

The roots and the future of mechanical spectroscopy

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Abstract

The origin of mechanical spectroscopy and its evolution over nearly 80 years are outlined. The first school on the anelastic behaviour of solids was founded by Clarence Zener in 1945 in Chicago, at which he was able to attract outstanding young researchers, who subsequently disseminated our culture all over the world. The study of the relaxation of plastically deformed metals provided early evidence of the existence of dislocations. The investigations of point defects and their complexes gave useful information on their dynamics even at very low concentration levels, where other techniques are often insensitive. The recent extensions of experiments to consolidated powders, either by sintering processes or by compacting procedures, and to viscous fluids deposited on vibrating substrates are opening new perspectives to the mechanical spectroscopy, as they allow anelasticity measurements to be applied to all frontier subjects of science in which bulky samples are not available; examples are the nanostructured and artificially structured materials, the organic and biological matter, the new gas-absorbing compounds, and the polycrystalline high T_C superconductors. Some new research lines are briefly mentioned, where anelastic spectroscopy has been applied as a necessary and complementary tool in combination with other spectroscopies.

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1. The origin

Kimball [1] was among the firsts who set-up an apparatus for measuring the elastic energy dissipation, and measured the internal friction of a revolving shaft supported in bearings. He unexpectedly found that the “internal frictional forces” were not like those of a viscous fluid, where the forces are greater the more rapid the deformation, but that the dissipative forces were the same whatever the speed of deformation. Indeed, at that time the elastic energy loss in solids was treated as a viscous friction, and this is the reason why the improper name “internal friction” was coined. Kimball and Lovell [2] measured the damping at small amplitudes and low frequency in 20 different materials and compared their results with previous data. Damping was considered approximately as a constant of the material at that time, but Read [3] demonstrated that the elastic energy dissipation of a material is markedly influenced by the growing procedures and the thermal and mechanical treatments.

A more appropriate apparatus was built in 1927 by Quimby [4], which consisted in a composite oscillator using a piezoelec-

tric quartz operating at a few tens of kilohertz, thus allowing concomitant measurements of elastic moduli and energy loss.

2. Clarence Zener

The first visible school on the anelastic behaviour of solids started by 1945 with Clarence Zener (Fig. 1), when he joined Cyril Smith in founding the “Institute for the Study of Metals” at the University of Chicago, in which other prominent Faculty members or young collaborators were working, like Enrico Fermi, Barret, Lawson, Nachtreib, Teller, Zachariason, Wentzel, Millikan, Mayer, Dijkstra.

Zener was able to attract in his group outstanding young researchers, like Nowick, Kê, and Wert. In 1948 Zener had just written his book on “Elasticity and Anelasticity of Metals” [5], in which he defined and theoretically described the anelastic behaviour of solids, thus originating a new discipline in condensed matter. In a later book of one of his former collaborators [6] the formal theory of anelasticity was developed, and its various manifestations in materials were unified in one theoretical basis.

The contribution of Zener to science was tremendously broad, and his career spanned more than 60 years. Before his gradu-

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Fig. 1. Clarence Zener in 1985.

ate degree at Harvard he published: “A theory of the electric breakdown of solid dielectrics”. After this paper a particular p–n junction, the *Zener diode*, was industrially fabricated. The Zener discoveries can be summarized as follows: Zener diode (1932), Zener thermoelastic effect (1937), Zener theory of anelasticity (1947), Zener relaxation (vacancy dynamics), Zener double exchange mechanism (1951, see “Section 19”), Zener drag mechanism (small precipitates may retard the grain boundary migration).

Zener is considered today as the founder of anelasticity, and Nowick as the scientist who developed the theory, compared it with experiments, and disseminated the information all over the world. This unsurpassed book [6] is no longer available, and any past effort of the authors to re-edit an updated version did not succeed, as it did not fit the economical interests of the publishers.

3. Bordoni peak and dislocation relaxations

One of the most exciting results, which gave impetus to anelasticity was the discovery in 1949 of the dislocation relaxation by Bordoni [7]. The thermally activated relaxation process first observed in lead and then in copper, aluminium, and sil-

ver by the same author, constituted the first real evidence of the existence of dislocations, whose presence was first suggested by Orowan [8], Polanyi [9], and Taylor [10] in order to interpret the plastic flow of crystals.

Bordoni had developed together with Nuovo [11,12], at the Institute of Acoustics “O.M. Corbino” of the Italian National Research Council (CNR) in Rome, an electrostatic way of exciting and detecting vibrations, by a frequency modulation device which they called “*Vibrometer*”; the free vibration modes of samples were achieved suspending them on nodal lines in order to reduce the spurious dissipation to minimum values. In that way it was possible to measure, in a wide temperature range, values of dissipation, Q^{-1} , as small as 10^{-5} (later reduced to 10^{-8}) for vibrations whose statistical amplitude may be comparable with the reticular constants.

In 1948 Bordoni started a systematic study of the dissipation coefficient and resonant frequency of several solids in order to determine their anelastic behaviour by applying the Zener relaxation theory to the experimental results. In order to decrease the difficulties he was aware to encounter, he decided to start with high purity elements and to extend measurements to low temperature, from 290 to 4.2 K. To this purpose he moved to the Low Temperature Laboratory of M.I.T. (Cambridge, USA) and took his “*Vibrometer*” and part of the measuring apparatus with him. He soon observed [7], in cold worked lead at about 35 K for 10 kHz, a trace of an unexpected feature in the dissipation curve, just emerging from the background and revealed thanks to the sensitivity of his electrostatic drive system (Fig. 2). On proceeding with copper, a huge effect appeared (Fig. 3).

This process, subsequently called the “Bordoni relaxation”, arouse enormous interest, stimulated theoretical works, and in some cases was matched with theoretical predictions. Mason in 1955 [13] interpreted the process as the dynamics of dislocation lines lying in a minimum energy position (Peierls valley)

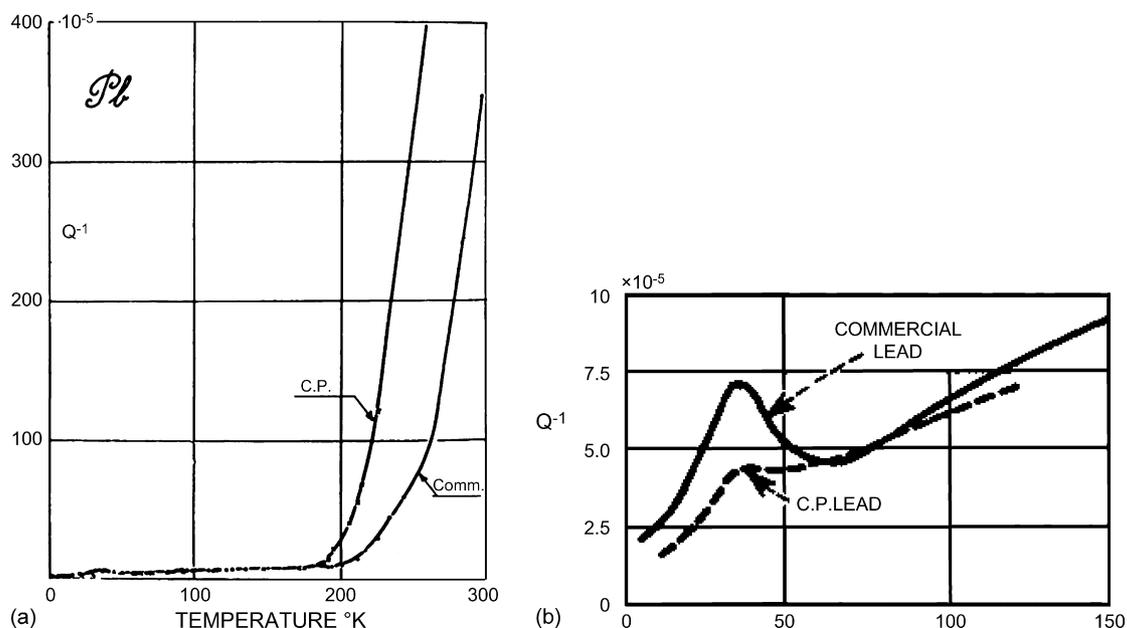


Fig. 2. (a) Elastic energy dissipation in cold worked lead. At 35 K a trace of a peak due to the Bordoni relaxation is visible; (b) the peak at 35 K [7] (written permission of the author).

