Acoustic and Dielectric Properties of Glasses at Low Temperatures

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Summary: Amorphous materials exhibit a variety of unusual low temperature properties. They are caused by low-energy excitations whose physical nature is still not fully understood. In this review, mainly measurements of the acoustic and dielectric properties of glasses are discussed, since these experiments have turned out to be very useful in investigating the origin of these anomalies.

1. Introduction

Amorphous materials have found a wide field of technical applications due to their broad spectrum of physical and chemical properties. Nevertheless, the investigation of their fundamental properties has attracted only a limited interest in the past. Nowadays, new technologies are going to be developed based on unique but not yet completely understood properties of amorphous substances. Consequently, the investigation of more fundamental aspects of amorphous materials has become more and more attractive.

In the present paper, the low temperature behaviour of amorphous materials will be discussed, which exhibit similar but "anomalous" properties. One year ago, H. Sussner, K. Dransfeld and the author have already given a brief and general survey of these anomalies [1]. In the meantime, new experiments have been carried out, deepening and extending the information on the physical nature of the low-energy excitations causing the anomalies. Therefore, after a short and general review, especially these recent results will be emphasized in this issue.

2. Review of the Thermal Properties of Glasses

In the past several years there have been intensive efforts to understand the thermal properties of glasses below 1 K. At these temperatures, thermal behaviour should be determined by the propagation of acoustic waves of long wavelength. Below 1 K the wavelength of the dominant phonons is larger than 1000 Å and therefore much larger than the scale of microscopic disorder. As a consequence, there should be little difference between thermal properties of amorphous and crystalline dielectrics. Especially the specific heat is expected to be proportional to T^3 in both cases.
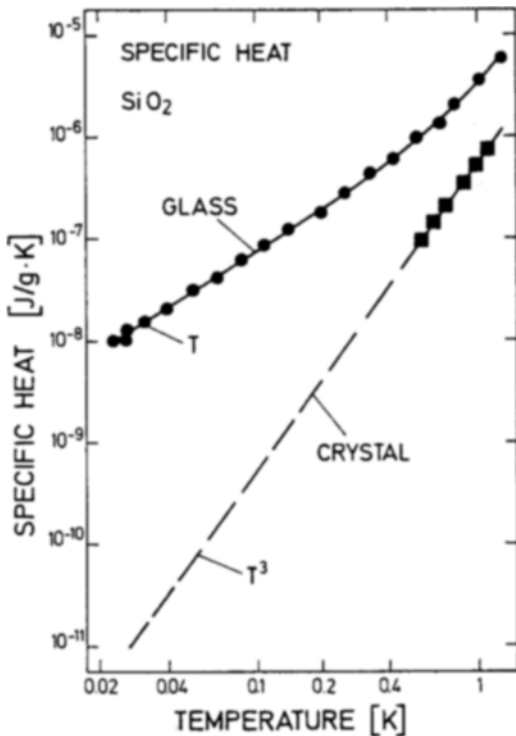
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Fig. 1
Specific heat of vitreous silica and crystalline quartz as a function of temperature (data from [4] and [3]). The specific heat of the pure crystal is proportional to T^3 above 0.6 K. Below this temperature no experimental data exist so far. Therefore the experimental curve has been extrapolated down to 20 mK. The specific heat of the glassy sample is roughly linear in T below 1 K.

Measurements of the specific heat of glasses [2, 3] show, however, that such arguments are too simple. In Fig. 1 the specific heat is plotted as a function of temperature for crystalline quartz [3] as well as for vitreous silica [4]. As expected the specific heat of the pure crystal is proportional to T^3 down to 0.6 K. The glassy sample, however, does not behave in the same way: its measured specific heat is linear in temperature and is much higher than that of the crystal. At a temperature of 30 mK, the specific heat of the glass is roughly 1000 times larger than the expected value. Moreover, the magnitude depends only weakly on chemical composition and impurity contents of the amorphous sample [2]. In the case of crystals, the specific heat differs considerably for various pure materials or for different impurity contents.

