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DYNAMIC PROPERTIES OF DISORDERED SOLIDS AT LOW TEMPERATURES

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Abstract.- Disordered solids 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 disordered solids are discussed, since these experiments have turned out to be very useful in investigating the origin of these anomalies.

1. Introduction.- During the last ten years amorphous solids have moved from a fringe zone to the center of interest in solid state science. In particular there have been intense efforts to understand the anomalous low temperature properties of glasses. These anomalies are unexpected for the following reason. At low temperatures the thermal behaviour of pure dielectric solids should be determined by acoustic phonons of long wavelength. Below 1 K the wavelength of the corresponding dominant phonons is larger than 1000 Å and therefore much larger than the scale of the microscopic disorder. As a consequence, at these temperatures and below there should be hardly any difference between the thermal properties of amorphous and crystalline dielectrics. Although there is great regularity in the thermal properties of amorphous materials, their behaviour — in contrast to expectation — is completely different from that of pure crystalline substances. This contradictory aspect has stimulated not only extensive work on thermal properties but also a new sequence of quite different investigations on the mechanical and dielectric properties of glasses below 1 K.

In this paper we will first describe the rather unexpected thermal and dynamic behaviour of nearly all glasses at low temperatures. Subsequently we will consider substances which are crystalline but contain defect states and finally a theoretical microscopic model is reviewed.

2. Specific Heat of Glasses at Low Temperatures.— As mentioned above the low temperature specific heat of pure dielectric solids was expect-
ed to be determined by acoustic phonons of long wavelength. Then, according to Debye's theory, the specific heat $C$ should be proportional to $T^3$. Incorporation of impurities should enhance the specific heat, but only in a limited temperature range. About ten years ago Zeller and Pohl /1/ discovered that many insulating glasses show an unexpected linear term in the specific heat below 1 K. This linear term not only dominates the contribution of thermal phonons but is hardly influenced by the incorporation of impurities /2/. At a temperature of 25 mK the measured specific heat of vitreous silica /3/ exceeds the Debye contribution of the phonons by more than a factor of 1000! More recently it has been demonstrated that superconducting amorphous metals also behave in a similar way /4/ even well below the transition temperature where the electronic specific heat can be neglected. This result strongly indicates that electrons do not contribute to the extra specific heat but that instead atomic motions may be responsible in amorphous insulators as well as in amorphous metals. In this context it is interesting to mention that a linear specific heat has also been found in crystalline ionic conductors (for example in $\beta$-alumina /5/) or quenched single crystals (for example in NbZr /6/) indicating that these materials are at least partially in a "glassy" state of disorder. We will discuss this point in more detail later.

The large extra specific heat clearly demonstrates the existence of a new type of low-energy states which is specific to the disordered state and does not exist in pure crystals. Surprisingly not only the temperature dependence of this extra specific heat is similar for all amorphous materials but also its magnitude. From these results one arrives at the conclusion that all these disordered solids contain roughly $10^{17}$ low energy excitations per cm$^{-3}$ uniformly distributed in the energy interval from 0 to 1 K. The total number of excitations is, however, probably considerably higher, since the density of states extends to higher energies and seems to increase quadratically /2/. Unfortunately no reliable estimate of this number can be given since at higher temperatures the extra specific heat is masked by the contribution of ordinary phonons.

Most of these low energy excitations interact - as we will see - strongly with the amorphous network, i.e. with the phonon modes. But for an appreciable number the interaction time with the "lattice" is much longer than 1 $\mu$s and extends to at least 1000 s. Consequently the specific heat depends on the time of measurement. Successful observations of such a time dependent heat capacity have recently been reported for fused silica by several groups /7/.
3. **Ultrasonic Properties of Insulating Glasses.** Attenuation /8/ as well as velocity /9/ of an ultrasonic wave are strongly affected by the interaction with these low-energy excitations. As a typical example, in Fig. 1 the attenuation of hypersonic waves is shown versus temperature /10/. Let us first focus our attention to temperatures below 1 K. A characteristic dependence on the acoustic intensity J is observed: At higher intensities the ultrasonic loss vanishes with decreasing temperature; at very low power levels the absorption increases again. This observation immediately rules out harmonic oscillators being responsible for the attenuation. It is compatible with the assumption that the ultrasonic absorption is caused by resonant transitions between two energy levels: At higher acoustic intensities both levels reach equal population because of the finite lifetime in the excited state (of the order of 10 μs in our example) and consequently the absorption falls. The population also varies with increasing temperature. In fact, the temperature dependence of the absorption α at low intensities /11/ (α = ωtanh(ωf/2kT)) and its intensity dependence /12/ (α ∝ 1/√J) strongly support that two level systems and not multi-level systems are present in glasses /13/.

