

voltage being a function of the quenching temperature [12].

The tetragonal distortion in  $\text{CuFe}_2\text{O}_4$  occurs as a result of a heavy concentration of distorting  $\text{Cu}^{2+}$  cations at the octahedral sites (B-sites), as evidenced in Table III. The concentrations of  $\text{Cu}^{2+}$  ions at B-sites is affected by temperature; becoming less and less for higher and higher temperatures. When the samples are quenched from elevated temperatures the cation distribution is frozen-in. When more than 25% of the  $\text{Cu}^{2+}$  ions migrate to A-sites, the tetragonal structure becomes cubic. Hence  $c/a$  values show temperature dependence.

Samples of  $\text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$  ( $x \neq 1$ ), slow-cooled and quenched, exhibit a cubic structure. The cation distribution given in Table III shows that in all these samples the concentration of  $\text{Cu}^{2+}$  ions at B-sites is less than 75%. Hence, these samples do not exhibit tetragonal distortion of the lattice and show a cubic structure.

The linear increase in  $a$  with the addition of  $\text{Zn}^{2+}$  in  $\text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$  can be attributed to the atomic volume differences wherein the atomic sizes do not appear to show any relaxation.

In  $\text{Cu}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$  samples more  $\text{Cu}^{2+}$  ions are transferred to A-sites on addition of Zn and on quenching the sample from  $800^\circ\text{C}$  compared with the transfer of  $\text{Cu}^{2+}$  ions in the slow-cooled and quenched  $\text{Cu}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$  samples. Hence, on quenching  $\text{Cu}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$  samples, the lattice parameter shows a larger change than the  $\text{Cu}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$  sample. As there is no significant

transfer of  $\text{Cu}^{2+}$  ions to B-sites on quenching the remaining samples, the lattice parameter also does not show a detectable change.

**References**

1. A. BERGESTEIN, L. CERVINKG, *Czech J. Phys. B* **11** (1961) 584.
2. N. NANBA and S. KOBAYASHI, *Jap. J. Appl. Phys.* **17** (1978) 1819.
3. T. YAMASHIRO, *ibid.* **12** (1973) 148.
4. K. K. LARROIA and A. P. B. SINHA, *IJPAP* **4** (1966) 187.
5. E. PRINCE and R. G. TREUTING, *Acta Crystall.* **9** (1956) 1025.
6. K. SAGAL and F. TEBELLEN, "Rontgenstruktur-analyse", (Springer, Berlin, 1958).
7. E. F. BERTANT, *J. Phys. Rad.* **12** (1951) 252.
8. C. DELORMA, *Bull. Soc. France, Min. Crist.* **81** (1958) 79.
9. N. S. SATYAMURTHY, M. G. NATERA and S. I. YOUSSEFFI, *Phys. Rev.* **181** (1969) 696.
10. M. A. GILLES, *J. Phys. Chem. Sol.* **13** (1960) 33.
11. R. S. TEBBLE and D. J. CRAIK, "Magnetic Materials", (Wiley-Interscience, New York, 1969) p. 262.
12. S. R. SAWANT and R. N. PATIL, unpublished work (1980).

Received 18 January  
and accepted 9 April 1981

S. R. SAWANT  
R. N. PATIL  
*Department of Physics,  
Shivaji University,  
Kolhapur 416004,  
India*

*Comments upon a statistical model of strength*

Recently, a general expression for the failure probability of a brittle material, based upon the presumed knowledge of the flaw-size distribution in the material, was formulated by Jayatilaka and Trustrum [1]. The resulting strength distribution was compared to the standard one given by Weibull [2]. Subsequently, Rickerby [3] extended this analysis to the case where a bimodal flaw distribution is existant in the material. He obtained the first correction to the Weibull distribution in the low strength regime.

In this note, several comments are made with regard to the applicability of these results in the low and high strength regimes.