Because of the much higher specific heat of glasses, additional low-energy excitations have to be present, that are different from ordinary phonons. Since the specific heat is linear in temperature below 1 K, the corresponding density of states must be constant in energy. From the magnitude of the specific heat the number of excitations can be deduced and about 10^{17} states per cm^3 and K are found. Measurements of the thermal conductivity of glasses [2–4a] have shown that these low-energy excitations do not contribute to the transport of energy. They scatter phonons [5] and reduce the conductivity well below the value of crystalline samples.

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3. Acoustic Measurements

The influence of these low-energy excitations on the propagations of phonons can be studied in more detail by ultrasonic experiments. For this purpose the velocity as well as the attenuation of ultrasound has been investigated in a variety of glasses [6—9]. The typical result is shown in Fig. 2, where the ultrasonic attenuation (or inverse mean free path) is plotted as a function of temperature. This experiment [10] has been carried out in vitreous silica applying longitudinal sound waves of 1 GHz and of two different intensities. A characteristic dependence of the attenuation on the power level is observed. At relatively high intensities (Curve 1) the acoustic absorption decreases steadily with decreasing temperature. Reducing the acoustic intensity the attenuation rises, i.e. the absorption becomes less and less saturated. For an intensity of 10^{-7} W/cm^2 (Curve 2) the absorption passes a minimum and increases again with decreasing temperature. The attenuation at higher intensities (Curve 1) in caused by a relaxation process [11] that we do not discuss here. We consider only the difference between Curve 2 and Curve 1, i.e. that contribution to the absorption which can be saturated by increasing the acoustic intensity. In contrast to the relatively high loss in glasses, the ultrasonic absorption in pure crystals in negligible and constant in this temperature range.
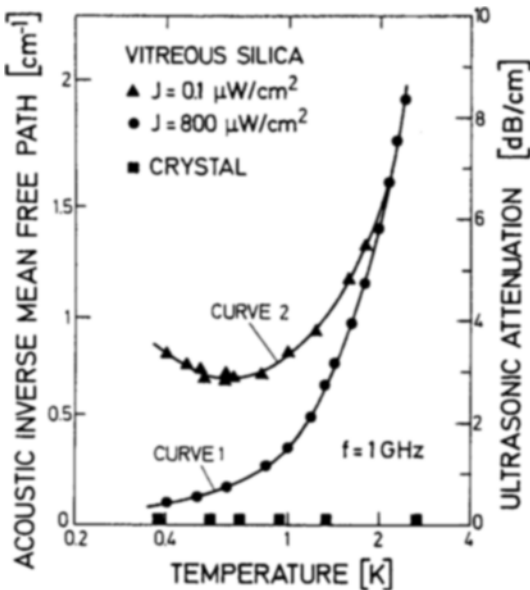

Fig. 2
Temperature dependence of the ultrasonic attentuation in vitreous silica for longitudinal waves of 1 GHz. Curve 1 represents the saturated attenuation, which is caused by a relaxation process. Curve 2 shows the measured attenuation in the almost unsaturated regime. Below 0.6 K the attenuation increases again. The full squares indicate the temperature independent attenuation in a pure quartz crystal (data from [10]).

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According to the measurements of the thermal properties, the low-energy excitations are spatially localized and hence can be treated as oscillators (see Fig. 3). At low temperatures the most likely interaction between such an oscillator and a phonon is the direct process. The phonon will be resonantly absorbed if its energy coincides with the level splitting E of the oscillator. Because of the broad distribution of the energy splitting, this condition will be fulfilled independently of the phonon energy. The cross-section of this process is extremely large: an oscillator having an energy splitting corresponding to 1 GHz exhibits a cross-section of the order of $10^{-13} \, cm^2$.

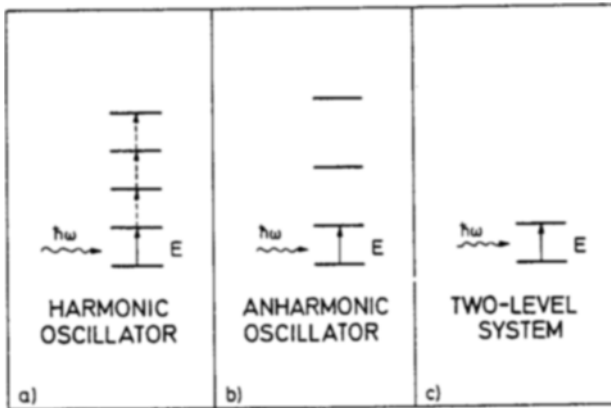| HARMONIC OSCILLATOR	ANHARMONIC OSCILLATOR	TWO-LEVEL SYSTEM
a)	b)	c)

Fig. 3. Schematic representation of the resonant interaction between phonons and different types of oscillators. The dashed arrows in a) indicate the increasing excitation of the harmonic oscillator by the absorption of several phonons.