![Fig. 1: Temperature dependence of the attenuation of longitudinal acoustic waves of two different intensities in vitreous silica. The full squares indicate the temperature independent attenuation in a pure quartz crystal (from /10/).](image)

The two-level systems also cause the steep rise of the attenuation at higher temperatures /14/. The sound wave modulates the level splitting of the two-level systems and thus disturbs the thermal equilibrium. The systems try to relax into the new equilibrium via the emission or absorption of thermal phonons. The resulting absorption is intensity independent since all thermally populated two-level systems contribute to this process. At low temperatures (T < 4 K) and hypersonic frequencies the condition ωτ ≫ 1 holds in silicate glasses, where τ is the relaxation time necessary for a two-level system to re-establish thermal equilibrium. In this regime the temperature dependence of the relaxation absorption reflects the energy
dependence of the relaxation rate. Since $\alpha = T^{3}$ is observed experimentally /15/ it follows that $\tau \propto e^{-E_0/T}$. This result is again in agreement with the assumption that two-level systems are responsible for the acoustic properties of glasses /13/. In summary, the ultrasonic absorption observed in glasses at low temperatures is caused by the interaction of the sound wave with a broad distribution of low energy excitations which are best described by two-level systems.

![Graph showing relative variation of longitudinal and transverse sound velocity as a function of temperature.](image)

Fig. 2: Relative variation of longitudinal and transverse sound velocity $\Delta v/v$ in borosilicate glass BK7, plotted as a function of temperature. The dashed-dotted lines are theoretical fits taking into account both the resonant and the relaxation interaction. The solid squares show for comparison the variation of sound velocity in a quartz crystal (from /13/).

Since the ultrasonic absorption depends on temperature the same must be true also for the velocity of sound since both quantities are linked by the Kramers-Kronig relation. Fig. 2 shows the temperature dependence of the velocity of sound in a borosilicate glass for both longitudinal and transverse sound waves /13/. In agreement with the Kramers-Kronig relation the sound velocity varies logarithmically with temperature below 1 K where the resonant absorption is dominant. At higher temperatures the contribution of the relaxation process predominates and the velocity decreases again. From the slope of the curve at 0.3K we can directly determine the product, density of states of the two-level systems times the coupling strength. This result is of importance in the discussion of the thermal conductivity. Interestingly the velocity of sound or the corresponding elastic stiffness of glasses decrease on cooling in contrast to that of crystalline materials which generally show no variation or the opposite behaviour at temperatures below 1 K.

4. Thermal Conductivity of Insulating Glasses.- In glasses thermal phonons are also scattered by two-level systems. Thus the thermal conductivity is limited to values much lower than that one of the corresponding crystalline materials. The heat conduction is proportional to the product of the phonon part of the specific heat, which shows the
classical $T^3$-dependence and the mean free path $\ell$ of phonons at thermal frequencies $\omega = kT/\hbar$. Since $a = \ell^{-1} = \omega \tanh (\hbar \omega / 2kT) = T$ (for details see ref./13/) the thermal conductivity of glasses should vary as $T^2$ in agreement with the observations /1-6/. Interestingly, the strength of the coupling between acoustic waves and two-level systems is of the same order of magnitude in all silicate and chalcogenide glasses. Consequently the heat conductivity of all these substances is almost identical below 1 K. Even glassy polymers and the lattice contribution of metallic glasses behave in the same way.

5. Dielectric Behaviour of Insulating Glasses.- If one places a sample of vitreous silica into a microwave cavity in order to investigate the interaction of electromagnetic waves with the two-level systems, observations almost identical with those in acoustic measurements become apparent. This is demonstrated by Fig. 3 where the dielectric absorption of microwaves of 10 GHz in vitreous silica Suprasil I (1200 ppm OH) is plotted versus temperature. The complete analogy becomes obvious by comparing Fig. 1 and 3. Nevertheless, there is an important difference. The magnitude of the dielectric loss depends on the amount of ionic or dipolar substances incorporated in the matrix of the glass. Thus the loss in borosilicate glass or Suprasil I (which contains roughly 1200 ppm of OH-impurities) is much higher than in highly pure vitreous silica (Suprasil W) or in As$_2$S$_3$. In short, the magnitude of the dielectric loss - in contrast to the acoustic loss - is not a universal property.

