idealized arrangement must exist, just as is found for GeTe itself. The unidexed reflections reported could not be indexed on the basis of an hcp structure related to the cubic close packed model.

At this stage more detailed statements about these structural distortions or the Ge atoms positions cannot be made except to point out that the indexed powder pattern indicates an almost body centred cell and so a body centred arrangement of Ge atoms might be expected. Although the proposed model for $GeTe_4$ has three-quarters of the possible octahedral Ge sites unfilled it is pertinent to note that the non-stoichiometry of GeTe also implies vacant Ge sites. Indeed it is possible that the build-up of vacant germanium sites along antiphase domain boundaries as postulated by Stoemenos *et al.* for GeTe, in fact gives rise to a slab of structure related to that of $GeTe_4$.

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Comments on "Glass-ceramics with random and oriented microstructures Part 2 The physical properties of a randomly oriented glass-ceramic"

Atkinson and McMillan have provided useful information on the mechanical, electrical and thermal properties of the glass ceramic material they studied [1]. However, consideration of their mechanical property results which are of particular interest to us, suggests that this aspect of their study is incomplete in a number of respects.

Before turning to a detailed consideration of their experimental data and its analysis it is appropriate to consider the theoretical background. A common basis for such analysis, as recognized by Atkinson and McMillan, is the Griffith equation:

$$\sigma = A_1\sqrt{(E\gamma/c)} \qquad (1)$$

where σ = the failure stress, A_1 = a flaw shape parameter, E = Young's modulus, γ = the fracture surface energy, and c is the flaw size. The first task is to determine whether or not the Griffith equation is valid for the particular conditions, or whether it can be made valid if appropriately modified. Validity can be established by measuring all parameters and showing that there is true equality.

Two conditions pertinent to the present material can make the above simple form of the Griffith equation invalid. The first is the contribution to failure that may be made to the failure stress by internal stresses resulting from the incompatible strains either between grains of the typically non-cubic phases that are produced, or between these phases and the residual glass matrix. Earlier work has shown that such stresses can add to the applied stress to aid failure [2] and more recent work corroborates this and shows that the extent to which these stresses add to the applied stress depends on the ratio of the flaw size to the grain size [3–5]. For fine grain bodies as in the materials of interest here, a contribution of the internal stress to failure may not disappear until flaw sizes of the order of 100 times the grain size has been reached [4, 5], in which case the Griffith equation can be modified by adding their contribution to the applied stress. The second somewhat related condition that can prevent the simple Griffith equation from being fully valid is if microcracks form. One may then be dealing with a large number of cracks, in which case the simple Griffith equation may no longer be valid and solutions for the multiplicity of cracks may not be available.

Even in the absence of sufficient data to check the equality of the Griffith equation there are experimental clues that either or both of the above effects may be occurring. First, fracture stresses of crystallized glasses are typically higher than the apparent glass because the Young's modulus and the fracture energy typically increase, while flaw sizes may not change significantly [6, 7]. Thus, for example, a drop in strength in the crystallized glasses below that of the parent glass as observed by Atkinson and McMillan implies the contribution of internal stresses or microcracks to the failure of the material. Second, Young's modulus falling below that of the glass (occurring in two of the heat treatments of Atkinson and McMillan) is a strong indication that microcracking is occurring. On the other hand, only one case of a low Young's modulus corresponds with a heat treatment giving a strength below that of the parent glass. The unusually low strength is not one of these cases and hence is not explained by an unusually low Young's modulus (see Table I), which could thus imply internal stresses. It should be noted that microcracking has been suggested as the cause of such deviations in Freiman and Henches' [6] study of Li_2O-SiO_2 glass-ceramics and the study of Freiman *et al.* on $BaO-SiO_2$ glass-ceramics [7], and was also indicated by Sahoo *et al.* [8]. It is further pertinent to note that in Freiman and Henches' Li_2O-SiO_2 studies that these deviations were suggested at mean free paths within an order of magnitude of those in the present study. Thus depending upon the actual grain size, the degree of nucleation and the particular heat treatments, microcracking may have contributed to some of the results of Atkinson and McMillan. For those cases where the Griffith equation is applicable, it is important to note that all of the parameters may depend on the microstructure.