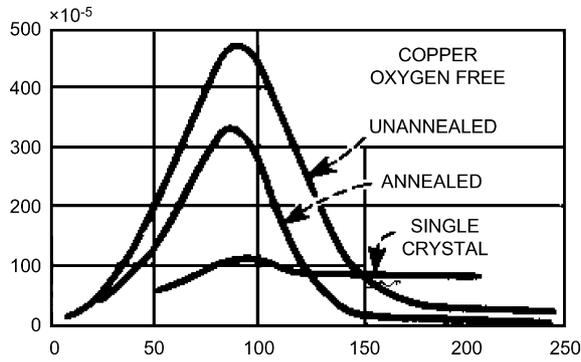


Fig. 3. The Bordoni peak in copper [7] (written permission of the author).

and anchored by pinning points, and Granato and Lücke in 1956 formulated a theoretical model of the vibrating string [14]. Seeger from 1955 interpreted this intrinsic relaxation in terms of the kink-pair mechanism [15–17]. Many other authors remarkably contributed to this effect and more generally to dislocation motion processes. Among them, Niblett [18], who confirmed the Bordoni peak and isolated a side peak on its low temperature side, Chambers [19], Nowick [20], Schoeck [21], Fantozzi et al. [22], Gremaud et al. [23], Rivière [24]. A detailed review on dislocation relaxations was given recently by Seeger [25] and by Gremaud [25].

4. Snoek peak

Relaxation of point defects was the other main subject, which determined, together with the dislocation relaxation, the abrupt rise of interest in the anelastic properties in solids and the development of our spectroscopy. Snoek was the first to show in 1941 [26] that the dynamics of point defects gives rise to an important class of relaxation phenomena, later called as the “Snoek effect”. This process is the elastic energy dissipation associated with the free motion of point defects. Indeed, any point defect introduces a distortion in the host lattice, represented by a second-rank tensor called “elastic quadrupole, λ ”. When the symmetry of the defect is lower than that of the lattice, the distortion according to the site occupied by the corresponding defect can have more than one crystallographic orientation. In the unstrained lattice all the λ orientations are energetically equivalent, but the application of an external strain differently interacts with the defect distortions according to their local orientations. As a consequence, the degeneracy of the site energies is removed and the energy levels are differently perturbed. If the Debye relaxation condition $\omega\tau = 1$ is fulfilled (ω angular vibration frequency, τ relaxation time of the mobile species) the elastic energy dissipated during the redistribution of atoms among the perturbed levels reaches its maximum.

The Snoek relaxation was first studied in bcc metals containing the heavy interstitial foreign atoms O, N, and C. Powers and Margarethe Doyle [27,28] carried out systematic investigations in transition metals and determined the relaxation parameters (pre-exponential factor, activation energy, and relaxation strength) associated with the hopping of O, N, and C, and the linear relationships between peak heights and interstitial

concentrations. In addition, they derived the diffusion coefficient of those impurities, assuming octahedral occupancy for the interstitials. They detected also that at high interstitial content the relaxation curves display a marked broadening. Later on Szkopiak repeated the measurements with a better definition [29,30].

Anelasticity is so sensitive to impurities that metallurgists used it to determine solute concentrations in metals at such low levels at which any other technique is insensitive. More recently it was shown that the Snoek maxima are broadened and shifted to higher temperature with increasing O content, because of the interactions between interstitial atoms [31–33].

5. Interaction of heavy interstitials (O, N, C) with substitutional solute atoms

Substitutional solutes have important effects in the modification of the mechanical properties and relaxation of metals, and the origin was identified in terms of *scavenging*, i.e. the reduction of the random interstitial concentration by the substitutional solute. Early general studies on the solution weakening can be found in papers by Hahn et al. [34], Armstrong et al. [35], Arsenault [36], and Ravi et al. [37]. An excellent review on the old investigations of the effects of substitutional atoms was given by Hasson and Arsenault [38]. A review on the same subject was given more recently by Numakura et al. [39].

Hasson and Arsenault showed that the addition of titanium to vanadium removes O and N from solid solution [40]. Extra relaxation peaks attributed to the motion of O and N in the vicinity of zirconium in niobium were reported by Bunn et al. [41] and Mosher et al. [42]. The effectiveness of substitutional titanium as a trapping centre for interstitial O and N and its consequences on relaxation, motion, and mechanical properties were first demonstrated by Cantelli and Szkopiak for niobium [43,44]. In particular, it was shown that the energy absorption spectrum is completely modified by the appearance of interaction peaks, or Snoek-type peaks, due to the stress-induced reorientation (Fig. 4) of single O (N) around single Ti atoms, and the respective binding energies were estimated.

The analysis of the Q^{-1} curves of the substitutional–interstitial (s–i) systems originally proceeded by the addition of Debye peaks associated with the corresponding interactions [42,43,45–47]. However, the synthesis of the experimental curves by superposition of several discrete single relaxation processes does not succeed at the higher s or i concentrations, as Enrietto concluded by varying the Mn and N contents in iron [48]. This is due to the remarkable broadening of the Q^{-1} curves due to the interaction among the relaxing complexes, which later could be fitted by introducing distributions of activation energies and relaxation times.

Several models were adopted to interpret the trapping effect of the substitutionals on interstitial O and N, giving rise to the “Snoek type effect”. Dijkstra and Sladek [45] assumed a deepening of the site energy and an increase of the saddle-point energy of the interstitial in the sites coordinated with the substitutional trap, in order to interpret the trapping of N by Mn in iron, and similar assumptions were adopted by Oriani [49]. Koiwa recon-

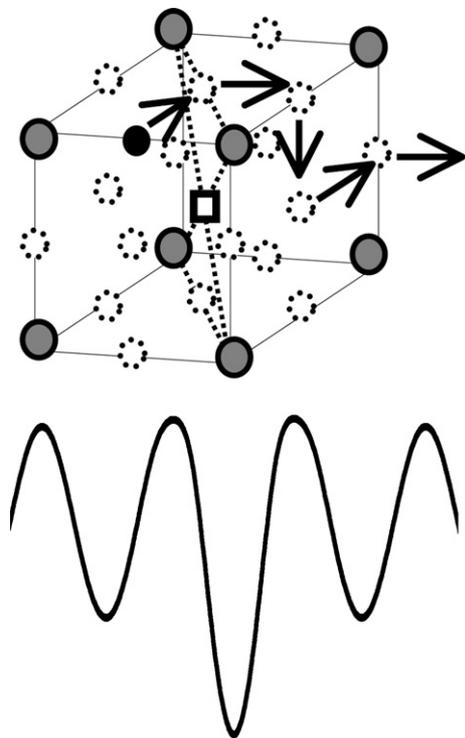


Fig. 4. Relaxation of O, N, C around substitutional atoms in metals. Grey circles are host lattice atoms, squares are substitutional Mn, Ti or Zr trapping centres, black circles are interstitial O, N, C atoms. Interstitial sites are indicated by dashed dots. A simplified potential profile is also drawn.

sidered the modellistic formulations and developed a model in which also the potential energy at saddle-points around the trap is lowered with respect to that of the interstitial free migration [50]. In addition, he proposed a method to calculate the relaxation processes [51], extending a previous approach proposed by Meijering [52]. Most recently, Blanter and coworkers and Golovin and coworkers re-examined the relaxation spectra induced by the substitutional–interstitial interactions [53,54], and carried out computer simulations of the relaxation effects taking into account long-range interactions among dissolved atoms [55–57].