The observed saturation immediately proves that these oscillators can not have equally spaced levels like harmonic oscillators (see Fig. 3a). Obviously they must have non-equally spaced levels like strongly anharmonic oscillators (Fig. 3b). A more careful analysis of the experimental data has shown that under most experimental conditions it is sufficient to consider only two levels. At low intensities the temperature dependence of the resonant absorption is simply given by the fact that the upper level of these two-level systems (2 LS) becomes more and more thermally populated at higher temperatures [5, 6, 9].

The strong and temperature dependent resonant absorption of sound waves in glasses is connected with a strong temperature dependence of the velocity of sound. Both quantities — absorption and sound velocity — are related via Kramers-Kronig relation. The variation of the sound velocity below 1 K has been observed for the first time in vitreous silica and is shown in Fig. 4 [12]. With decreasing temperature the velocity
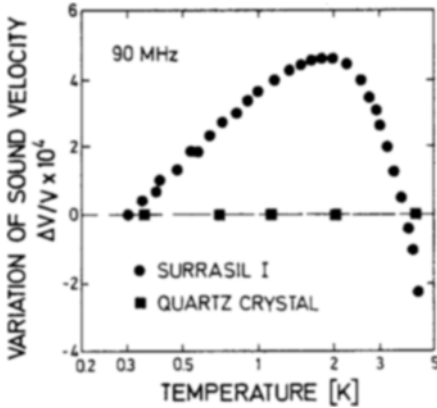
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Fig. 4
Relative variation of longitudinal sound velocity $\Delta v/v = (v(T) - v(T_0 = 0.3 \text{ K}))/v(T_0 = 0.3 \text{ K})$ in vitreous silica plotted as a function of temperature (data from [12]). The full squares show for comparison the temperature independence of the sound velocity in a quartz crystal.

of sound passes a maximum and decreases steadily below a few Kelvin, whereas the velocity in the crystalline phase is practically constant. The variation at higher temperatures is caused by the relaxation process mentioned before and will not be discussed here. The slope of the curve at the lowest temperatures is directly determined by the strength of interaction between phonons and 2 LS which also determines the magnitude of the resonant absorption. Using this value for longitudinal and transverse waves the observed heat conductivity below 1 K can be explained quantitatively [13]. It is also worth mentioning that this anomalous temperature dependence of the velocity of sound has been observed quite recently also in the glassy metal NiP [14]. This result indicates that free electrons do not significantly influence the anomalous behaviour of amorphous materials.

4. Dielectric Absorption

Those acoustic measurements that have been discussed above and other acoustic experiments [15—17] which will not be mentioned in this paper, have given a great deal of information about the dynamical behaviour of the 2 LS. Nevertheless, their atomic nature is still unknown and electromagnetic experiments have turned out to be helpful in the investigation of this question.