Turning now to Atkinson and McMillan's analysis, they rejected the equation:

$$\sigma = A_2 d^{-1/2} \tag{2}$$

TABLE I Original data(1) calculations

Heat treatment temperature (° C)	Hardness ($kg\,mm^{-2}$)	Young's modulus ($\times 10^{0}\,N\,m^{-2}$)	Fracture stress ($\times 10^{7}\,N\,m^{-2}$)	Mean free path, λ (μm)	γ/c(5) ($J\,m^{-2}\,\mu m^{-1}$)	γ(6) ($J\,m^{-2}$)	c'(7) (μm)	γ(8) ($J\,m^{-2}$)
640	640	3.5(2)	9(3)	0.25	0.23	6.9	45	10.4
690	660	8	7(4)	0.28	0.06	1.8	26	1.6
720	730	7	17	0.18	0.41	12.3	16	6.5
760	630	12	20	0.13	0.33	9.9	20	6.4
810	590	4.5(2)	17	0.18	0.64	19.2	36	23.0
870	510	9	15.5	0.18	0.27	8.1	20	5.5

(1) Basic data read as well as possible from data plots of Atkinson and McMillan [1]
(2) Values below that of parent glass ($E = (5.4 \pm 0.6) \times 10^{10}\,N\,m^{-2}$)
(3) Value slightly below that of parent glass ($\sigma_f = (9.7 \pm 0.6) \times 10^{7}\,N\,m^{-2}$)
(4) Value below that of parent glass ($\sigma_f = (9.7 \pm 0.6) \times 10^{7}\,N\,m^{-2}$)
(5) Calculated from Equation 1 assuming $A_1 \sim 1$
(6) Calculated from γ/c assuming $c = 30\,\mu m$
(7) Calculated from Equation 5, assuming $A_6 = 140$; i.e. so the average flaw size is again about $30\,\mu m$
(8) Calculated from γ/c assuming $c = c'$

where A_2 = a constant of proportionality and d = the grain size. This rejection was based only on their evaluation of strength and grain size data, i.e. neglecting their significant, nearly three-fold variation in Young's modulus, and the undetected but also possibly significant variations in fracture energy, as shown in Table I and discussed below.

Thus, while their experimental data allows them to reject Equation 2, it does not allow them to reject the possible correlation of d with the flaw size. However, this rejection of Equation 2 is most likely correct based on more recent results considering the ratio of the likely flaw sizes (20 to 50 μm) to the grain sizes ($\approx 1\,\mu$m). Flaw sizes larger than grain sizes are essentially independent of the grain size and grain size controls strength only when the flaw size is similar to or less than the grain size [9–11].

Atkinson and McMillan next considered the relationship:

$$\sigma = A_3 \lambda^{-1/2} \tag{3}$$

where A_3 = a constant, and λ = the mean free path between crystalline phase. Two factors should be considered in applying this relationship. The first is that there is an upper limit of mean free path beyond which this cannot apply. When λ is large in comparison with the flaw size, the particles have no effect on the flaw. This limit is not pertinent in the present case. The second factor is that the flaw size and mean free path should only be directly related when λ is within a few times the flaw size since the flaw size is in fact dependent on the spacing between particles limiting its size. Thus, in analogy with the question of grain size–flaw size correlations as the flaw becomes substantially larger than the mean free path, it is difficult to conceive how the flaw is limited by the spacing between the grains surrounding the flaw when it was not inhibited by such spacings through or around which the flaw has already propagated. In the present case mean free paths are of the order of 0.25 μm, about two orders of magnitude below the expected flaw size. Hence one may question the applicability of Equation 3 unless the mean free path dependence arises from other than flaw correlations, for example due to internal stresses or microcracking.