6. Cannelli–Verdini peak

The first observation of anelastic relaxation in the hydrogen/deuterium–metal systems was reported in 1965–66 by Cannelli and Verdini at the Corbino Institute of CNR, on Ta and Nb [58–60]. The authors undertook experiments on samples subjected to H electrolytic charge, to try whether it was possible to observe a Snoek peak due to the motion of interstitial hydrogen. The first repeated attempts did not display any effect on the anelastic spectrum ascribable to hydrogen. Evidently, the barrier of the surface oxides constituted a serious difficulty, which was not properly faced due to the status of the art at those early times. Only after obstinate insistence and on acquiring experience step-by-step, an unexpectedly developed peak appeared eventually around 100 K in the kHz range (Fig. 5). The authors, using the classical Arrhenius relationship for the relaxation time, obtained activation energies $E_H = 0.12 \pm 0.01$ eV and

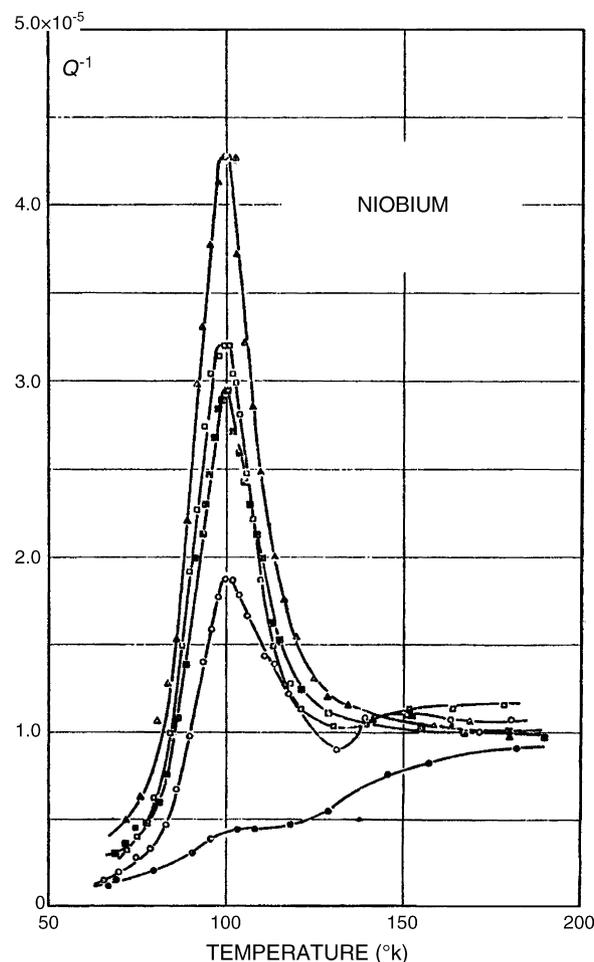


Fig. 5. The Cannelli–Verdini peak in niobium due to the reorientation of H around interstitial O acting as a trapping centre [58–60] (written permission of the author).

$\tau_0 = 1.6 \times 10^{-12}$ s for H in tantalum, and $E_H = 0.18 \pm 0.01$ eV and $\tau_0 = 4.2 \times 10^{-15}$ s for niobium. They also found, surprisingly, that the ratio of the prefactors of the H and D isotopes is 80 instead of $\sqrt{2}$, as the ratio m_D/m_H of the isotope masses predicts on the basis of the classical theory. This result arrived unexpectedly, as nobody in the world suspected at that time that hydrogen may have a quantum behaviour in the matter. Indeed, also the τ^{-1} versus $1/T$ plot (Fig. 6), that Cannelli and Verdini fitted by a straight line, clearly suggests an upward deviation from linearity, starting at about 80 K. The possible onset of this deviation was pointed out by Nowick and Berry [6], who suggested measurements at lower frequencies to ascertain whether the deviation was due to quantum tunnelling. This low temperature relaxation was called the *Cannelli–Verdini peak*, as a recognition of a discovery which opened the era of the quantum behaviour of hydrogen in solids, and stimulated further intense interest in the phenomenon and the formulation of quantum models and theories.

At the beginning the Cannelli–Verdini relaxation was broadly believed [6] to be the H Snoek peak, i.e. the analogous of the well known O, N, and C Snoek peaks observed above room temperature in bcc metals, and which was still missing from the

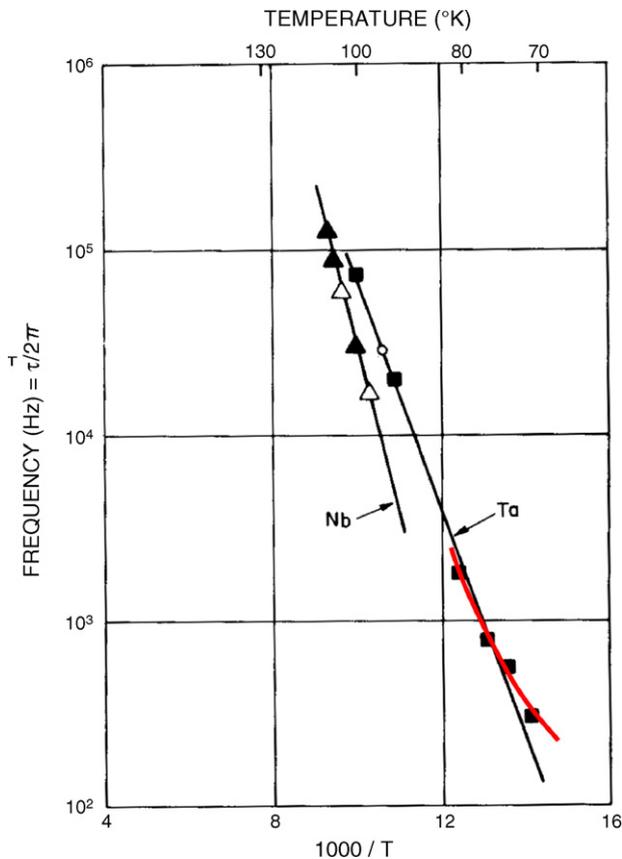


Fig. 6. Rate of the O–H relaxation as a function of reciprocal temperature for niobium and tantalum [59,60]. At low temperature a deviation from the classical Arrhenius law is visible (written permission of the author).

observation. However, after the discovery of the Gorsky effect in 1968–1969 (see later) it became clear that the Cannelli–Verdini relaxation had to be ascribed to a different mechanism. The Gorsky effect, which provided the first bulk measurement of the H diffusion coefficient, free of complications from surface barrier effects, gave an activation energy for long-range diffusion of H in niobium of about 0.11 eV, against 0.18 eV for the Cannelli–Verdini process found 2 years earlier. In 1970 [61] and in 1973 [62] it was suggested that the acoustic absorption might not be caused by free-hydrogen but by the H motion around traps, possibly O, N, or C. Debates and speculations about the nature of the Cannelli–Verdini peak went on until Schiller and Schneiders [63], in 1975, using the Bordoni technique [11] (in the early sixties Schiller was sent to the Corbino Institute of Acoustics in Rome by Professor Seeger to pick up the anelastic relaxation methodology), clearly demonstrated that the H relaxation is caused by the stress-induced reorientation of H around interstitial O acting as a trapping centre. Those authors observed the peak in samples containing both H and O, but revealed no peak in samples containing various amounts of H, which were previously oxygen outgassed at 2300 K in ultra-high vacuum.

The indications of the τ^{-1} deviation from linear behaviour at low temperature of the O–H relaxation did not escape from the observation of Birnbaum, who extended the experiments to low frequencies (10^{-3} Hz), thus shifting the peak down to about 35 K [64,65]. The plot of the hopping rate in the temperature

range 35–250 K clearly revealed a significant deviation from classical Arrhenius law. The $\tau^{-1}(T)$ curves were fitted with the model of Flynn and Stoneham [66] for the polaron-like hopping. The relaxation due to the H reorientation around interstitial impurities has been found also in vanadium [67,68] and in hcp yttrium [69].

7. The precipitation peak

Cannelli and Mazzolai first observed a sharp increase of Q^{-1} and a frequency inflection in the Ta–H system, when they cooled down the system [70]. The temperature of the Q^{-1} and f inflections appeared to be quite well correlated with the $\alpha/(\alpha + \beta)$ solvus line of the Ta–H compound. The peak was later attributed [71] to the motion of the dislocations produced by hydride precipitation and dragging interstitial H, and was called *the hydrogen cold-work peak*. The same effect was detected in V–H [72], V–D [67] and Ta–D [73] and was successfully used to determine the solvus lines.

