Low-temperature internal friction and sound velocity in Zener alloys

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In an attempt to identify the kind of disorder that leads to glasslike lattice vibrations in certain crystals, we have studied the low-temperature elastic properties of Ag:Zn and Cd:Mg alloys known to show Zener relaxation, which is believed to result from the relaxation of elastic dipoles. Although low-energy excitations were found, they are different from those observed in other crystals in which glasslike excitations have been previously reported.

I. INTRODUCTION

Low-temperature elastic properties of glasses and amorphous solids have been studied extensively for the last decades. The characteristic elastic properties that distinguish a glass from a crystal can be summarized as follows.[1-3]

(i) A temperature-independent plateau in the internal friction Q^{-1} is found in the temperature range $T < 10$ K. The value of Q^{-1} is typically of the order of 10^{-3} in insulating glasses and $\sim 10^{-4}$ for metallic glasses.

(ii) Below a certain temperature, called the crossover temperature T_{co}, Q^{-1} decreases and approaches a power law:

$$Q^{-1} \propto T^n . \tag{1}$$

For insulating glasses, $n \approx 3$ and $T_{co} \propto \omega^{1/3}$, ω being the measurement frequency. For metallic glasses T_{co} is much smaller and Q^{-1} stays almost constant to very low temperatures, unless ω is in the GHz range; at these very high frequencies and at very low temperatures $Q^{-1} \propto T$.

(iii) The temperature variations of the sound velocities v in both dielectric and metallic glasses are more pronounced than in crystals. Typically for $T > 5$ K, v in glasses follows a linear relation of the type (Bellessa effect)

$$\frac{v - v_0}{v_0} = \frac{\Delta v}{v_0} = \alpha(T - T_0) , \tag{2}$$

where T_0 is some reference temperature, and v_0 the sound velocity at T_0. $\alpha \approx (100-300) \times 10^{-6}$ K^{-1}.

At lower temperatures, depending on the measuring frequency, the sound velocity shows a maximum around a certain temperature T_m. For $T < T_m$, v follows a $\ln T$ temperature dependence given as

$$\frac{v - v_0}{v_0} = \frac{\Delta v}{v_0} = C \ln \left[\frac{T}{T_0} \right] . \tag{3}$$

The constant C is closely related to the plateau of the internal friction. For insulating glasses, $Q^{-1} \approx \pi C/2$ and for metallic glasses $Q^{-1} = \pi C$. The close relation between the low temperature $\ln T$ variation of the sound velocity and the value of the internal friction plateau observed for $T < 10$ K is an important characteristic of glass.

(iv) At low temperature ($T < 1$ K) and high frequencies ($> 10^8$ Hz) the ultrasonic attenuation ($= \omega Q^{-1}/v$) in glasses depends on the measurement power, and at high enough power it can be saturated.

(v) According to the tunneling model, which has been proposed to explain these phenomena, the above properties arise from the same broad spectrum of low-energy excitations ["two-level-systems" (TLS)], which also give rise to the characteristic thermal properties of glasses through which these excitations were first observed (a specific heat varying as T and a thermal conductivity varying as T^2). In this model, C in Eq. (3) is connected to the spectral density $\bar{P}$ of the TLS and to the coupling energy γ through

$$C = \frac{\bar{P} \gamma^2}{\rho v^2} , \tag{4}$$

where ρ is the mass density. Both $\bar{P}$ and γ have remarkably similar values in all glasses.[4] It is this similarity that poses the greatest difficulty to our understanding of the physical nature of these excitations.[5]

In recent years, it has been found through elastic and thermal measurements that not only amorphous solids, but also certain disordered insulating and metallic *crystalline* solids exhibit the same properties as summarized above, which are therefore briefly referred to as "glasslike."