If 2 LS carry electrical charges or exhibit an electrical dipole moment, they are expected to interact with electromagnetic radiation in a completely analogous way as they do with elastic waves. Especially a saturation in the absorption of electromagnetic radiation should occur in the microwave range. So far only one experiment is known [18] and will be briefly discussed here. In Fig. 5 the dielectric absorption (or inverse mean free path) of microwaves at 10 GHz in vitreous silica Suprasil I is plotted for two different intensities. Completely analogous to the
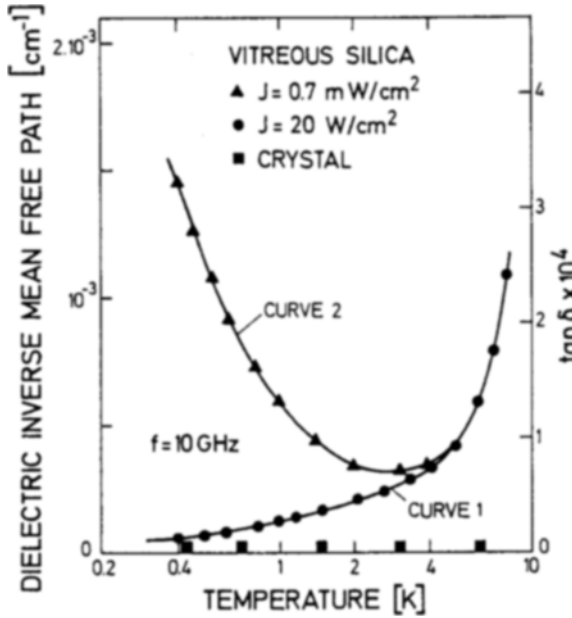
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Fig. 5
Temperature dependence of the dielectric absorption in vitreous silica Suprasil I for microwaves of 10 GHz. As in the acoustic case Curve 1 represents the saturated absorption and Curve 2 the attenuation in the unsaturated regime. Below 3 K the absorption increases again. The full squares show the negligible attenuation in a pure quartz crystal (data from [18]).

acoustic absorption a strong dependence on microwave intensity is observed. At higher intensities the dielectric absorption decreases steadily (Curve 1) with decreasing temperature, but at low intensities it increases again below 3 K (Curve 2). As in the acoustic case the absorption in the corresponding crystals is negligible in this temperature range.

From the magnitude of the absorption the coupling parameter $n_e \mu'^2$ for the coupling between the 2LS and electromagnetic waves can be derived, where n_e represents the density of states of those 2LS that are electrically active and μ' is the average induced electrical dipole moment of a 2LS. μ' is uncorrected for the local field but an average over the random spatial orientations has been carried out. Using the experimental value of $n_e \mu'^2 = 1.5 \cdot 10^{-4}$ and assuming that n_e is identical to the density of states deduced from specific heat we obtain $\mu' = 0.5$ Debye.

Here the interesting question arises: Are the 2LS observed in acoustic and in electric experiments the same? The answer to this question has been given by the "cross"-experiment [19]. In this experiment 2LS in the sample are excited by a relatively intense electromagnetic field. Simultaneously, the absorption of a weak acoustic pulse of nearly the same frequency is measured. If the 2LS interact with both types of fields, the electromagnetic radiation should cause a decrease of the acoustic absorption and vice versa [19–21]. The result of such an experiment in borosilicate
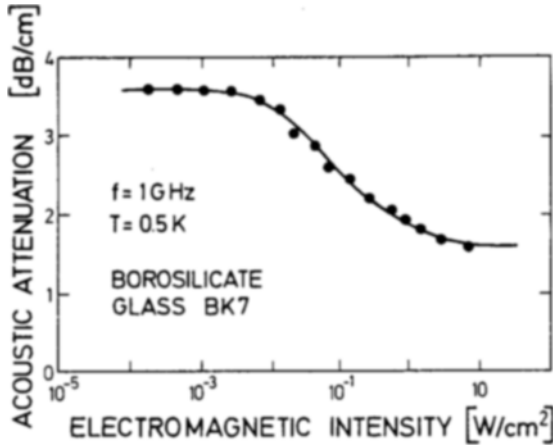
Fig. 6
Resonant ultrasonic absorption in a borosilicate glass BK7 sample as a function of the applied electromagnetic intensities. From the difference of the attenuation at low and high electromagnetic intensities the fraction of those 2LS can be deduced, which couple only to an elastic but not to an electromagnetic wave (data from [20]).

glass BK7 is shown in Fig. 6. The acoustic absorption decreases with increasing electromagnetic power as soon as the intensity exceeds a certain critical value, i.e. as soon as the 2LS become saturated by the electromagnetic pulse. This result is a clear indication for the fact that the same 2LS are involved in both absorption processes. The acoustic absorption, however, does not go to zero, even at relatively high electromagnetic intensities. A simple explanation can be given if we assume that only that fraction of 2LS couples strongly to the oscillating electric field which happens to carry ions or polar impurities.