Jayatilaka and Trustrum [1] obtained the following expression for the cumulative failure probability,  $P_f$ , for a system containing  $N$  cracks:

$$P_f = 1 - [1 - F(\sigma)]^N, \tag{1a}$$

where

$$F(\sigma) = \int_0^x du \left(1 - \frac{u}{x}\right) \frac{u^{n-2} e^{-u}}{(n-2)!} \tag{1b}$$

and

$$x \equiv \sigma^2 \frac{\pi c}{K_{IC}^2}. \tag{1c}$$

In Equations 1a to c,  $F(\sigma)$  is the cumulative failure probability for a single crack up to stress  $\sigma$ ,  $K_{IC}$  is the critical stress intensity factor and  $c$  and  $n$  are parameters in the flaw-size distribution. One may integrate Equation 1b to obtain,

$$F(X) = 1 + \frac{(n-1)}{x} (e^{-x} - 1) + e^{-x} \left\{ \sum_{j=1}^{n-2} x^{n-j-2} \left[ \frac{(n-1)}{(n-1-j)!} - \frac{1}{(n-j-2)!} \right] \right\} \quad (1b^1)$$

Jayatilaka and Trustrum [1] argued that for large  $N$  Equation 1a may be written as

$$P_f \approx 1 - e^{-NF} \quad (2)$$

and hence for small  $x$  (and large  $N$ ) they find

$$\ln(1 - P_f) = -N \left[ \frac{x^{n-1}}{n!} - \frac{x^n (n-1)}{n! (n+1)} \right] \quad (3)$$

The first term on the right-hand side of Equation 3 may be considered as the Weibull term and the second as the correction.

Equation 3 is correct to  $O(x^n)$ , except for the case  $n = 2$ . This is a result of the fact that Equation 2 derives from the small  $\sigma$  (and not large  $N$ ) approximation. In order to obtain a consistent expansion in  $x$  valid to  $O(x^n)$ , one must expand the  $\ln$  term as well as  $F$ .

$$\begin{aligned} \ln(1 - P_f) &= N \ln(1 - F) \\ &= N \left( -F - \frac{F^2}{2} - \dots \right) \quad (4) \end{aligned}$$

If  $n > 2$  then only the first term in the expansion shown in Equation 4 need be retained to obtain a result valid to  $O(x^n)$  since  $F \sim x^{n-1} + O(x^n)$ . However, for  $n = 2$  the  $F^2$  term contributes to the first

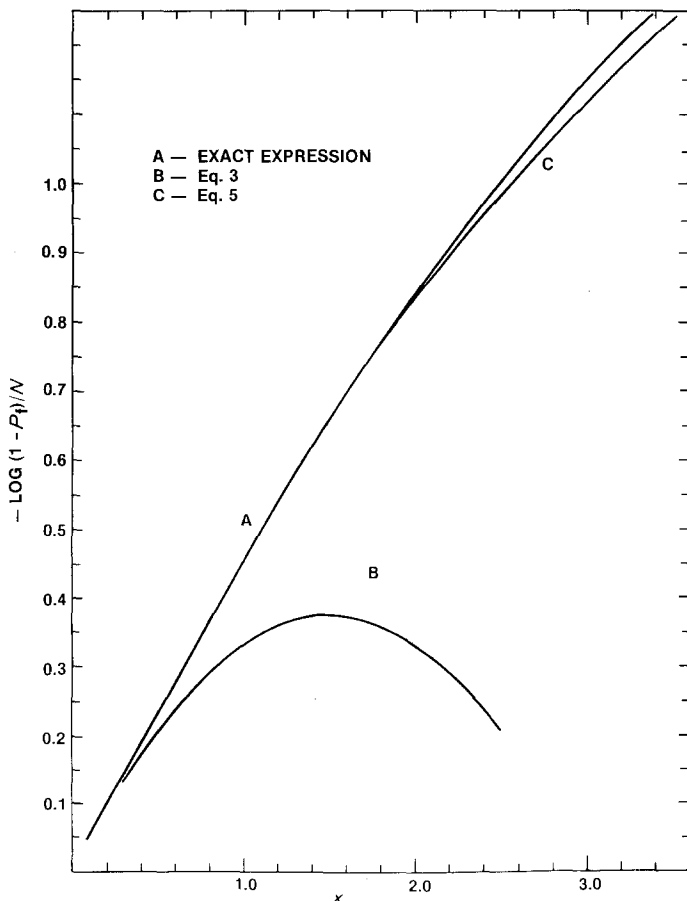


Figure 1 -  $\ln(1 - P)/N$  against  $x$  for  $n = 2$ .