Among the insulating crystals showing "glasslike" properties two of the more thoroughly studied examples are $(KBr)_{1-x}(KCN)_x$ (Ref. 6 and 7) and $Ba_{1-x}La_xF_{2+x}$ (Ref. 8). In $(KBr)_{1-x}(KCN)_x$ the glasslike properties, nearly independent of x, occur in the composition range $x > 0.25$. They are believed to arise from reorientation by tunneling of elastic dipoles associated with CN^- molecule ions, which substitute for Br^- ions in the KBr lattice.[9] In $Ba_{1-x}La_xF_{2+x}$ it has been shown that the onset of glasslike thermal and elastic properties can occur for x as low as 0.045. However, the characteristic density of states of the low-energy excitations, i.e., truly glasslike

properties, which are nearly independent of x, were only reached for $x > 0.30$. In this crystal La^{3+} substitutes for Ba^{2+} and a F^- is incorporated interstitially next to a La^{3+} for charge balance. The tunneling in this case can be envisioned as arising from reorientation of La-F defect pairs or aggregates thereof. The above two examples suggest that reorientation of groups of atoms between equivalent energy minima in these crystals can give rise to tunneling states similar to those found in amorphous solids. A similar conclusion has also been reached in a study of the thermal properties of $Rb_{1-x}(NH_4)_xH_2PO_4$ mixed crystals, in which glasslike properties were found for $x = 0.35$ and 0.72.[10]

Among the metallic crystalline alloys that have glasslike properties we mention IVB-VB alloys like Nb-Zr (Refs. 11 and 12) and Nb-Ti (Refs. 13 and 14). In these alloys the tunneling states are believed to arise from a diffusionless structural transformation (between the ω and the β phases). In a recent review of the literature[15] it has bee noted that in addition to the IVB-VB alloys, A-15 compounds such as Nb_3Sn (Ref. 16) and V_3Si may also have glasslike properties, although in the latter case the situation appears somewhat controversial.[17]

The existence of glasslike excitations in a wide variety of disordered crystals further increases the puzzle of their origin. It is a fruitful investigation to classify the various types of disorder in crystals that lead to these excitations. Since in all of these crystals distortions by elastic dipoles, and possibly interactions between such dipoles, can be envisioned, we decided to investigate the question of whether alloys showing Zener relaxation may also have glasslike excitations. They are a large class of alloys that have been extensively studied over the last four decades at higher temperatures after it had been discovered by Zener that in α brass (Cu:Zn) an internal friction peak exists above room temperature (typically around ~ 700 K).[18] These relaxations are believed to arise from a thermally activated stress-induced reorientation of elastic dipoles consisting of solute atom pairs present in the solid solution in a nearest-neighbor configuration (Ref. 19, Chap. 10). In the following we call these materials Zener alloys; a listing can be found in Chap. 10 of Ref. 19. Typical activation energies with these relaxations are in the range of 1 eV. At low temperatures ($T < 10$ K) reorientation by thermal activation is frozen out, but tunneling can conceivably take place. If there is a high enough tunneling probability and if these defects are strongly coupled to the lattice, one might envision that this tunneling might give rise to glasslike excitations. At high concentrations, interactions between the dipoles can also be expected. It is perhaps of interest to mention here that in $Ca_{1-x}Y_xF_{2+x}$ at small concentrations of yttrium ($x \approx 10^{-5}$) a relaxation peak has been observed at ~ 600 K (Ref. 19, Chap. 11). $Ca_{1-x}Y_xF_{2+x}$ has the same structure as $Ba_{1-x}La_xF_{2+x}$, which has glasslike low-energy excitations for large lanthanum concentrations.

We have measured low-temperature internal friction and the speed of sound in two Zener alloys, Ag:Zn and Cd:Mg, using a torsional oscillator technique ($f \sim 60$ kHz). We have chosen to use elastic measurements because in a metallic system this is the best way to search

for these excitations, since in thermal measurements contributions from conduction electrons often mask the effects of the TLS. In Ag:Zn we have studied three samples with Zn concentrations 12, 24, and 47 at. %, and also pure Ag for comparison. In Cd:Mg we have studied only one sample containing 29 at. % Mg. These particular Zener alloys have been thoroughly studied at higher temperatures.[19] They have been found to have high strengths of relaxation, which is measured by the relative change of the elastic compliance arising due to defect reorientation. This indicates a strong coupling of the dipoles to the lattice.

