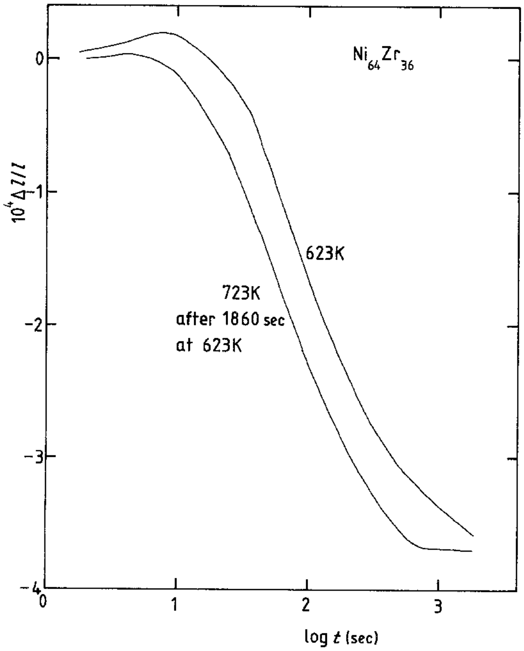

Figure 5 Isothermal length changes of $Ni_{64}Zr_{36}$ taken successively at 623 K and then at 723 K on one sample.

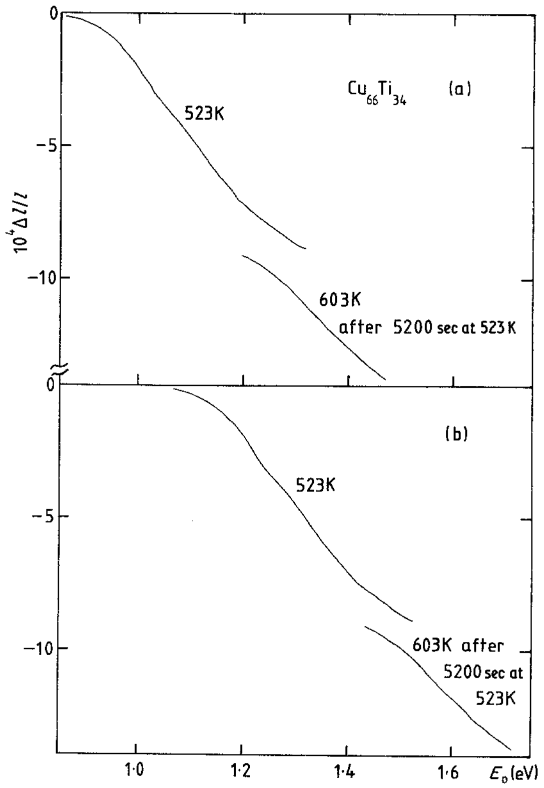

Figure 6 The data of Fig. 4 plotted as a function of E_0 with (a) $\nu_0 = 10^9\ \text{sec}^{-1}$ (b) $\nu_0 = 10^{11}\ \text{sec}^{-1}$.

