Umari and Pasquarello Reply: In our Letter [1], we deduced a fraction $f \sim 0.75$ of B atoms in boroxol rings in vitreous B_2O_3 through a joint analysis of experimental Raman and NMR spectra. In the previous Comment [2], Swenson and Börjesson claim (i) that our estimate is only based on the analysis of Raman spectra which are notoriously difficult to calculate, (ii) that we inappropriately obtained the value of $f \sim 0.75$ on the basis of the Raman spectrum of a model structure with $f = 0.09$, and (iii) that ^{11}B NMR spectra are insensitive to f. We here show that these claims are unsubstantiated.

The accuracy of Raman intensities and frequencies as obtained within density functional schemes has amply been demonstrated for a variety of systems including molecules [3], crystals [4], and vitreous materials [5].

The vibrational mode associated to the boroxol peak is well localized. Indeed, molecules containing boroxol rings with different terminating ligands all yield a boroxol Raman peak within only 4 cm^{-1} [6] from the boroxol frequency in v-B_2O_3. The incoherent Raman scattering of boroxols is also supported by experiment [7]. This supports our assumption that the Raman activity of the single boroxol ring is largely independent of the value of f [1].

Our estimate of f is not only based on the Raman spectrum, but also on the interpretation of ^{11}B NMR chemical shifts. We showed that the isotropic chemical shift of a ^{11}B atom linearly depends on the average B-O-B angles of its first-neighbor O atoms [1]. When the B-O-B angle distributions for O atoms inside and outside of the boroxol rings have different mean values, two peaks appear in the NMR spectrum. For our model, the average B-O-B angles for O atoms inside and outside of boroxol rings are $119.7° \pm 0.5°$ and $134.4° \pm 9.2°$, respectively. Using the corresponding angular distributions together with $f = 0.75$, the simulated NMR spectrum shows the characteristic double-peak shape (Fig. 1) observed in the experiment [8]. The two peaks derive from B atoms inside and outside of boroxol rings and correspond to different average B-O-B angles: $\theta_{\text{boroxol}} = (2 \times 120° + 134°)/3 = 125°$ and $\theta_{\text{nonboroxol}} = 3 \times 134°/3 = 134°$. The chemical shift separation between the two peaks agrees closely with experiment [1].

Using the same B-O-B distributions for O atoms inside and outside of boroxol rings (Fig. 1) but for $f = 0.09$, the simulated spectrum shows a single peak with a slight shoulder on the opposite side with respect to the experiment. Furthermore, when the same angular distribution is taken for both kinds of O atoms as proposed by Swenson and Börjesson [2], the simulated spectrum does no longer depend on f and shows a single symmetric peak, in stark contrast with the experimental result [8].

In conclusion, our work shows that NMR provides a powerful probe for f contrarily to the claims of Swenson and Börjesson [2]. In retrospect, ^{11}B NMR spectroscopy provides the most direct probe for accessing the value of f through the integrated areas under the two peaks in the spectrum, without requiring the estimate of coupling factors as for the Raman spectrum.

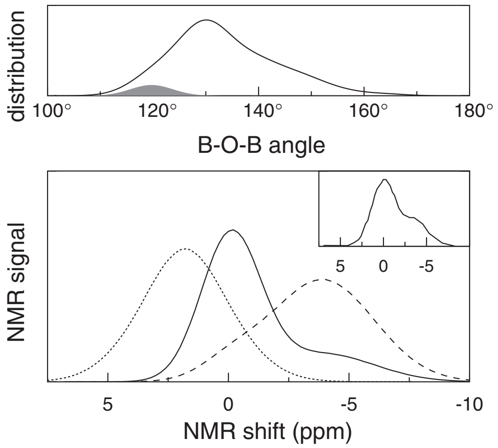

FIG. 1. Top: B-O-B bond angle distribution in our model of v-B_2O_3; the contribution from O atoms in boroxol rings is highlighted. Bottom: simulated NMR spectrum for $f = 0.75$ (solid line) and $f = 0.09$ (dashed line). The dotted line corresponds to a bond angle distribution centered at 120° with a FWHM of 20° for all O atoms [2]. Inset: experimental spectrum [8].

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[1] P. Umari and A. Pasquarello, Phys. Rev. Lett. **95**, 137401 (2005).
[2] J. Swenson and L. Börjesson, preceding Comment, Phys. Rev. Lett. **96**, 199701 (2006).
[3] D. Porezag and M. R. Pederson, Phys. Rev. B **54**, 7830 (1996); A. Stirling, J. Chem. Phys. **104**, 1254 (1996); P. Umari, X. Gonze, and A. Pasquarello, Phys. Rev. B **69**, 235102 (2004).
[4] P. Umari, A. Pasquarello, and A. Dal Corso, Phys. Rev. B **63**, 094305 (2001).
[5] P. Umari, X. Gonze, and A. Pasquarello, Phys. Rev. Lett. **90**, 027401 (2003); L. Giacomazzi, P. Umari, and A. Pasquarello, Phys. Rev. Lett. **95**, 075505 (2005).
[6] J. Goubeau and H. Keller, Z. Anorg. Allg. Chem. **272**, 303 (1953).
[7] G. Simon *et al.*, Phys. Rev. Lett. **96**, 105502 (2006).
[8] R. E. Youngman and J. W. Zwanziger, J. Non-Cryst. Solids **168**, 293 (1994).