8. Gorsky effect

A stress field producing a non homogeneous dilatation in a crystal containing point defects can give rise to a thermally activated relaxation process due to the stimulated long-range diffusion of the mobile species, whatever their symmetry; the only condition, which however is quite generally fulfilled, is that the point defect should produce a local dilatation or contraction of the lattice. Specifically, the bending of a rectangular bar (Fig. 7) produces a dilatation gradient across its thickness h , and consequently the defects migrate from the less energetically favoured compressed region to the dilated region. This effect was predicted by Gorsky in 1935 [74], but remained undiscovered for more than 30 years. The reason was the enormously long time required to the particles until then considered (gold in copper in the Gorsky theory) for migration over the macroscopic distance h .

The Gorsky relaxation was experimentally observed for the first time by two different methods. Schaumann et al. [75,76] used long rods folded in the form of springs and conducted elastic after effect measurements by an inverted torsion pendulum

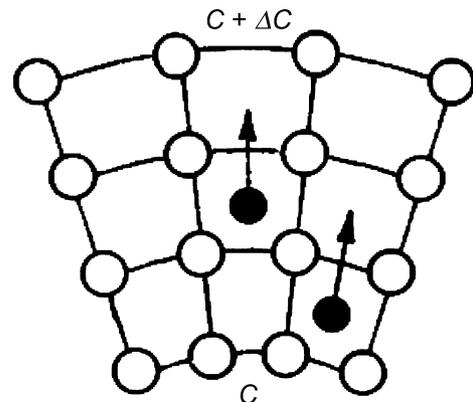


Fig. 7. Migration of interstitial atoms upon sample bending, according to the Gorsky relaxation.

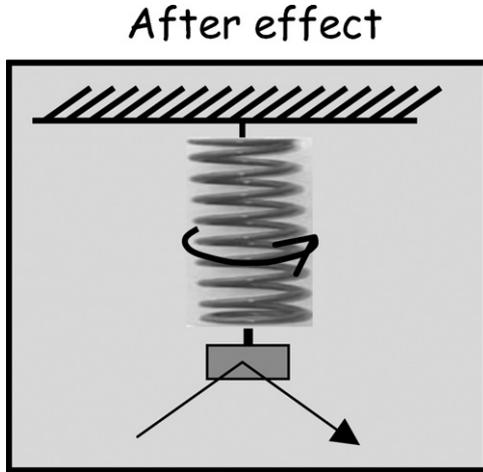


Fig. 8. Study of the Gorsky effect by elastic after-effect. The sample is a rod folded in the form of a spring. After torsion, the recovery vs. time is monitored optically and supplies the relaxation time of the H long-range migration [76].

(Fig. 8). Cantelli et al. [77–80] used rectangular samples as considered in the Gorsky theory and conducted on them dynamic measurements of Q^{-1} (Fig. 9); the samples were sheets with thickness of a few micrometers, clamped at one end and excited with flexural vibrations.

The Gorsky theory was formulated for a sheet subjected to bending, and for flexural vibrations the dissipation coefficient by dynamical measurements was predicted to be:

$$Q^{-1}(T) = \frac{\theta}{T} \sum_{n=1,3,5,\dots} \frac{1}{n^4} \frac{2\omega\tau_n}{1 + \omega^2\tau_n^2} \quad (1)$$

with:

$$\tau_n = \frac{h^2}{n^2\pi^2 D(T)} \quad (2)$$

where θ is a constant, ω the angular vibration frequency, h the thickness of the rectangular bar, $D(T)$ the diffusion coefficient of the mobile particle, and τ_n are the relaxation times contributing to the process. As the contribution of the higher order terms is only 1%, the process is substantially governed by a single relaxation time and Eq. (1) can be truncated to the first term. The knowledge of the first term τ_1 in Eq. (2) allows the absolute value of the diffusion coefficient to be determined, with no need of assumptions concerning the particle occupancy in the lattice.

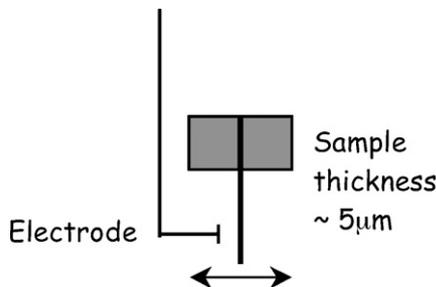


Fig. 9. Study of the Gorsky effect by dynamical energy loss measurements [77–80].

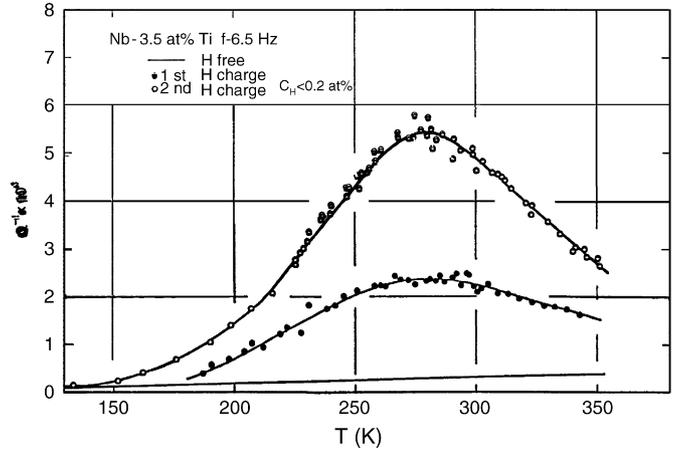


Fig. 10. The Gorsky relaxation peak in Nb–3.5 at.%Ti [87].

By introducing τ_1 in (1) approximated by the first term one obtains:

$$\ln D = \ln \frac{\omega h^2}{\pi^2} - \text{arc cosh} \frac{T_{\max} Q^{-1}(T_{\max})}{T Q^{-1}(T)} \quad (3)$$

where T_{\max} is the absolute temperature at which the condition $\omega\tau = 1$ is satisfied.

The dynamical method presents several advantages with respect to the quasi-static one by the torsion pendulum. In fact, in the former case the compressed and dilated regions are produced directly by the flexural vibration, and the Gorsky theory can be applied straightforward without use of correction parameters. In addition, Eq. (3) shows that the diffusion coefficient can be obtained not only at the temperature at which $\omega\tau = 1$, but at any other temperature where the dissipation process dominates over the background (Fig. 10). Owing to the sensitivity of the dynamical measurement, this fact allows the diffusion coefficient to be obtained over nearly three orders of magnitude at one sample frequency (Fig. 11), and on changing vibration frequency the range of D is extended. On the other side, all the samples used for the after effect measurements [76] contained dislocations. In fact, after the plastic deformation of the wires to form long coiled

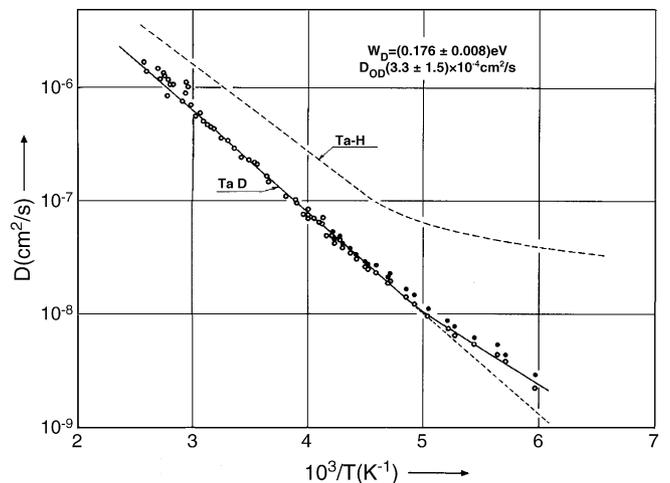


Fig. 11. Diffusion coefficient of H in tantalum from the Gorsky effect [79,80].

springs, the high temperature dislocation annealing could not be conducted, as the thermal treatment rendered the springs not self-sustained. In addition, due to the indirect relation between spring twisting and dilatation, the results needed a correction factor to fit the Gorsky τ relation.