correction to the Weibull term. To illustrate this point,  $[-\ln(1 - P_f)]/N$  was plotted for  $n = 2$  in Fig. 1. It is observed that Equation 3 deviates from the exact result by a wide margin, while the correct  $O(x^2)$  expression,

$$\frac{-\ln(1 - P_f)}{N} = \left(\frac{x}{2} - \frac{x^2}{24}\right) \quad (5)$$

agrees well with the exact result. Thus, in the special case  $n = 2$  the first-order correction to the Weibull term given by Jayatilaka and Trustrum [1] will be in error. In general, (for  $n \geq 2$ ) corrections of  $O(n - 1)$  and higher to the Weibull distribution must account for all appropriate terms in the expansion given in Equation 4 in a consistent manner.

In the case of the bimodal version of this flaw distribution (as used by Rickerby [3]),

$$f(a) = \frac{P_1 c_1^{n_1-1} a^{-n_1} e^{-c_1/a}}{(n_1 - 2)!} + \frac{P_2 c_2^{n_2-1} a^{-n_2} e^{-c_2/a}}{(n_2 - 2)!} \quad (6)$$

it is easy to show that

$$\ln(1 - P_f) = N \ln \left\{ 1 - P_1 \left[ F(x, n_1) + \frac{(1 - P_1)}{P_1} F(\alpha x, n_2) \right] \right\}, \quad (7)$$

where  $F$  is the distribution given by Equation 1b<sup>1</sup> and  $\alpha \equiv c_2/c_1$ . The approximate form which  $\log(1 - P_f)$  assumes for small  $x$  is not only dependent upon the small  $x$  behaviour of  $F$ , but also upon the values of the parameters  $\alpha, n_1, n_2$ , and  $P_1$ . For example, if  $n_2 \gg n_1$  and  $1 \gg \alpha$  (and  $P_1$ , not too small), then for small  $x$ ,  $F(\alpha x, n_2)$  will not contribute to  $\ln(1 - P_f)$ . This case would correspond to the situation where the second distribution is centred about a very small flaw size and the distribution decays rapidly with increasing flaw size. Rickerby [3] obtained an expression for the first-order correction to the Weibull distribution, for the case of a bimodal flaw distribution, for  $n_2 > n_1$  and small  $x$ . However, by performing a careful  $x$  ordering procedure one may show that this expression is valid only under limited circumstances. For example, if  $\alpha = 1$ , then his expression will be correct only if  $n_2 \approx n_1 + 1$ . For  $\alpha \neq 1$ , there will be

a similar restriction upon the relationship between  $n_1$  and  $n_2$ . Thus, there exist a myriad of cases and the correct small  $x$  approximation depends upon the values of the parameters  $(\alpha, n_1, n_2, P_1)$  characterizing the distribution.

One may experimentally probe the small flaw region of a distribution by using small samples and thereby avoiding the large flaws in at least a number of samples. For sufficiently large  $x$  one may show (employing Equation 1b<sup>1</sup>) that

$$\ln(1 - F) = \ln \left[ \frac{(k + 1)}{x} \right]. \quad (8)$$

Although it is difficult to unambiguously ascertain that one is probing the high-strength regime, results on glass fibre strengths seem to indicate that this regime has been probed [4]. Here however, the strength distribution (at least at the highest strengths) often appears to be of the Weibull form [4, 5] and unlike the result predicted by Equation 7. In Fig. 2 this point is illustrated by showing the results of some fibre strength measurements made in our laboratory. Several features should be noted. First, the high-strength regime is most likely being probed since some of the reported strengths are a reasonable fraction of the theo-

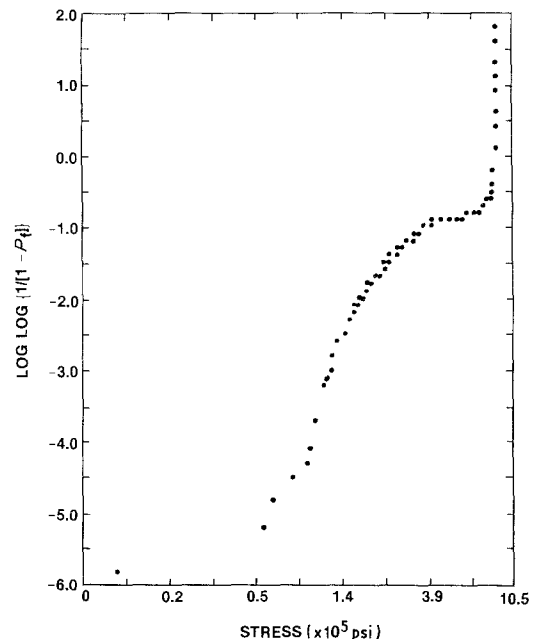


Figure 2  $\ln \ln [1/(1 - P)]$  against stress ( $10^5$  psi) for glass fibre.