II. EXPERIMENTAL

The alloys were prepared by induction melting at the Metals Facility of the Cornell Materials Science Center. They were prepared in the form of cylinders of diameter ≈ 0.4 cm. The samples were analyzed for uniformity of composition by x-ray diffraction and chemical tests. The transverse sound velocity v (related to the shear modulus) and the internal friction Q^{-1} were determined by using a composite oscillator technique described in detail elsewhere,[20] with modified electronics.[21] In this method, the sample (cut to the proper length, one half of a wavelength) and a quartz crystal (diameter ≈ 0.4 cm, length ≈ 2.7 cm) were made into a composite torsional oscillator. The sample length was adjusted so that the composite oscillator has a resonance frequency (f_{comp}) at room temperature, which is within 1% of the bare quartz-crystal resonance frequency (f_{td}). This adjustment ensures that the junction between the crystal and the sample has almost zero strain, and its contribution to the total internal friction is therefore very small. This junction was made with Stycast epoxy and a thin indium foil between the transducer and the sample to make sure that the stress produced by thermal expansion mismatch did not break the bond during cooling, which otherwise invariably happened. The transducer crystal itself was mounted on a thin Be-Cu pedestal.[20] The composite oscillator was driven by a pair of electrodes, and its motion was detected by another pair put in quadrupolar configuration. The sound velocity change and the internal friction Q^{-1} of the samples were determined from the composite oscillator resonance frequency (f_{comp}) and the quality factor (Q_{comp}) through the following relations:[20]

$$\Delta v / v = \left[\frac{I_{sa} + 1.06 I_{td}}{I_{sa}} \right] \frac{\Delta f_{comp}}{f_{comp}} , \qquad (5)$$

$$Q^{-1} = \left[\frac{I_{sa} + 1.06 I_{td}}{I_{sa}} \right] Q_{comp}^{-1} , \qquad (6)$$

where I_{sa} and I_{td} are the moments of inertia of the sample and the transducer, respectively. The connection between f_{comp} ($\approx f_{td}$) and f_{sa} has been shown to be (Ref. 14, p. 52)

$$f_{comp} = \frac{I_{td} f_{td} + I_{sa} f_{sa}}{I_{td} + I_{sa}} , \qquad (7)$$

for cylindrical rods, where f_{sa} is the resonance frequency

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TABLE I. Information on the samples investigated. I_{sa} and I_{td} are the rotational inertias of sample and quartz transducer, respectively. f_{comp} is the measured resonant frequency of the composite oscillator at 300 K; v_t is the transverse speed of sound at 300 K; Δ is the relaxation strength of the Zener relaxation at 20 °C.

| | Dimension | | | | | | | | |
| | Length | Radius | Density | I_{sa} | I_{td} | f_{comp} | $\dfrac{v_t}{10^{-5}}$ | | Δ |
Sample	(cm)	(cm)	(gm/cm^3)	(10^{-2}gm cm^2)		(Hz)	(cm/sec)	Structure	($\times 10^3$)
Ag	1.47	0.22	10.50	5.49	2.16	55 607	1.598	fcc	
Ag$_{88}$Zn$_{12}$	1.24	0.21	9.73	3.68	2.16	66 066	1.606	fcc	NA
Ag$_{76}$Zn$_{24}$	1.27	0.20	9.10	2.90	2.16	65 830	1.627	fcc	222[a]
Ag$_{53}$Zn$_{47}$	1.48	0.22	8.52	4.63	2.56	56 217	1.632	fcc	NA
Cd$_{71}$Mg$_{29}$	1.11	0.20	6.07	1.80	2.58	56 358	1.170	hcp	270[a]

[a]Ref. 19 (p. 263).

of the sample itself. Thus, f_{sa} can be determined with the aid of Eq. (7), and from f_{sa} the transverse speed of sound, $v_t = 2Lf_{sa}$, where L is the sample length. Relevant information on the samples are given in Table I together with their room-temperature transverse sound velocities. The sound velocity of silver measured by us agreed with the accepted value to within 1%.[22] The precision in v is estimated to a few ppm and that in Q^{-1} to $\sim 1\%$. The measurements from 2–300 K were carried out in an insertable cryostat[23] and below 2 K in a dilution refrigerator.

