Comment on "High-Frequency Dynamics in Metallic Glasses"

A recent Letter reports x-ray Brillouin data on a metallic glass, $Ni_{33}Zr_{67}$ [1]. Longitudinal acoustic (LA) excitations of energy $\hbar\Omega$ are found well above an independently observed boson peak (BP), located at $\hbar\Omega_{BP} \simeq 3$ meV. The authors claim that $Ni_{33}Zr_{67}$ is strong in the sense of Angell [2]. From the linewidth Γ of the acoustic signal, they also claim a Ioffe-Regel (IR) crossover, $\Gamma = \Omega/\pi$, at $\hbar\Omega_{IR} \simeq 23$ meV [3]. The latter occurs at a large scattering vector $Q \simeq 14\,\mathrm{nm}^{-1} > Q_p/2$, where Q_p is the position of the main peak in the static structure factor $S(Q)$. In this Comment, we remark that the 3 meV feature corresponds to a rather small excess of modes. It is a very weak BP and $Ni_{33}Zr_{67}$ is a fragile glass. We also point out that for $Q \geq Q_p/2$, the observed linewidth Γ does not mainly reflect mode damping. Hence, it does not determine a meaningful Ω_{IR} and no IR crossover occurs there on the LA mode of $Ni_{33}Zr_{67}$.

Our first point is that the BP is weak. Ni_xZr_{100-x} alloys were extensively studied for the past three decades, experimentally and with simulations. Experiments are preferable here for quantitative estimates. Consider the temperature dependence of the specific heat $C(T)$ at low T. An excess of modes at ~3 meV should produce a hump in C/T^3 at ~7 K. $C(T)$ in $Ni_{33}Zr_{67}$ is complicated by a superconducting transition at $T_c \simeq 2.7$ K [4]. However, in the normal state—above T_c or at a field above the second critical field—one finds that $C \simeq \gamma T + \beta T^3$, at least from 2 to 10 K [4,5]. The large $\gamma \simeq 4.48\ \mathrm{mJ/mol\,K^2}$ mainly arises from the electronic contribution, while β is slightly greater than the Debye value $\beta_D = C_D/T^3$, where C_D is the Debye specific heat. A good value of β_D might be that directly observed on $C(T)$ well below 1 K, deep in the superconducting state where the electronic contribution vanishes, $\beta_D \simeq 0.185\ \mathrm{mJ/mol\,K^4}$ [4]. Otherwise, one can use the value $0.159\ \mathrm{mJ/mol\,K^4}$ corresponding to a Debye temperature $\theta_D = 230$ K. The latter is derived from the experimental elastic moduli extracted from [1,6]. Plotting $(C - \gamma T)/T^3$ vs T, using C from [5,7], we find a small hump in the region from 7 to 11 K, peaking at $\beta_{max} \simeq 0.22\ \mathrm{mJ/mol\,K^4}$. Using either value of β_D, the excess $(\beta_{max} - \beta_D)/\beta_D$ is very small, ~0.2 or ~0.4, respectively. According to [8], this places $Ni_{33}Zr_{67}$ among the very fragile glasses, like CKN or OTP.

However, Scopigno *et al.* [1] claim that $Ni_{33}Zr_{67}$ is strong, with a fragility index $m \simeq 25$. At first, this seems to disprove [8]. However, the evidence for m in [1] is indirect, based either on a disputable wide extrapolation of simulation results or on an empirical relation [9]. There exists a direct measurement on $Ni_{60}Zr_{40}$ giving $m \simeq 90$ in Fig. 10 of [10], in excellent agreement with the small excess noted above. Instead of a failure of [8], it rather seems that [9] fails in this hyperquenched glass.

To summarize, the BP being so weak, the hybridization mechanism described in [11] can hardly be active. The absence of IR-crossover effects agrees with observations in the first pseudo-Brillouin zone [1]. Consider now spectra for Q near and above $Q_p/2$ [1]. Figure 5 of [12] shows that these spectra should acquire a sizeable width, just as observed [1]. The origin of this broadening lies in diffuse umklapp scattering. Static reciprocal-space vectors $\mathbf{G}$, distributed spherically according to $S(G)$, combine with modes of wave vector $\mathbf{q}$, to produce scattering at $\mathbf{Q} = \mathbf{G} + \mathbf{q}$ [13]. As Q nears $Q_p/2$, the densely distributed sheets at $|\mathbf{G}| \simeq Q_P$ combine with phonons with $|\mathbf{q}| \sim Q_p/2$. The signal integrates then over a progressively larger spread of q values, increasing the apparent $\Gamma(Q)$. Hence, the crossover criterion $\Gamma = \Omega/\pi$, in which Γ should reflect real damping, becomes meaningless beyond $Q_p/2$. In fact, if a IR crossover would exist at all, it should already appear in the first pseudo-Brillouin zone, i.e., for $Q < Q_p/2$. In this respect, we note that no data are obtained in [1] for $Q < 1.8\ \mathrm{nm}^{-1}$, while a BP at ~3 meV suggests a crossover wave vector of only ~1 nm^{-1}.

To conclude, $Ni_{33}Zr_{67}$ has a very weak BP and no IR crossover was observed on the LA mode. A IR crossover is expected at $\Omega_{IR} \simeq \Omega_{BP}$ if and only if the BP contains a sufficient excess of modes [11], which might not be the case here. The discussion in Scopigno *et al.* [1] should be considerably revised.

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[1] T. Scopigno, J.-B. Suck, R. Angelini, F. Albergamo, and G. Ruocco, Phys. Rev. Lett. **96**, 135501 (2006).
[2] C. A. Angell, J. Non-Cryst. Solids **131-3**, 13 (1991).
[3] The value of $\hbar\Omega_{IR}$ in the text of [1] is too small by a factor π, as seen from their Fig. 3a.
[4] H. W. Gronert *et al.*, Z. Phys. B **63**, 173 (1986).
[5] C. Sürgers *et al.*, Phys. Rev. B **40**, 8787 (1989).
[6] Y. D. Dong *et al.*, J. Non-Cryst. Solids **43**, 403 (1981).
[7] K. S. Gavrichev *et al.*, J. Phys. Condens. Matter **16**, 1995 (2004).
[8] A. P. Sokolov *et al.*, Phys. Rev. Lett. **78**, 2405 (1997).
[9] T. Scopigno *et al.*, Science **302**, 849 (2003).
[10] R. Busch *et al.*, Acta Mater. **46**, 4725 (1998).
[11] B. Rufflé *et al.*, Phys. Rev. Lett. **96**, 045502 (2006).
[12] J. Hafner and M. Krajčí, J. Phys. Condens. Matter **6**, 4631 (1994).
[13] J. Hafner, J. Phys. C **14**, L287 (1981).