Similar to the variation of the velocity of sound in the acoustic case, a temperature dependent velocity of light is observed. In Fig. 4 the variation of the dielectric constant $\varepsilon$ (which determines the light velocity in the solid) is shown for vitreous silica (Suprasil W) and As$_2$S$_3$ at a frequency of 10 GHz. At the lowest temperature again
the slope of the curve in Fig. 4 is steeper the higher the content of polar impurities. Clearly, of all the low-energy excitations present in the glass sample only those are "seen" by the electric field which carry electrical dipoles or charges.


So far we have discussed the interaction of the two-level systems with external elastic or electric fields. But an interaction also exists among the two-level systems which is probably elastic in origin. This additional aspect is taken into account by using the Bloch equations in order to describe the dynamical behaviour of the two-level systems. In analogy to paramagnetic ions in a magnetic field we have to distinguish between $T_1$ and $T_2$, the longitudinal and transverse relaxation time, respectively. $T_1$ is the spontaneous lifetime caused by the emission or absorption of thermal phonons and is identical with the relaxation time we have discussed so far. $T_2$ is determined by the interaction between the two-level systems.

In principle both quantities can be measured by applying more than one acoustic or electric pulse to the sample. The analysis of such experiments is, however, complicated by the fact that spectral diffusion plays an important role in glasses. A more convenient way is to cool down the sample to the Millikelvin range. There the relaxation times are long enough to exceed the duration of applied acoustic or electromagnetic pulses. Under this condition the two-level systems can be excited coherently, i.e. a macroscopic elastic or electric polarization is generated in the sample and different techniques are available to study this quantity. Here we only want to
mention the measurement of its decay ("free induction decay"), the generation of echoes (spontaneous as well as stimulated echoes), and the investigation of self-induced transparency (in sound propagation) /19/.

Echoes in glasses have been studied in many experiments /20/.

Thus $T_1$ and $T_2$ have been measured in vitreous silica down to temperatures of 4 mK /21/.

Here we want to discuss another aspect: It is well-known that the dipole moment of the interacting system can be deduced from the maximum in the amplitude of the spontaneous echo, which is obtained by varying the applied field strength. In Fig. 5 the result of such an experiment at 19 mK is shown for vitreous silica containing different impurities /22/.

All samples exhibit a maximum at a relative field amplitude of 0.3. A second maximum at 0.04 is present if the sample contains OH-impurities. This result supports the interpretation of measurements of the dielectric properties. Obviously the two-level systems in vitreous silica exhibit an electrical dipole moment which is enhanced if they carry a polar impurity.

7. Glassy Metals.- As already mentioned above, amorphous superconducting metals exhibit a linear specific heat well below $T_C$ /5,23/. Since its magnitude is comparable to that in ordinary glasses it seems that two-level systems are present also in amorphous metals in roughly the same number as in vitreous silica. Below 1 K the heat conduction shows the same $T^2$-dependence /5,24/ as known for amorphous dielectrics indicating that in amorphous metals also heat is mainly transported by phonons whose mean free path is limited by scattering on two-level systems. Detailed studies /25/ of the temperature variation of the sound velocity showed similar results as in ordinary glasses. For the ultrasonic absorption a temperature and intensity dependence was found similar to that one shown in Fig. 1 for vitreous silica /26/.
But there is a basic difference: The saturation effect is observed at much lower temperatures and, even more important, saturation occurs at completely different acoustic intensities. While in vitreous silica the resonant absorption at 1 GHz and 0.5 K becomes saturated at an intensity of $10^{-7}$ W/cm$^2$ one needs an intensity which is three orders of magnitude higher in PdSi at 0.06 K /26/. This demonstrates that in normal conducting metals the relaxation times are—probably by the presence of the conduction electrons—shortened by several orders of magnitude relative to ordinary glasses, where the two-level system can only relax via phonons.

If the conduction electrons are condensed to Cooper-pairs by cooling a superconducting amorphous metal well below $T_C$ one would predict /27/ that the relaxation time should increase by several orders of magnitude finally reaching the value of ordinary glasses. Therefore a drop in the relaxation absorption is expected at $T_C$ since below these temperatures the condition $\omega T \gg 1$ should hold. In Fig. 6 we show the ultrasonic absorption in amorphous PdZr /38/. The most striking feature is that at $T_C$ there is no change of the absorption. It only falls well below $T_C$. This result demonstrates how effective free electrons are in reducing the relaxation time of two-level systems: Although the number of unpaired electrons drops rapidly below $T_C$ those which are left over, are still capable of shortening the relaxation time to such an extent that the condition $\omega T > 1$ is not fulfilled until $T = T_C/2$ is reached. At the lower temperatures phonons determine the relaxation rate. Applying a magnetic field of 8 Tesla makes this sample normal conducting and the unpaired electrons give rise to a strong absorption down to the lowest temperatures.