There is a second relationship of strength to the mean free path not discussed by Atkinson and McMillan. This results from the possible dependence of γ on mean free path [12]; i.e.

$$\gamma = \gamma_0 + A_4/L \tag{4}$$

where γ_0 = the fracture energy of the matrix L = particle spacing and A_4 = a constant. Here flaw sizes substantially larger than the mean free path are allowed and one considers the effect (on the fracture energy) of the crack front interacting with the particles. Freiman and Hench found neither Equation 3 nor 4 fit their Li_2O-SiO_2 data very well. As will be shown below, Equation 4 would not fit Atkinson and McMillan's data either.

Atkinson and McMillan apply Equation 3 to their data since they did indeed find a correlation between strength and the inverse square root of the mean free path. It is at this point that their approach may be questioned. First, while the data shows a dependence of σ on $\lambda^{-1/2}$, the line does not pass through zero as required by Equation 3, but in fact has a negative intercept. Thus, it also does not fit Equation 4 which gives a positive intercept. Atkinson and McMillan neglect the non-zero intercept and assume that strength is directly correlated with fracture energy, a situation contrary to both the analysis given below, and the wide variation in Young's modulus (see Table I), and thus calculate a fracture energy from the slope of their σ versus $\lambda^{-1/2}$ plot. They obtain a value of 0.2 J m^{-2} and suggest that this low value is consistent with fracture initiation occurring in the glass phase. This is unlikely since no silicate glass system, or in fact any ceramic glass system, is known which has such a low fracture energy. Typical fracture energies to be expected are at least 20 to 30 times the values that they calculate [13].

The importance of considering the above parameters can be seen by attempting to further analyse the data of Atkinson and McMillan. First, assuming that the basic Griffith Equation holds and that the flaws are of a simple, regular shape (for example a typical penny shape), we can calculate the ratio of the fracture energy to the flaw size from their strength and Young's modulus data, obtaining the results shown in Table I. Furthermore, based on fracture energy measurements in other similar systems including the LiO_2-SiO_2 system [6] one can calculate the size of such simple flaws to be of the order of 30 μm. Such sizes are substantiated by fractography, which is generally applicable to glassy or fine grain bodies [11, 14]. Fig. 1 is an example, showing the failure-initiating flaw in glass-ceramic samples fractured after either tumbling with abrasive or diamond grinding. It should be noted that while tumbling of samples with abrasive grit in a mill is a convenient method for obtaining a population of samples that do not have too wide a spread of strength, it commonly produces a flaw shape which is of the size suggested, but is more difficult to characterize adequately numerically for exact calculation since the flaw is not a simple planar flaw, often being part of a Hertzian cone-type crack. On the other hand, machining of ceramics, typically by diamond grinding, usually produces simple, elliptically shaped flaws which can usually be characterized quite adequately for numerical analysis, see [10] and Fig. 1b.

Assuming that the flaw size is constant at a typical value of 30 μm, which as discussed above is a reasonable value for similar systems, the fracture energies γ, can be calculated for each heat treatment (Table I). Two resultant values are clearly extreme. The very high value is for a heat treatment having an unusually low Young's modulus. Such a high apparent fracture energy is