III. RESULTS AND DISCUSSION

In Fig. 1, we show the internal friction, Q^{-1} obtained on the bare quartz crystal transducer and also on a pure BaF$_2$ crystal, which had been bonded to the transducer in the same way as all other samples studied here. Above 100 K, the rapid rise in Q^{-1} is due to the Stycast bond between the transducer and the Be-Cu pedestal. Below 20 K, which is our region of interest, Q^{-1} is smaller than
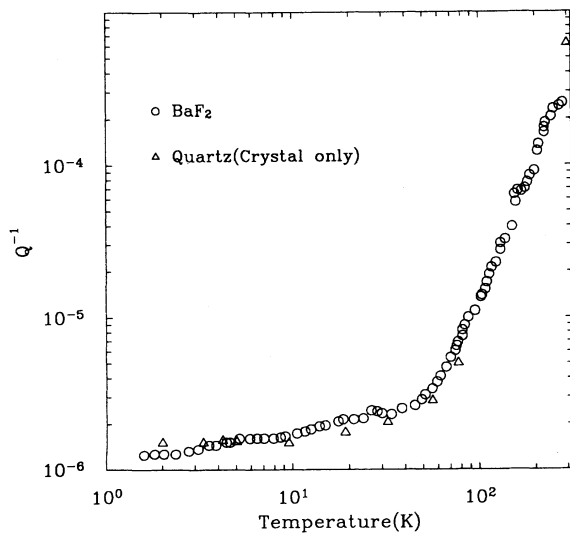
2×10^{-6}. This gives a lower limit of the internal friction that we can measure, or the background loss in our apparatus.

In Fig. 2 we show the internal friction of the three Ag:Zn alloys. Data for amorphous silica and quartz are also shown for comparison. We note the following features.

(a) For 12 at. % Zn and 24 at. % Zn, Q^{-1} below 10 K approaches a nearly temperature-independent value of $\approx 10^{-5}$. This is about 5–10 times larger than the background (see Fig. 1), but about 50 times smaller than that of amorphous silica and about one order of magnitude less than the Q^{-1} typically observed in metallic glasses.

(b) There are small peaks in Q^{-1} around 20 and 40 K.

(c) On substitution of more Zn (47 at. %), Q^{-1} at lower temperature actually decreases and the peak in Q^{-1} near

FIG. 1. Internal friction (Q^{-1}) of two crystals, quartz and BaF$_2$ [for the latter, using Eq. (6) to calculate Q^{-1} from the measured Q^{-1}_{comp}]. BaF$_2$ data are from Ref. 8. The rise at higher temperature ($T > 100$ K) is due to losses in the bonds.
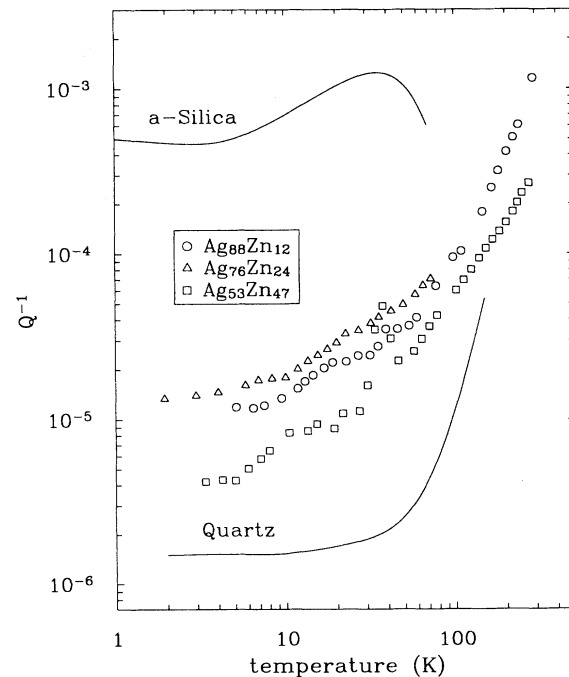

FIG. 2. Q^{-1} of Ag:Zn alloys; data for amorphous silica and quartz, Ref. 20, are shown for comparison.

40 K becomes sharper.

In Fig. 3 we show Q^{-1} of $Cd_{71}Mg_{29}$, which we believe to be the Zener alloy with the largest relaxation strength known. Q^{-1} shows a sharp peak at around 50 K, much like the Ag:Zn alloys, and below 10 K it becomes almost temperature independent with $Q^{-1} \approx 10^{-5}$. This value continues down to 0.1 K, the lowest temperature measured.

To contrast the behavior of these alloys with that of a pure metal we have shown in Fig. 4 the internal friction of pure silver. Also shown are published data for silver measured by a vibrating-reed technique.[24] They are about four times larger, although the temperature dependences observed in both measurements are similar. In both samples, the magnitude of Q^{-1} is larger than in the Zener alloys. The peak of internal friction at ~ 75 K is believed to be caused by dislocations.[19] Their concentrations are probably different in the two samples. The long tail in Q^{-1} is probably enhanced by a secondary peak at around 20 K. These peaks are suppressed on alloying and show up only as small peaks in the 20–40 K region; see Fig. 2. Such peaks in Q^{-1} were also observed in BaF_2:La,[8] where their nature is unknown.