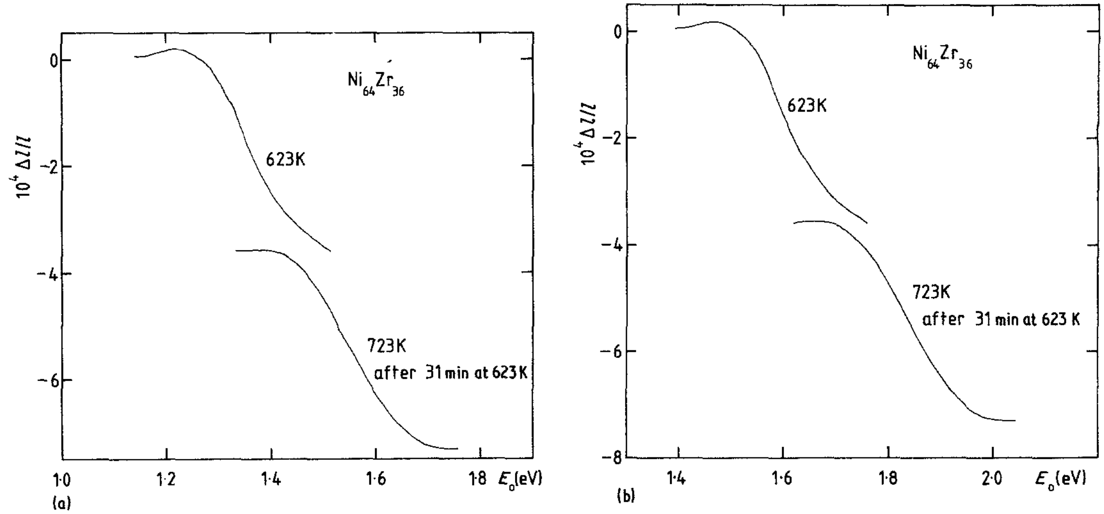

Figure 7 The data of Fig. 5 plotted as a function of E_0 with (a) $\nu_0 = 10^9$ sec^{-1} (b) $\nu_0 = 10^{11}$ sec^{-1}.

reversible component on cycling between two temperatures 100 K apart is much less than this measured expansion, and hence this expansion may contain an instrumental contribution. An alternative possibility is that the reversible processes are all to be found in the low energy region of the spectrum. This is discussed further below.

Cahn *et al.* [4] and Sinning *et al.* [11] describe an experiment to determine the magnitude of any reversible component to the length change. They cycle the temperature between 473 and 573 K holding for 13 min at each temperature. The specimen used had a pre-anneal at 623 K for at least 60 min. Fig. 8 is based on the original data of Sinning *et al.* [11]. The curves (marked (a)) for the amorphous material were reproducible between runs, as were those taken later for the crystalline material (marked (c)). Assuming the run for a crystallized specimen can be taken as a reference and only reflects instrumental changes which are common to runs on amorphous or crystalline material, then the difference between Curves (a) and (c) at a given temperature represent the reversible component due to changes in CSRO. The maximum value of the reversible component is thus found to be only 1% of the total length change on isothermal annealing. Assuming that the crystalline material exhibits no length changes due to changes in CSRO this value should be taken as an upper bound estimate to allow for instrumental effects which may be present. This is considerably less than the 3.5% expansion, relative to the total length change, noted above in Fig. 1. The range of E involved in this experiment (1.127 to 1.523 eV)

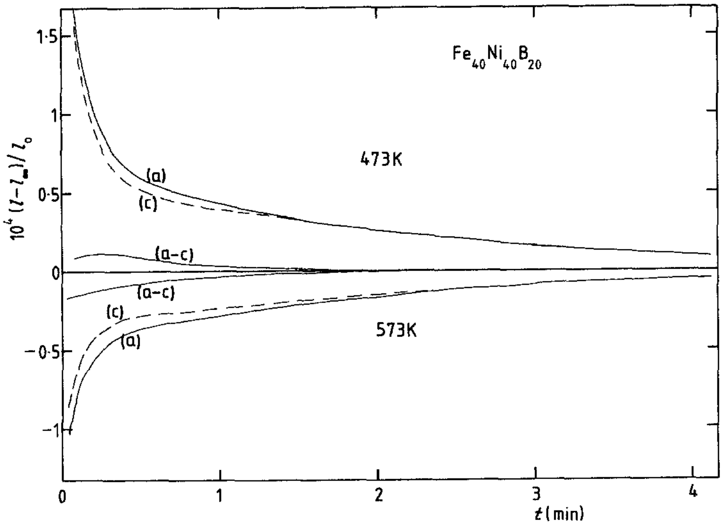

Figure 8 Reversible transients in length measurement of $Fe_{40}Ni_{40}B_{20}$ during cycling between 473 and 573 K, after Sinning *et al.* [11] (see text). (a) amorphous sample. (c) crystallized sample. (a—c) difference between (a) and (c). l_∞ = final length for each isothermal run. l_0 = initial specimen length.

is not the same as that for the expansion in Figs. 1 to 7, however, and may support the idea that the reversible processes are grouped at the low energy end of the spectrum.