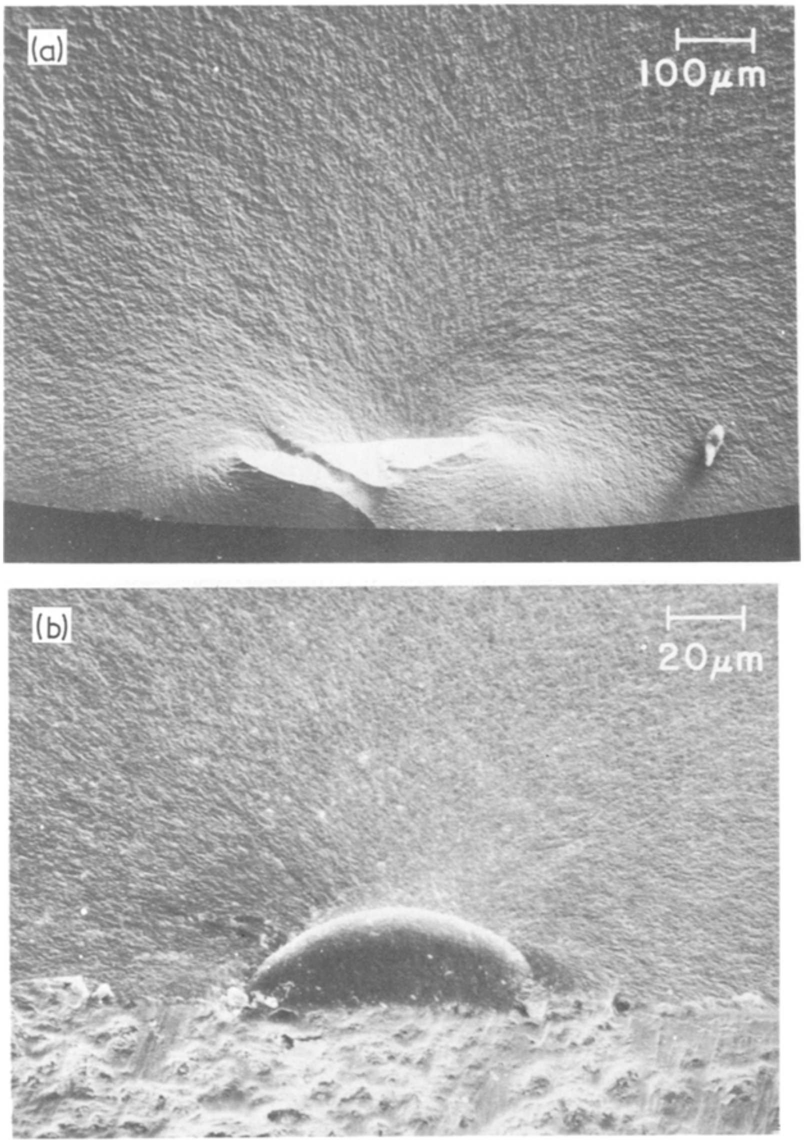

Figure 1 Keatite glass-ceramics fracture origins from (a) tumbling round rods with an abrasive and (b) diamond grinding parallel with the tensile axis prior to flexure testing. The specimen in (a) had a fracture stress of 19 000 p.s.i. and the one in (b) 14 000 p.s.i. (which gives a calculated fracture energy of ~ 5 J m^{-2} from the observed flaw size and shape).

consistent with microcracking, as is the low modulus. The other extreme value of fracture energy, which is unusually low, is for the heat treatment that gave an unusually low strength. This lower apparent fracture energy would be consistent with internal stress effects, as is the low fracture strength. Thus, the major deviations are consistent with two of the three heat treatments showing significant deviations in Young's modulus and strength.

It should be noted that if internal stresses or microcracking are significant, then the common tendency for an approximately constant flaw size may not be valid. Probable variations in flaw sizes can be estimated using relationships developed for indentation-caused cracks. Such relationships, which have also been used to calculate flaw sizes from impact and abrasion, give [15]

$$c = A_5(H^2/E\gamma)^{1/3} \sim A_6(H/E)^{2/3} \qquad (5)$$

where H = hardness and A_5 and A_6 are proportionality constants. Table I shows flaw sizes and fracture energies using Equation 5. This makes the two cases that were extreme using a constant flaw size, even more extreme. It also reduces the somewhat high values of γ for the 720 and 760° C heat treatments to values that are probably more realistic. This variable flaw estimate also increases the fracture energy for the 640° C heat treatment which had a low Young's modulus, and somewhat low strengths. The variable flaw treatment thus gives extreme fracture energies for all samples having either low Young's moduli, strength or both.