Also shown in Fig. 4 are data for metallic glass, $Pd_{76}Si_{16}Cu_6$,[25] obtained by the vibrating-reed method. At low temperatures, its internal friction exceeds that of the silver. In metallic glasses below 10 K, Q^{-1} changes by $\approx 10\%$ per decade in temperature, while in pure silver the change is approximately a factor of 4. Both in the Ag:Zn alloys and in Cd:Mg the changes are around $\approx 30\%$. Thus, while a "plateau" in Q^{-1}, with a temperature dependence similar to metallic glasses, and very different from that of pure silver, is found in the Zener alloys below 10 K, Q^{-1} is about one order of magnitude less than in metallic glasses in the same temperature region.

The existence of a nearly temperature independent internal friction in the Zener alloys at low-temperature points to the existence of low-energy excitations with a broad energy and relaxation time distribution. However, given the low value of Q^{-1} we conclude that the excitations are not glasslike. At best, this internal friction can
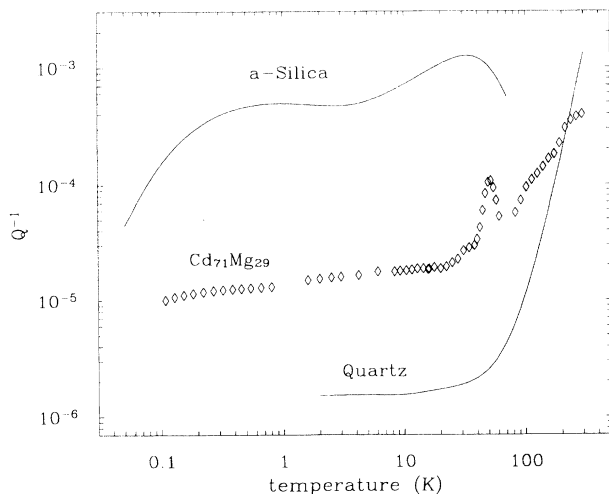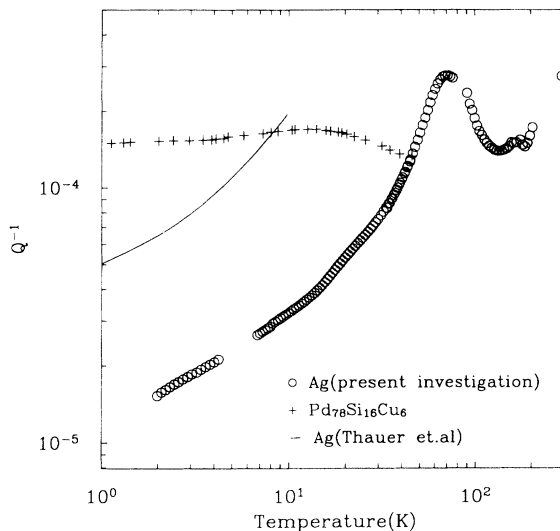

FIG. 4. Q^{-1} of pure silver. Data for $Pd_{78}Si_{16}Cu_6$ metallic glass are from Ref. 25 ($f = 1030$ Hz). The graph also shows Q^{-1} obtained in Ref. 24 by a vibrating reed technique ($f = 500$ Hz).