retical strength. Next, one notes that at the highest strengths Weibull statistics are obeyed quite well, with deviations occurring as one proceeds to lower strengths. These results are fairly typical for fibres and thus seem to suggest that the size distributions employed above are probably inappropriate for the description of flaws in glass fibres.

## References

1. A. De S. JAYATILAKA and K. TRUSTRUM, *J. Mater. Sci.* **12** (1977) 1426.
2. W. WEIBULL, *J. Appl. Mech.* **18** (1951) 293.
3. D. G. RICKERBY, *J. Mater. Sci.* **15** (1980) 2466.
4. F. V. DIMARCELLO, A. C. HART Jr, J. C. WILLIAMS and C. R. KURKJIAN, in "Fiber Optics, Advances in Research and Development", edited by B. Bendow and S. S. Mitra, (Plenum Press, New York, 1979), p. 125.

5. H. SCHONHORN, C. R. KURKJIAN, R. E. JAEGER, H. N. VEZIRANI, R. V. ALBARINO and F. V. DIMARCELLO, *Appl. Phys. Lett.* **29** (1976) 712.

Received 27 February  
and accepted 26 March 1981

MICHAEL C. WEINBERG  
GTE Laboratories,  
40 Sylvan Road,  
Waltham, MA 02254, USA

## Reply to "Comments on a statistical model of strength"

An implicit premise of the statistical theory of strength [1] is that the flaw density in the material is sufficiently high that the probability  $F$  of a given flaw propagating will be small. Under these circumstances Equation 2 of Weinberg [2] should closely approximate the failure probability  $P_f$  for the entire specimen [3]. This is true for low values of  $F$  (i.e. large  $N$ ), rather than necessarily for small stress,  $\sigma$ , as claimed by Weinberg [2]. The separate approximation leading to his Equation 3, however, does depend on the smallness of the parameter  $x = \sigma^2 \pi c / K_{IC}^2$  (where  $c$  is a parameter in the flaw size distribution and  $K_{IC}$  is the Mode I critical stress intensity factor), and the upper limit of its applicability is  $x = (n + 1)/n$  [4] (where  $n$  is a parameter in the flaw-size distribution), corresponding to the maximum in Curve B of Fig. 1 of Weinberg [2].

Weinberg [2] has noted that for the special case where  $n = 2$ , his Equation 3 is inexact because the term in  $x^n$  is improperly approximated. Similar problems would arise for higher values of  $n$  only if higher order terms were considered. As relatively few flaws are required to be present in a specimen for the approximate analysis to be valid [3], and flaw densities are high in typical brittle materials [5, 6], more extensive order analysis will not generally be necessary.

For a bimodal flaw-size distribution the stress

dependent correction term affects the relative contribution to the overall failure probability [4]. Provided that the small  $x$  restriction is maintained the validity of Weinberg's [2] Equation 7 will not be limited in the manner suggested. The contribution of higher order terms will be negligible compared with the first two terms, under small  $x$  conditions, for both component flaw populations. Therefore, whichever population is dominant, the major contribution to the failure probability will still be well approximated by the first two terms in each case. The determination of the relative importance of the respective populations is already embodied in the existing theory.

The experimental data presented for glass fibres are indicative of a high density of rather small flaws leading to the high stress Weibull type behaviour, together with occasional large flaws in only some of the specimens causing lower stress failures [7]. Results of indentation strength tests correlate well with the previously proposed corrected theory [8], but lie in an intermediate stress range between experiments on fibres and large flexural or tensile specimens. It is debatable whether the statistical theory can truly be considered appropriate to failures due to isolated large flaws in the fibres, since the existence of a plateau between the high and low stress data suggests that these more severe flaws fall in a discrete size range rather than forming a continuous distribution. Nevertheless, the gradually decreasing slope of the lower stress data would be expected, on the basis

of Equation 7 of [2], for a bimodal distribution in which there was little or no overlap between the large and small size range flaw populations.