The Gorsky relaxation time can be correctly measured also on monitoring the time-dependent recovery of the deflection of rectangular bars by an electrostatic bridge. However, the dynamic measurement of the energy dissipation of a vibrating thin sheet still remains the most favourable. In fact, recalling that τ is the relaxation time associated with the long-range diffusion from one side to the other side of the sample, one would have, for instance in Nb–H at 300 K, a Gorsky relaxation time $\tau = 3.62 \times 10^{-3}$ s for a 5 μm thick vibrating sheet against a value of five orders of magnitude higher ($\tau = 1.45 \times 10^2$ s) for a 1 mm deflected bar.

Sinning [81] identified an anelastic relaxation process in several hydrogenated polycrystalline alloys as due to the H long-range diffusion within the grains under flexural vibrations, i.e. the analogue of the Gorsky effect, but with the H diffusing from the compressed to the expanded side of a grain instead of the whole sample.

9. Thermoelastic effect

The diffusion of heat in solids can produce a relaxation effect known as the thermoelastic relaxation. Strain inhomogeneities in a vibrating bar give rise to an alternating heat current. The theory of this process was developed by Zener [82,83] and is formally like to that of the Gorsky effect. The only difference consists in the different law of the diffusion coefficient, which in the case of heat presents a complex regime: in metals it is generally nearly constant from 350 down to 100 K and assumes an hyperbolic increase below this temperature. For such a reason the thermoelastic relaxation cannot be observed as a function of temperature but only as a function of frequency. Berry [84] verified Zener's prediction by elastic energy dissipation measurements at room temperature by varying frequency. A complete verification of the thermoelastic effect came from Cannelli and Cannelli [85,86], who conducted a systematic investigation in niobium, tantalum and vanadium as a function of frequency, and determined the thermal diffusivity and the difference in molar heat capacity of these metals in a wide temperature range.

10. Trapping of H by substitutional solute atoms

The trapping of H by substitutional impurities was first reported for Nb–Ti–H dilute alloys in 1977 [87], and recently reviewed [88]. It was found by Gorsky effect measurements that the H diffusion coefficient progressively and noticeably decreases with increasing Ti concentration and concomitantly the activation energy for diffusion increases (Fig. 12). By applying a trapping model [50] the value $E_B = 0.06 \pm 0.01$ eV for the binding energy of H to Ti was obtained. Such a deepening of the barrier height with respect to the H free migration ($E_M = 0.11$ eV) is quite large. The consequent measurements of the relaxation spectrum in those alloys [89] revealed that additions of Ti con-

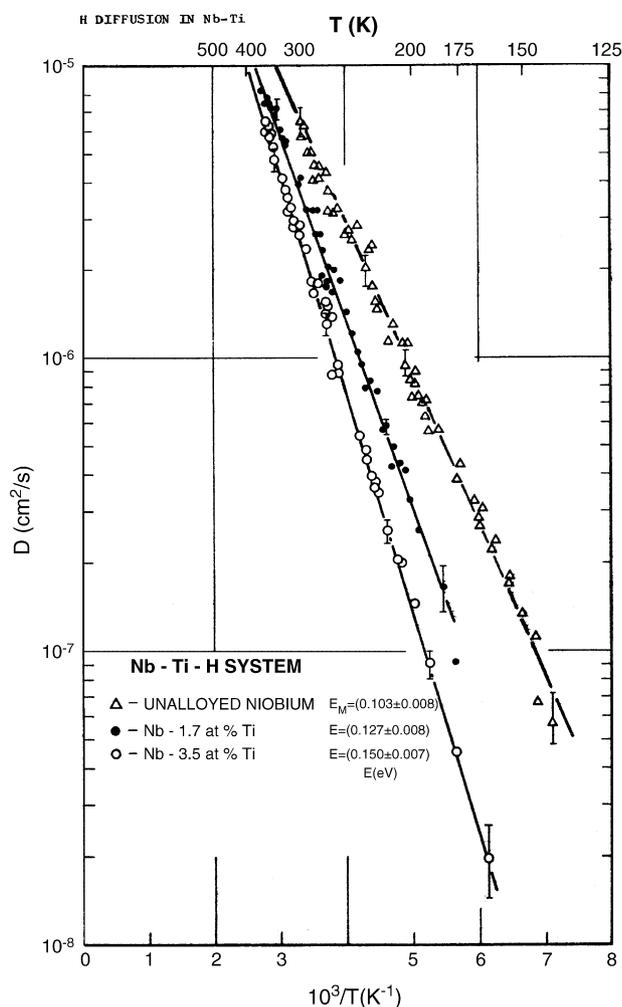


Fig. 12. H long-range diffusion coefficient in niobium by varying Ti concentration from Gorsky effect measurements [87,88].

tents as small as 2 and 5 at.% to niobium completely suppress the Cannelli–Verdini peak due to the relaxation of H around interstitial O, indicating that H is removed from the sites coordinated with O. In addition, two new interaction peaks appear at low temperature separated by about 50 K. The peak at the higher temperature (between 160 and 110 K) is dominant and markedly shifts to low temperature with increase of H content, down to a saturation value. An attempt to interpret the peak shift in terms of discrete peaks caused by different high order Ti-H_n complexes was not satisfactory [90]. An interpretation of the peak temperature dependence on the H content succeeded later on by formulating a statistical model based on the Fermi–Dirac statistics, and assuming that the energies of the free sites and trap sites are distributed according to density-of-state functions [91].

The anelastic measurements [89] indicated that substitutional Ti is a very effective trapping centre for H, which is able to remove this element from solid solution and to retain it in its neighbourhoods in the ratio 1:1, thus inhibiting hydride precipitation. In particular, in Nb–5 at.%Ti containing 4.2 at.%H, the precipitation, expected at 300 K in pure niobium, did not occur even on cooling down to 50 K. The presence of interac-

tion peaks and their shifts with the H content was found a few years later also in V–Ti dilute alloys [92]. The symmetry of the substitutional–interstitial complex was investigated by acoustic measurements in single crystals by Cannelli et al. [93] and Yoshinari et al. [94].

Recently, Yoshinari and co-workers [95] measured the Gorsky effect in the Ta–O–H and Ta–Nb–H systems to study the trapping effect of interstitials and substitutionals on H. By comparison with Nb–Ti [87–89] it is seen that Ti is a more effective trapping centre for H.

11. Acoustic emission from hydride precipitation

The stress wave emission occurring during the nucleation and growth of microcracks generated by severe hydride precipitation in metals (niobium, tantalum and vanadium) was discovered in 1979 [96–98]. Fig. 13 shows the acoustic emission total count rate, and the Q^{-1} and f curves on cooling a niobium sample containing 5.6 at.%H. The hydride precipitation temperature is monitored by the Q^{-1} and f inflections; a few kelvin below intense acoustic emission starts due to the cracking of the material caused by precipitation. The statistical analysis of the acoustic signals revealed that the metal–H systems during hydride formation show self-organized criticality (SOC) behaviour [99]. SOC systems organize themselves into a stationary critical state in which a minor event starts off a chain reaction that can affect any number of elements [100,101]. It is of relevant importance that the hydride precipitation follows the same Gutenberg–Richter law, which is operative in earthquakes [102] and in the market movements [101].