be the sign of an incipient glassiness, as perhaps seen in $Ba_{1-x}La_xF_{2+x}$ for small x ($< 20\%$). This conclusion is further supported by measurements of the temperature dependence of the speed of sound in the Zener alloys. In Fig. 5, we show the low temperature (30 K $> T > 2$ K)
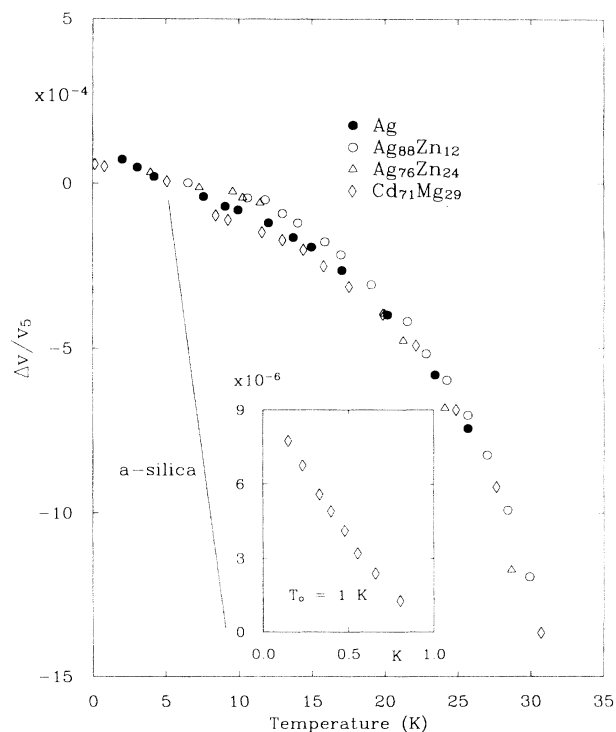

FIG. 5. Sound velocity change [Eq. (7)] for pure Ag, two Ag:Zn alloys, and $Cd_{71}Mg_{29}$ $T_0 = 5$ K. The data for amorphous silica (Ref. 20) are shown for comparison. They follow a straight line between 2 and 20 K. The inset shows the linear change in sound velocity in the Cd:Mg alloy below 1 K. Note the different vertical scale. At 5 K, the resonance frequency of this sample was 60 231.69 Hz, and at 1 K, 60 232.89 Hz.

FIG. 3. Q^{-1} of $Cd_{71}Mg_{29}$ for a-SiO$_2$ and quartz as in Fig. 2.

dependence of the sound velocity in the form of $\Delta v / v_0$ [see Eqs. (2) and (3)], with the reference temperature $T_0 = 5$ K (1 K for the inset). In the same graph we have also shown data for amorphous silica for comparison. Both electrically insulating and metallic glasses show a linear temperature dependence [see Eq. (2)] with $\alpha \simeq 300$ ppm/K for a-silica (between 2 and 20 K, Ref. 20) and $\alpha \simeq 100$ ppm/K for $Pd_{78}Si_{16}Cu_6$ (not shown in Fig. 5).[25] The behavior of the Zener alloys is quite different and resembles that of the pure metal, silver, as seen in Fig. 5. The relative change in sound velocity from 5 to 30 K is only $\approx 1.5 \times 10^{-4}$, which is more than one order of magnitude smaller than in glasses. In the Cd:Mg alloy, where the data extend to 0.1 K, we find the linear temperature dependence to persist down to the lowest temperatures, but with a very small $\alpha \approx 10$ ppm/K. But even this small temperature dependence is amazing. As T approaches zero, $\Delta v / v_0$ in a metallic crystal is expected to show the behavior

$$\frac{\Delta v}{v_0} = \alpha T^2 + \beta T^4 , \qquad (8)$$

as has been seen in a few cases above 4.2 K.[26] The linear dependence observed here implies the existence of low-energy excitations.[27] In a metallic glass one observes a maximum in the sound velocity at $T \approx T_m$ (~ 1 K) and the transition to a logarithmic temperature dependence below T_m [Eq. (3)]. (It is interesting to note that such a

behavior has, in fact, been seen in the crystalline alloys Be:Cu and in coin silver (Ag:Cu) in the mK temperature range.[28]) In the tunneling model, as reviewed in Refs. 1–3, the internal friction in the plateau region ($Q^{-1} = \pi C$ for amorphous metals) is a measure of the quantity $\bar{P}\gamma^2$ [Eq. (4)]. Since in our Zener alloys Q^{-1} in the plateau region is an order of magnitude smaller than in metallic glasses, we have to conclude that $\bar{P}\gamma^2$ in these alloys is at least ten times smaller, if the tunneling model applies at all. In that case it is likely that the T_m for these alloys would indeed occur below 0.1 K.

To conclude, we have not found evidence of glasslike lattice vibrations in Zener alloys, although some low-energy excitations with a broad energy distribution do exist. Thus, it appears that interacting elastic dipoles alone, as they certainly exist in these alloys, are not enough to generate glasslike excitations. Conceivably, their interactions are not strong enough in the Zener alloys. As a result, only relatively small and composition-dependent concentrations of low-energy excitations exist in these crystals.

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