**References**

1. W. WEIBULL, *Ingeriörsvetenskapsakad. Handl.* Number 151 (1939).
2. M. C. WEINBERG, *J. Mater. Sci.* 16 (1981) 3499.
3. A. De S. JAYATILAKA and K. TRUSTRUM, *ibid.* 12 (1977) 1426.
4. D. G. RICKERBY, *ibid.* 15 (1980) 2466.
5. A. S. ARGON, *Proc. Roy. Soc. A* 250 (1959) 482.
6. T. R. WILSHAW, *J. Phys. D* 4 (1971) 1567.
7. R. E. MOULD, *J. Appl. Phys.* 29 (1958) 1263.

8. D. G. RICKERBY, in "Advances in Fracture Research", Proceedings of the 5th International Conference on Fracture, Cannes (Pergamon Press, Oxford, 1981).

*Received 29 June  
and accepted 30 June 1981*

D. G. RICKERBY  
*Materials Science Division,  
Commission of the European Communities,  
Joint Research Centre,  
21020 Ispra, Varese,  
Italy*

*X-ray characterization of SrCeO<sub>3</sub> and BaCeO<sub>3</sub>*

The compounds SrCeO<sub>3</sub> and BaCeO<sub>3</sub> have been examined by numerous authors in order to determine their crystal structures. Both compounds exhibit non-ideal perovskite-type crystal structures; with regard to their symmetry, however, a great deal of the data reported in the literature are often in disagreement.

SrCeO<sub>3</sub> has been assigned, with varying lattice parameters, a cubic cell [1, 2], a tetragonal cell [2, 3], an orthorhombic cell [4–7] and a monoclinic cell [8–10]. According to Preda and Dinescu [2], SrCeO<sub>3</sub> undergoes a phase transition from a high-temperature cubic structure, obtainable by quenching, to a low-temperature tetragonal structure, obtainable by slow cooling.

BaCeO<sub>3</sub> has been assigned, with varying lattice parameters, a cubic cell [1–5, 11, 12], a tetragonal cell [2], an orthorhombic cell [6] and a monoclinic cell [9, 10]. For BaCeO<sub>3</sub>, too, Preda and Dinescu [2] have found evidence of a phase transition from a high-temperature cubic structure, obtainable by rapid cooling, to a low-temperature tetragonal structure, obtainable by slow cooling.

Because of their interesting electrical characteristics, which have been pointed out by Longo *et al.* [13], SrCeO<sub>3</sub> and BaCeO<sub>3</sub> appear to be suitable materials for use as high-temperature semiconductors; therefore, the present investigation was undertaken in order to determine the crystal structures of the two cerates under different

operating conditions and to verify the existence of the phase transition reported by Preda and Dinescu [2].

The raw materials used were CeO<sub>2</sub> (99.9% pure) and reagent grade SrCO<sub>3</sub> and BaCO<sub>3</sub>. To prepare the stoichiometric compounds in the mole ratio of 1 : 1, the starting materials were weighed, mixed and homogenized by hand-mixing in agate mortars for 4 h, pressed into discs and air-fired at 1400°C for long time periods to ensure the completion of the reactions; equilibrium was considered to have been attained when the X-ray diffraction patterns of specimens subjected to successive heating and cooling treatments showed no further change.

The specimens were subjected to different cooling treatments: namely, some of them were quenched in water at 20°C, some were cooled in air, some were allowed to cool in the oven, and some were annealed at a temperature of 450°C for

TABLE I Crystal data of SrCeO<sub>3</sub>

Parameter	Value
<i>a</i>	5.997 ± 0.002 Å
<i>b</i>	12.308 ± 0.004 Å
<i>c</i>	8.615 ± 0.003 Å
<i>V</i>	635.88 Å <sup>3</sup>
FW	275.74
<i>Z</i>	8
δ <sub>calc</sub>	5.76 g cm <sup>-3</sup>
δ <sub>exp</sub>	5.68 g cm <sup>-3</sup>

*V* = volume, FW = formula weight, *Z* = number of formula weights per unit cell, δ<sub>calc</sub> = calculated density and δ<sub>exp</sub> = experimental density.