From the above it can be concluded that for most of the range of E scanned in an isothermal experiment any reversible component in length change, which would manifest itself in ΔP for a given E_0, being a decreasing function of temperature, is likely to be lost in instrumental error and differences between specimens. ($Q(E)$ at the start of the experiment is determined by the quench rate, and this may vary along a reel of material.)

It is clear that the data in Figs. 1 to 7 do demonstrate that the concept of a master curve, in the case where the temperature dependence of $q_s(E, T)$ is negligible, is valid. If the temperature dependence was resolvable then the curves would be systematically displaced with respect to one another, the curve for the highest temperature showing the smallest $\Delta l/l$ for a given value of E_0 (from Equation 3).

Some of the isothermal data in Figs. 1 to 7 show an upward bending at longer times. It is believed that this may be instrumental in origin as its magnitude was variable between specimens. The initial increase in gradient of the data for pre-annealed specimens reflects the effect of the pre-anneal and has been discussed elsewhere [11, 12].

The van den Beukel *et al.* data [1], replotted in Fig. 1 have been corrected in two ways. From the work of Mulder *et al.* [16] it is possible to calculate the total length change from the initial ribbon to the end of the anneal. The values of $\Delta l/l$ plotted take this into account by the final point of the original data being replotted as this total length contraction and then earlier points being calculated with respect to this final point. Leake *et al.* [8] have discussed the effect of heating rate on the true annealing time. In the case of the data of van den Beukel *et al.* [1] the 20 min period during which the temperature stabilizes is approximately equivalent to a 20 min pre-anneal at the given annealing temperatures. In calculating E_0, 20 min is added to the times plotted in their data. The effect is most significant for the shorter times.

The data for the Cu–Ti alloy plotted in Fig. 6 support the concept of a master curve despite this alloy showing strong chemical order in diffraction experiments [17]. There is therefore difficulty in rigorously ascribing reversible behaviour with changes in CSRO as from the data available to date on this alloy showing strong chemical order, there is no enhanced reversibility on properties. Cowlam [18] has suggested that the order parameter may have only a small temperature-dependence in the temperature range studied.

Woldt and Leake [19] have discussed resistivity data on $Fe_{40}Ni_{40}B_{20}$ which shows reversible behaviour on cycling the temperature. They make out a case for $\overline{c(E)}q(E, T)$ $(= p_0(E)$ in their paper) being a function of E. The results of Figs. 1 to 7 support this viewpoint. The gradient $\Delta P/E_0$ at any instant, in the step function approximation, is $\overline{c(E)}q(E, T)$ from Equation 3. In the region of data where $\Delta l/l$ is linear with $\log t$ then the gradient is constant and Equation 5 can be used implying that $\overline{c(E)}q(E, T)$ is constant. For small E the gradient decreases. It can well be assumed that $q(E, T)$ and $q_s(E, T)$ tend to zero as E tends to zero on statistical grounds.

From their analysis van den Beukel *et al.* [1] claim that for anneals at temperatures below 578 K there is a larger contribution from CSRO changes, well above the level detectable in the experiment (of the order of 25% of total Δl at 546 K). They do remark that this contribution is surprisingly large. If the CSRO component is largely reversible, our value of 1% would be in sharp disagreement with these findings. They perform an analysis on the part of their Young's modulus data which they ascribe to CSRO changes and demonstrate that the activation energy is not constant throughout an isothermal anneal, in accordance with Gibbs *et al.* [3].