12. Coherent tunnelling of hydrogen

The extension of elastic energy dissipation to the liquid helium temperatures in niobium containing O and H in the kHz (Fig. 14) [103–105] and MHz [106] range revealed new thermally activated relaxation processes around 3 K, which denoted a non-classical dynamics of hydrogen. Such measurements, combined with specific heat [107] and neutron spectroscopy [108] results, gave the first evidence that at liquid helium temper-

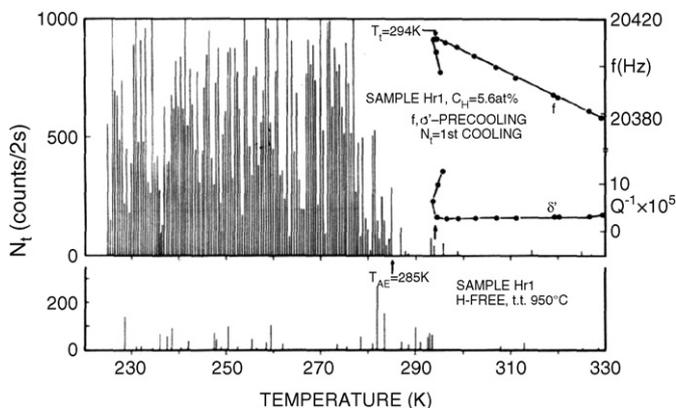
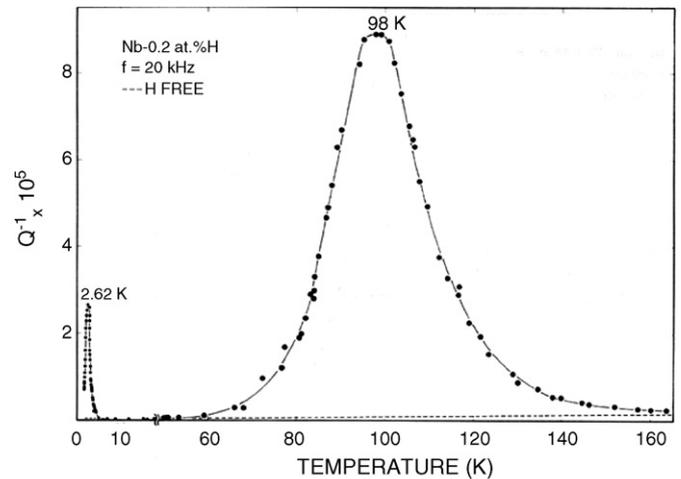


Fig. 13. Elastic energy loss, vibration frequency and total ringdown count rate of the bursts in niobium with 5.6 at.%H [96]. The lower part of the drawing represents the background emission of the H-free sample.



Internal friction spectrum of the Nb–O(N)–H system.

Fig. 14. Extension of the dissipation curve of Nb–O–H to liquid helium temperatures [103].

atures H forms two-level systems (TLS) in a pair of equivalent sites near the trapping impurity (Fig. 15). The tunnelling process appears only when also the Cannelli–Verdini peak at 100 K is present, indicating that the two effects are different manifestations of the same O–H complex; at the higher temperatures H visits the sites coordinated with the O trapping centre and possesses the thermal activation for dissociation via incoherent tunnelling. Instead, when temperature is lowered down a few kelvin, H is confined in sites near the trapping impurity, where it delocalizes itself due to the reduced interaction with the phonon or electron bath. The Q^{-1} experiments of Drescher-Krasicka et al. [109] and of Cannelli et al. [105] demonstrated that the relaxation rate τ^{-1} for H tunnelling in niobium and tantalum is dominated by the interaction with the conduction electrons.

The case of the interstitial–H pair giving rise to a TLS is rather different from the more symmetric substitutional–H complex. In the latter case, symmetry reasons suggested that H may tunnel at low temperature among the four tetrahedral sites of the {100} cube faces, which are symmetrically arranged with respect to the substitutional atom. Indeed, the formation of four-level tunnel systems (FLS) has been demonstrated by studying the Nb–Zr [110] and Nb–Ti systems [111,112]. It was also found

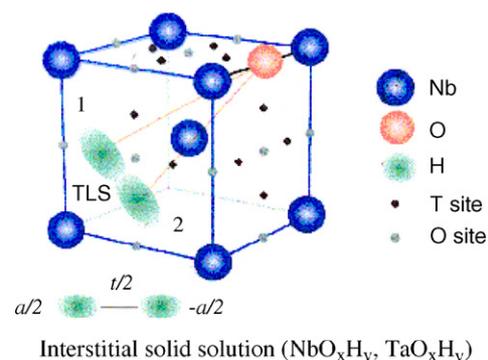


Fig. 15. Coherent tunnelling of H between two nearly equivalent sites in a dilute Nb–O alloy [105,88].

that the H transitions among the quantized energy levels of the FLS are assisted by the interactions with the conduction electrons [113]. Specific heat measurements in $\text{Nb}_{0.95}\text{Ti}_{0.05}\text{H}_x(\text{D}_x)$ revealed finite values of low energy excitations down to the lowest mK region [114], and this was later recognized to be expected by four level systems [111,113]. A review of the tunnelling of H and D in metals was given in [88].

13. High T_C superconductors

13.1. $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$

Anelastic relaxation experiments in ceramic superconductors started promptly after the discovery of high T_C superconductors. In order to obtain appropriate vibrating samples for the anelastic measurements the starting powders were sintered and compacted in the form of parallelepipeds. Cannelli et al. first reported the oxygen Snoek relaxation in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ in the nearly stoichiometric state ($x=0$). The peak appears around 55 K at ~ 1 kHz and is approximately single [115]. The activation energy of the jumping process of residual free oxygen in the CuO_x basal planes (Fig. 16) was 0.11 eV, and the diffusion coefficient resulted in a surprisingly high value, $D=4 \times 10^{-8} \exp(-0.11 \text{ eV}/kT) \text{ m}^2/\text{s}$ [114], which extrapolated to room temperature is comparable with that of hydrogen in transition metals. At the doping levels at which the cuprate is superconducting ($x > 0.5$) the O Snoek peak is suppressed as a negligible number of isolated O atoms is available, and peaks related to O jumps between off-centre positions within the Cu–O chains in the basal planes appear between 35 and 110 K. This zig-zag chain dynamics is a thermally activated process and has been investigated by various authors [116–121]. Energy dissipation measurements above room temperature

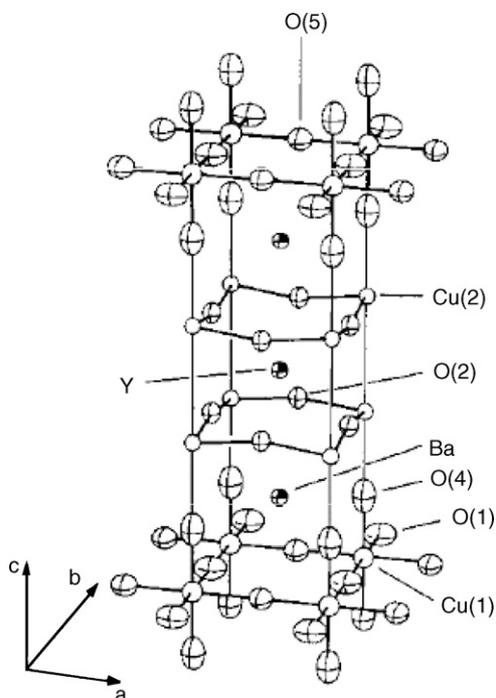


Fig. 16. Unit cell of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$. The $\text{Cu}(1)$ – $\text{O}(1)$ sequence gives rise to the zig-zag chains in the Cu – O_{6+x} basal plane.

were carried out by after effect [122], pendulum [123–126], and resonant bar [127–130]. Most experiments reported only one thermally activated process, the so called PH2, appearing at about 750 K in the kHz region. After exploring the complete range of x an adjacent but distinct peak, called PH1, was found at about 600 K in the low temperature side of PH2 [127,130,131], which increases while PH2 disappears (Fig. 17) during its measurement due to O outgassing [131]. Process PH2 was assigned to the hopping of O in the Ortho-I phase existing for $x \sim 0.8$ and constituted by filled Cu–O chains in the CuO_{6+x} plane. Peak PH1 was ascribed to the reorientation of O in the Ortho-II phase, constituted by alternately filled Cu–O chains in the CuO_{6+x} plane. A review of the dynamics and phase transformations in the 123 ceramic superconductors by anelastic relaxation was given in [132].