5. Measurements of the Dielectric Constant

It would be of great interest to find out whether the magnitude of the dielectric absorption is also "universal" and hence independent of chemical composition or impurities contents of the sample. The result of the "cross"-experiment already seems to indicate the opposite. A clear answer is given by the measurements of the real part of the dielectric constant. Because of the Kramers-Kronig relation the real and imaginary part of the dielectric constant are closely related and both quantities reflect the coupling between 2LS and electromagnetic radiation. The temperature variation of the dielectric constant has been measured in a variety of amorphous materials [22–24]. The qualitative behaviour is always the same (see Fig. 7) and very similar to the acoustic case: on cooling the dielectric constant decreases, passes a minimum and increases again. As an example in Fig. 7 the temperature dependence of the dielectric constant is plotted for crystalline quartz, vitreous silica Suprasil I and amorphous PET (polyethylene terephtalate) [23, 24].
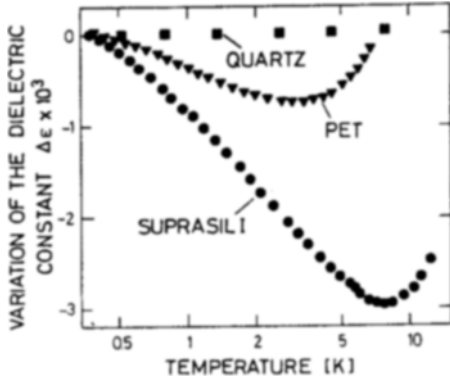
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Fig. 7
Temperature dependence of the dieletric constant
$\Delta \epsilon = \epsilon(T) - \epsilon(T_0 = 0.4 \text{ K})$ of crystalline quartz, vitreous silica Suprasil I and amorphous PET (polyethylene terephtalate) (data from [23, 24]).

In contrast to the acoustic case the magnitude of the observed effect and hence the dielectric coupling depends strongly on chemical composition and the content of charged impurities. This remarkable result is especially clearly seen in vitreous silica where the coupling strength depends linearly on the concentration of OH^--ions [23].

In Fig. 8 the coupling strength of different samples of vitreous silica as given by the slope of the curves for $\Delta \epsilon$ at 0.4 K is plotted as a function of the OH^--contents. It seems very unlikely that both quantities, n_e and μ' depend on c in such a way that the product $n_e \mu'^2$ should be exactly proportional to the concentration.

Therefore we assume that probably either n_e or μ'^2 alone exhibit the observed dependence on the OH^--concentration. Let us develop a geometrical model of the 2LS: In Fig. 9 the 2LS are represented by hatched areas whereas the randomly oriented dipoles of the OH^--ions are given by small arrows. The mean distance d between the randomly distributed ions depends of course on the sample and is
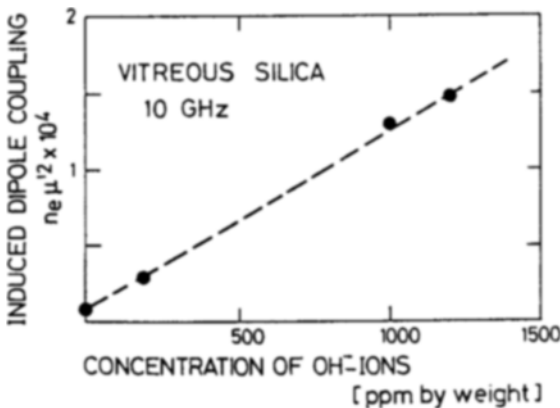