All the data we have presented here they would ascribe to having a large contribution from CSRO. Using their technique of taking cuts at constant $\Delta l/l$ and plotting the corresponding $\ln t$ against $10^3/T$ we obtain the results plotted in Figs. 9 and 10. The activation energy is agains seen to vary during an isothermal experiment in accordance with the ideas of van den Beukel *et al.* [1]. It should be noted that the values of Q calculated in Figs. 9 and 10 are often higher than any values plotted as E_0 in Figs. 1 to 7. There is a question as to whether the approach of taking cuts across the data is valid when the activation energy is varying with time [20].

In our data we have quantified the reversible component as undetectable as far as the data of Figs. 1 to 7 are concerned, and thus there should

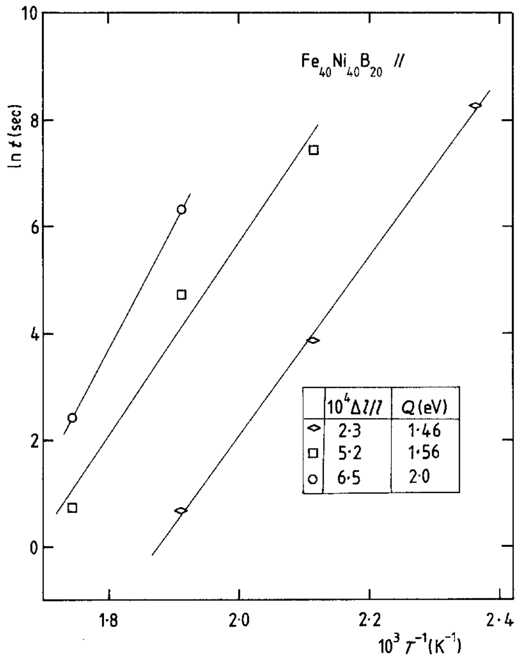

Figure 9 Arrhenius plots of ln *t* against T^{-1} for cuts at constant $\Delta l/l$ after van den Beukal and Radelaar [2], taken from the data of Fig. 1 along the specimen length (||).

be no effect of reversible CSRO changes and the temperature dependence of $q_s(E, T)$. By the argument of van den Beukel *et al.* the data should be demonstrating only irreversible TSRO changes.

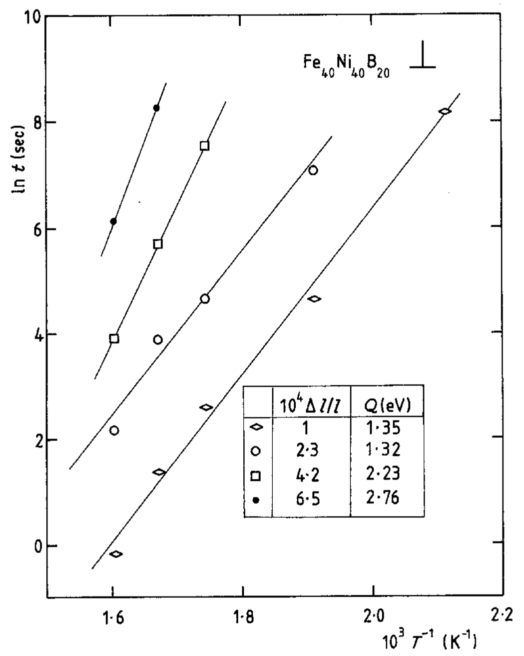

Figure 10 As Fig. 9, but for length changes across the specimen width in Fig. 1.

However, we find an activation energy varying with time. The way in which the data on a range of alloys, including all the data of van den Beukel *et al.* [1], group on to a master curve in accordance with the AES model for this case strongly supports the view that the whole process of $\Delta l/l$ against time should be explained in terms of a spectrum of activation energies. As stated by Gibbs [5] TSRO and CSRO changes are unlikely to occur separately in general, and the parameterization of the AES model is sufficient to account for the effects of changes in nearest neighbour number, spacing and identity. Hence the AES model is capable of producing a unified approach to relaxation data and is to be preferred to an approach which makes a sharp distinction between CSRO and TSRO changes.

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