13.2. Doped La_2CuO_4

The lanthanum cuprate La_2CuO_4 , if doped with Sr ($\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, LSCO) or Ba ($\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, LBCO) becomes superconducting at temperatures lower than 40 K. Its structure is formed by layers of CuO_6 octahedra intercalated by La atoms, as shown in Fig. 18. It has been shown that the octahedra of undoped La_2CuO_4 are not straight but tilted [133,134]. As they are relatively rigid and hinged to each other at their corners, the tilt of one of them propagates to the surrounding ones, resulting in a long-range-ordered pattern of tilts. Anelastic relaxation combined with ^{139}La NQR (nuclear quadrupole relaxation) experiments demonstrated that the tilting is not rigid but presents a collective dynamics, resulting in an intense relaxation process with an activation energy of 0.23 eV, which was identified as the thermally activated tilt motion of a fraction of the CuO_6 octahedra in double well potentials [135,136]. Moreover a quantum tunnelling process due to the local dynamics of the tilts of the octahedra has been reported at the liquid helium temperatures [137].

The phase diagram of LSCO is essentially characterized by (Fig. 19): (1) a high temperature tetragonal (HTT) to low

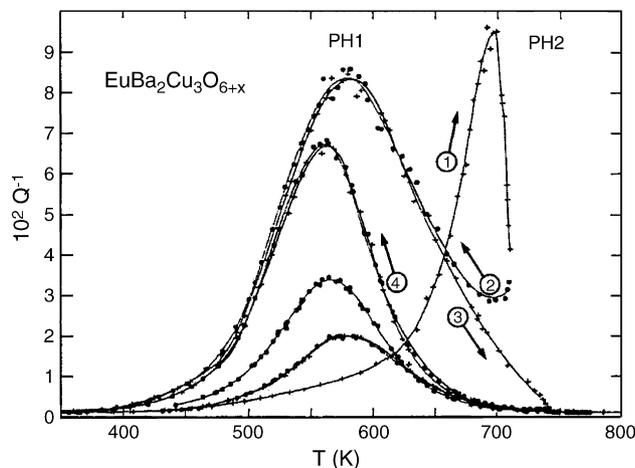


Fig. 17. Evolution of PH2/PH1 in a sample of $\text{EuBa}_2\text{Cu}_3\text{O}_{6+x}$ with decreasing x , starting from $x=0.9$ [131].

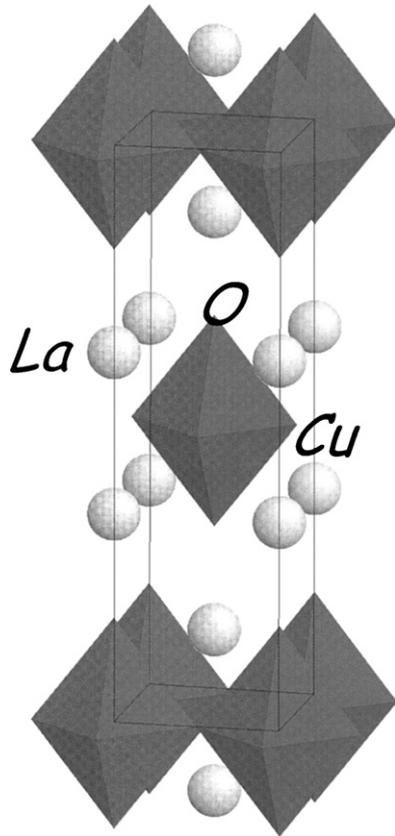


Fig. 18. Structure of La_2CuO_4 and CuO_6 octahedra.

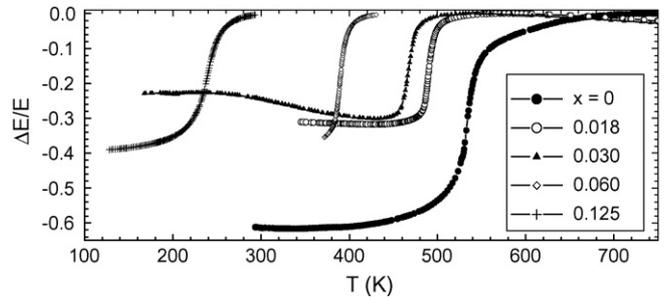


Fig. 20. Modulus inflections revealing the high temperature tetragonal to low temperature orthorhombic phase transformation of La_2CuO_4 [136].

the non-superconducting antiferromagnetic phase at low Sr doping including a spin-glass area, and a cluster spin-glass region which partially interpenetrates the superconducting one. Also the transition to these inhomogeneous magnetic phases have been studied by anelastic spectroscopy; in fact, these transitions are accompanied by an increase of the elastic dissipation due to the stress-induced movement of the domain walls [138–140].

Finally, anelastic spectroscopy detected a thermally activated peak in LSCO centered around 80 K at 1 kHz, attributed to a polaronic mechanism, which was identified with the disordered charge stripes overcoming pinning centers [141].

14. New perspectives of mechanical spectroscopy in nanoscience

Mechanical spectroscopy experiments making use of vibrating samples require specimens with extended dimensions, also in order to decrease the background dissipation. This limitation may preclude the possibility of measuring samples in which the crystal growth can be achieved only on a millimetre scale. Mizubayashi et al. surmounted this problem by glueing or mechanically clamping to massive blocks vibrating samples having lengths from a few millimetres to 0.3 mm (often the biggest obtainable single crystals) [142].

Sometimes the samples are available only in the form of powders, and in some other cases it is of no meaning to look for bulky samples, as their working state is in form of powders. This is the case of solid state hydrogen reservoirs, where hydride precipitation brittles and fragments the materials. A way of obtaining extended samples from powders is that to consolidate them by the sintering process. This procedure has been used for the high T_C superconductors and for the materials for the lithium batteries (Section 16).

When materials are not sinterable, they can be consolidated by pressing the powders either as they are, or after mixing them with potassium bromide (KBr), which is a rather neutral mean having a compacting function. This procedure was first introduced to study the organic molecules [143] and the alanates, the new class of hydrogen absorbers (Section 15), where the samples were nano- and micro-structured powders.

When the material is processed to form a gel, it can be spread onto a known substrate. If the substrate vibration is able to transfer the alternating stress into the gel, a mechanical spectroscopy experiment can be conducted; this has been demonstrated to be

temperature orthorhombic (LTO) phase transformation, which can be easily detected by anelastic spectroscopy by means of the large modulus variation associated with the transition (Fig. 20); (2) a curve delimiting the superconducting region; (3)

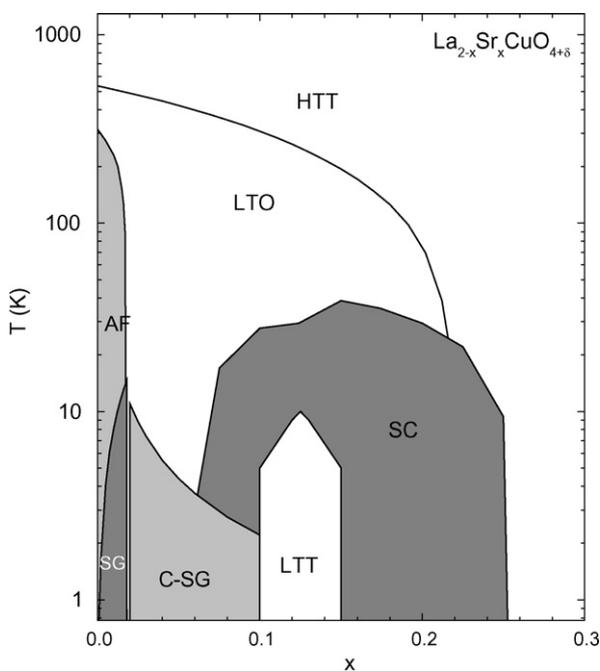


Fig. 19. Phase diagram of the high T_C superconductor $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$.

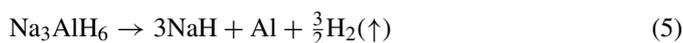
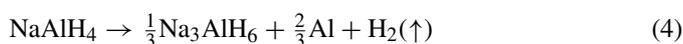
feasible in the case of biological matter (Section 20). Deposition on substrates is useful to study hydrogen in semiconductors, organic matter, and carbon nanotubes, too.