Fig. 8
Coupling constant $n_e \mu'^2$ of vitreous silica as a function of the concentration of OH^--ions (data from [23]).
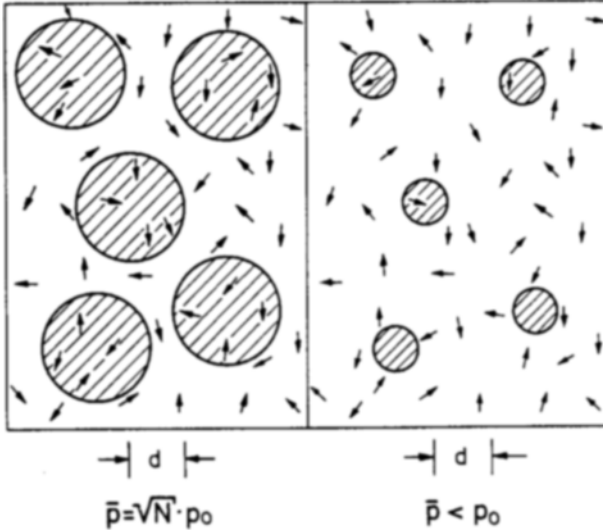
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Fig. 9. Schematic representation of 2LS (hatched areas) and randomly distributed and oriented dipole moments of OH⁻-ions for two different cases: a) D > d, b) D < d; where D is the spatial dimension of the 2LS and d the mean distance between OH⁻-ions.

roughly 20 Å for Suprasil I containing 1200 ppm of OH⁻-ions. In the left side of Fig. 9 we first assumed that the spatial dimension D of the 2LS is much larger than the mean distance of the ions. In this case every 2LS is carrying an average number N of ions whose mean value is proportional to the concentration c. Because of the random orientation of these N dipole moments an average dipole moment $\bar{p} = \sqrt{N} \cdot p_0$ is expected for the 2LS, where p_0 is the dipole moment of an individual OH⁻-ion. Although this model leads to the correct dependence of the coupling on the OH⁻-concentration it is contradicted by two experimental observations. Firstly it had been shown by the "cross"-experiment that not all 2LS are coupled to an electromagnetic wave. Although this experiment has not yet been carried out in vitreous silica, the results should also be relevant for this material, since the concentration of ions and polar impurities in borosilicate glass is much higher than the concentration of OH⁻-ions in vitreous silica. Secondly average dipole moments $\mu' = 0.5$ Debye and $\mu' = 0.2$ Debye are found for vitreous silica Suprasil I and for vitreous silica with 180 ppm of OH⁻-ions, respectively, using the density of states from specific heat measurements. Although the exact value of the dipole moment depends on the local environment of the OH⁻-ions, it can be estimated from measurements in crystals. For example a dipole moment of 3.8 Debye, uncorrected

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for the local field, is found for an individual OH^--ion in KCl [25]. The value deduced from our experiment is much smaller. Consequently, the assumption $D > d$ cannot be correct.

The opposite situation, namely $D < d$, is represented by the right side of Fig. 9. Not every 2LS that is present in the sample also carries an ion. Therefore, we expect $n_e \propto c$ and the dipole moment of an individual 2LS should be of the order of p_0. In our estimate of $\mu' = 0.5$ Debye we have assumed that n_e is identical with the density of states deduced from specific heat. As a consequence we have over-estimated the value of n_e and therefore, we have obtained $\mu' \ll p_0$.

It should be added that actually $\bar{p}$ and μ' do not represent the same quantity although they are closely related. It would be more accurate to compare $\bar{p}$ with the average permanent dipole moment μ that can be deduced from the relaxation process which dominates the acoustic and dielectric behaviour at higher temperatures [11, 12, 23]. From our measurements we know, however, that μ is larger than μ' by less than a factor of two [23, 24]. Therefore, our arguments hold for both quantities μ' and μ.

Since only the last interpretation agrees well with all experimental facts, we draw the important conclusion that the extent D of the 2LS is apparently smaller than $d = 20$ Å in our special example of vitreous silica Suprasil I. This result excludes several large scale cluster models for the 2LS, but we do not yet have, at present, a full insight into the nature and microscopic structure of the 2LS.

6. Conclusion

In conclusion we want to say that glasses at low temperatures exhibit many properties that are fundamentally different from those of their crystalline counterparts. To a large extent, thermal and acoustic properties are insensitive to the chemical composition of these substances and can therefore be considered as characteristic of the glassy state. Dielectric measurements, however, are very sensitive to specific impurities and are therefore able to narrow down more and more the number of possible kinds of defects, giving rise to the low-energy excitations. Although the formal phenomenological description of the observations in terms of "two-level systems" has been very sucessful, we have to admit, that we are still far from an understanding of the low temperature properties of amorphous materials on an atomic scale.

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