8. Low Temperature Anomalies in Crystalline Materials.—The question arises whether these low temperature anomalies are only observed for
amorphous materials. We have already mentioned that the fast ionic conductor β-alumina and quenched crystals of NbZr also show a linear specific heat /5,6/. These materials also show a thermal conductivity and acoustic properties very similar to those of ordinary glasses. Here we want to discuss briefly two experimental results, namely the velocity anomaly of the fast ionic conductor Li₃N and of quenched NbZr.

In Fig. 7 the variation of the sound velocity with temperature is shown for Li₃N /29/. Qualitatively the behaviour is the same as that of glasses (see Fig. 2), but there are quantitative differences: the position of the maximum is shifted to lower temperatures by a factor of five and the slope of the logarithmic rise is considerably smaller than in glasses. It seems that the density of states of the two-level systems is considerably smaller than in ordinary amorphous substances. In Fig. 8 the velocity is plotted for rapidly quenched NbZr /30/. For the first time the variation of the velocity of sound was observed in a superconducting material exhibiting the low temperature anomalies. Below 1 K two remarkable features are found: The absolute value of the velocity as well as the slope of the rise depends on the state of the sample, normal or superconducting. This is a consequence of the relaxation process whose contribution to the velocity is negligible in the superconducting state (since $\omega t \gg 1$) but is relatively strong in the normal state since unpaired elec-
trons enhance the relaxation rate.

There are several additional examples which demonstrate that a distribution of two-level systems can exist in crystalline materials. In all cases these crystals exhibit either disordered sub-structures (as for example β-alumina), randomly distributed defects (as in the case of neutron irradiated quartz crystals /31/) or contain metastable phases (as in quenched Nb₃r). Although disorder is a necessary condition, it is not sufficient: Recent experiments on the one-dimensional ionic conductor Hollandite show no linear specific heat /32/. In summary, low temperature anomalies similar to those in amorphous materials can also occur in crystalline materials, but the exact presuppositions are not yet known.

9. On the Nature of the Low Energy Excitations.- The universality of these low temperature anomalies suggests that the two-level systems in amorphous solids must be a natural consequence of the metastable state of glassy materials, which have many configurational minima of the free energy, which are almost but not exactly equivalent. In a simple approximation it has been proposed /33/ that in amorphous solids certain atoms or groups of atoms are able to move in a double well potential. At low temperatures these particles jump over the barrier between the two wells. Instead they are thought to be able to go from one well to the other by quantum mechanical tunneling. Because of the randomness of the amorphous network the parameters of the different tunneling systems are expected to vary slightly. The basic assumption /33/ is now, that the asymmetry in depth of the minima as well as the resulting tunnel splitting, are uniformly distributed. This assumption leads to good agreement with all the experiments described above. The nature of the tunneling particles, however, is not yet known. In vitreous silica it is likely /34/ that the rotary motion of a SiO₄-tetrahedron is responsible. This motion is probably made feasible by the bending softness of the bridging oxygen bonds. In other materials one can find clusters of similar size which can rotate from one minimum position to the next without an excessive energy barrier between both positions. In this view it is not surprising that in amorphous silicon and germanium where cluster formation does not seem to be possible two-level systems apparently do not exist either /35/.

In general, more is known about the nature of the tunneling particles in disordered crystals. For example, in the fast ionic conductor Li₃N it is very likely the tunneling of hydrogen impurities between neighbouring nitrogen ions which gives rise to two-level systems /29/. As in this specific case the tunneling systems in crystals can
usually be attributed to well-defined defects. However, it is completely unclear why under such circumstances a broad distribution of tunneling splitting exists.

10. **Summary.** - In summary we want to say that disordered solids at low temperatures exhibit many properties that are fundamentally different from those of perfect crystals. In amorphous materials thermal and acoustic properties are insensitive to the chemical composition to a large extent and seem to be a characteristic of the glassy state. In disordered crystals the magnitude of the anomalies can in generally be varied by varying the content of impurities, the duration of irradiation etc. Dielectric measurements, however, are very sensitive to specific impurities and provide additional information on the nature of low-energy excitations. Although the formal phenomenological description of the observations in terms of "two-level systems" has been very successful, we have to admit that we are still far from a complete understanding of the low temperature properties of disordered solids on an atomic scale.

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**References.**

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