In summary, neither of the above analyses gives a good correlation of flaw size and mean free path, again suggesting that correlation of λ with strength may be due to other causes. Furthermore, assuming either constant or variable flaw sizes gives reasonable fracture energies of a few J m^{-2}, except for bodies showing deviations in strength, Young's modulus or both. These deviations are consistent with possible internal stresses or microcracking. Finally, these observations clearly show the utility of more comprehensive measurements; i.e. at least including fracture energy, and flaw measurements along with strength and Young's modulus measurements.

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Reply to 'Comments on "Glass-ceramics with random and oriented microstructures Part 2 The physical properties of a randomly oriented glass-ceramic"'

We agree that our data on mechanical properties are incomplete in the sense that we did not undertake an exhaustive study of these. However, as will be obvious from our paper, the mechanical strength investigations formed but a small part of an overall study of the properties and microstructures of a glass-ceramic composition.

We rule out the occurrence of microcracking in our materials since a detailed study of all the glass-ceramics by electron microscopy was undertaken [1] and the presence of microcracks would have been readily detected. There is no doubt however that the Li_2O-SiO_2 glass-ceramics of Freiman and Hench [2] were grossly microcracked as is clearly shown by the micrographs in the paper. Cracks are clearly visible in these materials even at a magnification as low as X350 and these have lengths of the order of 30 μm. The evidence for microcracking of the $BaO-SiO_2$ materials of Freiman *et al.* [3] seems much less certain though we do not contest the contention of Freiman and Rice that these were in fact microcracked. It should be pointed out, however, that both the Li_2O-SiO_2 and $BaO-SiO_2$ materials largely contained crystals having a spherulitic morphology and this is likely to result in microcracking and/or high internal stresses. The glass-ceramics we produced contained lathlike and equant crystals of small dimensions and there was no evidence of spherulitic morphology whatsoever.

We wish to make it clear that while we discount the applicability of the equation:

$$\sigma = K_1 d^{-1/2}$$

We do not reject the possible correlation of d with flaw size because the mean free path, λ, is dependent on both d and V_f, the volume fraction of crystalline phase.

We agree that if the flaw sizes were indeed two orders of magnitude greater than the mean free path values, there would be difficulty in understanding how the flaw size could be limited to the spacing between the grains. We believe, however, that there is no evidence whatsoever that flaws of this magnitude exist in our materials. Furthermore, the evidence for the existence of flaws having these dimensions in other glass-ceramics is not soundly based. We are unable to understand how the work of Freiman and Hench [2] can be used on the one hand to support the contention that microcracking leads to deviation of mechanical properties and can also be used to support the proposition that all glass-ceramics contain flaws of a size of about 30 μm. Surely, fracture energy measurements on grossly microcracked materials will only yield information concerning the extent of microcracking and will indicate an approximately constant "flaw size". Later in their comment, Freiman and Rice allow the possibility that flaw sizes may not be constant, especially for microcracked materials, yet they use mechanical property data obtained for microcracked materials to support their contention of constant flaw size. Use of our hardness data to calculate a mean flaw size in apparent agreement with the value suggested earlier does not add anything because the value obtained for flaw size depends directly on the value obtained the constant A_6 and no justification is given for the value chosen by Freiman and Rice.

We have no comment to make on the fact that our data do not fit the Lange equation except to add that the results of Hing and McMillan [4] did not fit this equation either.

The calculations given in the comment unfortunately do not advance the understanding of the microstructural dependence of mechanical properties of glass-ceramics. This may not be surprising if, as we believe, the estimates of flaw sizes are unsound. What has been clearly established by experimental study is the relationship between σ and $\lambda^{-1/2}$ as given in Fig. 4 of our paper. This same relationship was found to hold for a different family of glass-ceramics by Hing and McMillan [4] and has been further confirmed in more recent unpublished work. The failure of the curve in Fig. 4 to pass through zero may indicate the existence of some bias in the data. We suggest that an approximately constant internal stress might account for this. If the stress varied for different heat treatments, it would have to be proportional to $\lambda^{-1/2}$ to account for the straight line relationship. While this cannot be ruled out, we can find no basis for a relationship of this kind.

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Pre-precipitation in Al—0.1 wt % Cr alloy

Tracer diffusion measurements in aluminium show that the 3d transition metals, particularly chromium, iron and manganese, diffuse with high activation energies [1–3]. Kinetic studies on supersaturated Al–Cr solid solutions lead to an activation energy of 3.14 eV for the decomposition process [4]. It would be interesting to check whether these large values of the activation energy have any bearing on the interaction between chromium atoms and vacancies in Al–Cr alloys. The pre-precipitation phenomenon in a quenched Al–0.1 wt % Cr alloy is studied in this investigation by electrical resistivity measurements and transmission electron microscopy. The isothermal annealing data are analysed to evaluate the magnitude of the chromium–vacancy binding energy.

The Al–0.1% Cr alloy was prepared from 99.999% pure aluminium and a master alloy containing 5% chromium. The ingot, after homogenization at 600° C for 120 h, was reduced in a number of stages to a 0.1 cm diameter wire. Electrical resistivity measurements were carried out at liquid nitrogen temperature on samples with a length to area ratio of $7.47 \times 10^3\,\text{cm}^{-1}$, using a precision Kelvin bridge. Samples for isochronal and isothermal annealing treatments were quenched from 500° C into iced brine at 0° C and the as-quenched resistivity ρ_q measured immediately. Isochronal treatments were carried out at intervals of 10° C in the temperature range 0 to 100° C for a fixed time of 5 min at each temperature; the resistivity ρ_T was measured after every step. Isothermal studies were made in the temperature range 0 to 30° C by measuring the resistivity ρ_t of the sample as a function of time. A final anneal at 70° C for 30 min was used to measure the resistivity ρ_∞, corresponding to the resistivity after completion of the recovery stage. The samples for electron microscopic examination were obtained by electro-polishing strips 3.0 cm × 1.5 cm × 0.02 cm quenched from temperatures in the range 500 to 600° C into brine at 0° C and aged for 24 h at 20° C.

The results of the isochronal annealing experiments are shown in Fig. 1 where the difference in resistivities, $\rho_q - \rho_T$, is plotted against temperature. There is a prominent recovery stage in the temperature range 0 to 40° C which is similar to that observed in a number of aluminium-base alloys [5]. The experimental data for the kinetics of this recovery stage are shown in Fig. 2 as plots of $\Delta\rho/\Delta\rho_0$ against time where $\Delta\rho = \rho_t - \rho_\infty$ and $\Delta\rho_0 = \rho_q - \rho_\infty$. The errors in the experimental points are small (< 5%) in the early stage of annealing, becoming significant (~ 15%) in the later stages. The kinetics are of the first order for long annealing times, as deduced from the linearity of the ln $(\Delta\rho/\Delta\rho_0)$ against time plots, with transients present in the early stages.

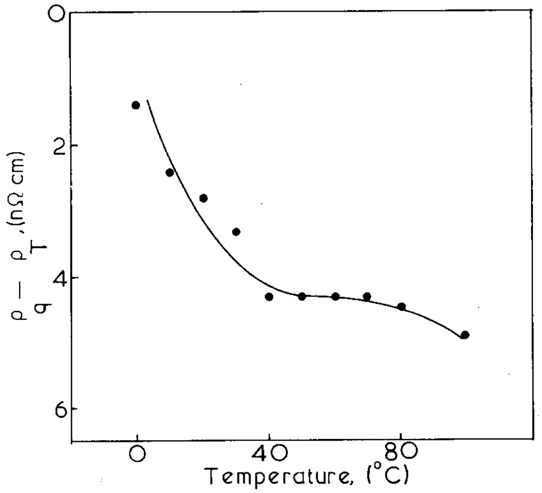

Figure 1 Isochronal annealing of Al–0.1% Cr alloy quenched from 500° C.