Those new procedures have allowed the mechanical spectroscopy to be applied to any frontier subject of modern science and technology; this makes it possible to supply, by an indispensable technique like ours, the needed information on the motion parameters and phase transformations of condensed matter.

15. Energy storage—hydrogen accumulation in solids

Hydrogen as energy carrier is arousing renewed interest due to the necessity of finding alternative energetic sources, not only because fossil fuels will be finally exhausted, but mainly in order to find a way towards the energetic independence, not influenced by the political instability on planetary scale, and in order to decrease the environmental pollution from fossil fuels. The choice of a hydrogen economy implies several problems connected with: (a) the hydrogen production with a process that should be energetically favourable and free from CO and CO₂ pollution as much as possible; (b) the storage in one of the three possible forms, gaseous, liquid or as solid hydride; (c) its utilization by feeding fuel cells to produce electric energy, or through direct reaction with oxygen in internal combustion engines. Of the three ways for hydrogen storage, the introduction in solids as a hydride appears rather promising because of a high massive storage capacity and safety. However, at present the solid-state tanks are not yet fully compatible with the requirements from current applications. The main requirements for such tanks are: (a) high storage capacity; (b) moderate absorption/desorption temperatures; (c) fast hydrogenation/ dehydrogenation kinetics; (d) high resistance to degradation and contamination on thermal and charge/discharge cycling. The use of nanostructured powders increases the surface/volume ratio and has beneficial effects on the absorption/desorption kinetics.

Sodium alanates, NaAlH₄, are considered among the most promising novel absorbers for solid-state hydrogen storage. The hydrogen release from these materials, which is contained in their formula units, occurs by means of three chemical decomposition reactions that take place at increasing temperatures:



The last reaction occurs at a temperature too high to be of practical interest. The addition of a catalyst, such as Ti or Zr, significantly decreases the H release temperatures, makes the decomposition reaction reversible, and enhances the kinetics of dehydrogenation and re-hydrogenation of the compound to rates that are of practical relevance [144]. Despite large efforts, the atomistic paths during the tetrahydride–hexahydride decomposition reaction, and the mechanism of action of the catalyst are still unknown. Various authors [145–147] invoked the existence of a highly mobile entity in order to explain the reverse transitions in (4) and (5). Recent mechanical spectroscopy data

allowed essential information to be obtained on the various decomposition steps and on the mechanism of action of the catalyst [148,149]. In this case, the samples were micro and nanostructured powders, which were pressed in order to obtain the extended and consolidated samples necessary for vibration. It was observed that heating sodium alanates to temperatures at which decomposition occurs causes the formation of a new species. This species gives rise to a thermally activated relaxation peak around 70 K at 1 kHz, denoting a very high mobility; the value of the prefactor of the relaxation time ($\tau_0 = 7 \times 10^{-14}$ s) is typical of a point defect complex, which, according to the observed deuterium isotope effect, involves hydrogen.

Fig. 21 shows the high temperature f curves for an alanate NaAlH₄ starting sample doped with 2% TiF₃. During the thermal cyclings up to 360 K the f curves show hysteresis loops which close on cooling back to room temperature, indicating practically no onset of the chemical reactions. Instead, the cycles extended to higher temperatures remain open and, principally, the elastic modulus markedly decreases from cycle to cycle; the former feature and the visible softening indicate a substantial change of the nature of the material, explained by the progressive formation of a new phase during decomposition, which is accompanied by the hydrogen evolution out of the sample according to Eqs. (4) and (5).

Each high temperature f measurement was followed by a low temperature run. Fig. 22 shows the low temperature dissipation curves of the NaAlH₄ samples doped with 2% TiF₃ after the corresponding thermal ageings reported in Fig. 21. The sample that previously displayed a closed loop when heated to 360 K (curve 1 in Fig. 21) showed a smooth background dissipation on cooling. After the thermal treatment to 380 K, a peak appears at ~ 70 K with a vibration frequency of 1 kHz (curve 2

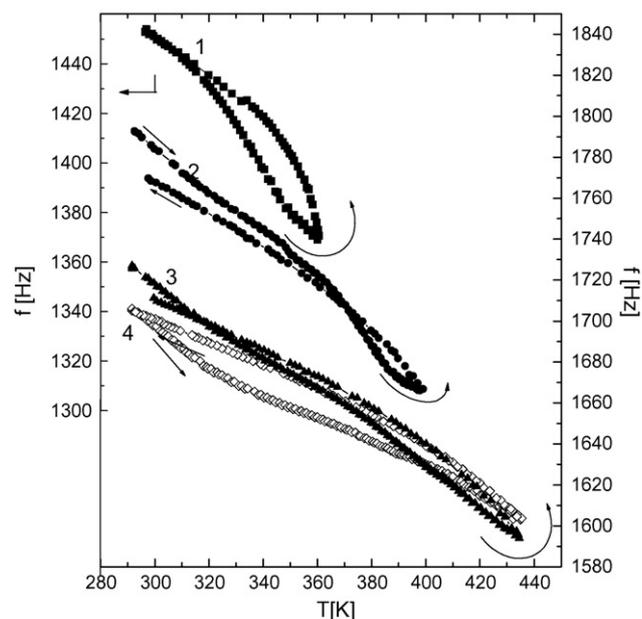


Fig. 21. Temperature dependence of the frequency of a NaAlH₄ sample doped with 2%Ti acting as a catalyst, during a thermal cycle up to 360 K (■, 1), 400 K (●, 2), 435 K (▲, 3), and 436 K (□, 4) [148].

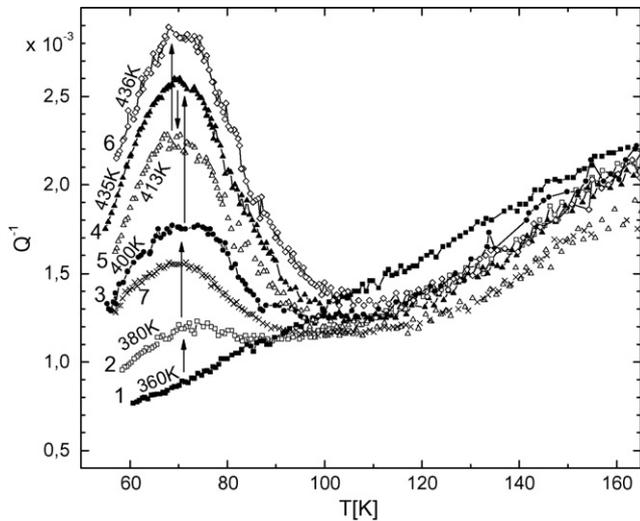


Fig. 22. Low-temperature dependence of the elastic energy loss. Sample of Fig. 21 after thermal treatments (TT) up to 360 K (■, 1), 380 K (□, 2); 400 K (●, 3); 435 K (▲, 4); 413 K (△, 5); 436 K (◇, 6). Sample b (mixed with KBr) after TT up to 436 K (x, 7) [149].

in Fig. 22), which develops in height after subsequent thermal treatments to progressively higher temperatures. The formation of such a new species and its evolution during the decomposition reactions in the Ti-doped alanate was observed for the first time by anelastic relaxation spectroscopy. Various possible sources of the process have been considered, taking into account the products of decomposition. After excluding any stoichiometric product of decomposition and even the involvement of catalytic Ti, it is concluded that the most likely cause of the observed process is a hexahydride stoichiometry defect of type AlH_{6-x} missing one or more H atoms, thus giving rise to local vacancy dynamics. The results show that not all the hydrogen released during the high temperature decomposition reactions evolves out of the samples as gas, but part of it remains in the lattice and, above room temperature, it diffuses on a long-range scale. At high temperature a spontaneous partial reverse decomposition reaction has been monitored by a peak decrease (Fig. 22, curve 5). At low temperature the long-range mobility of H is frozen and only a local dynamics around an Al atom takes place. In addition, the anelasticity measurements demonstrated that the AlH_{6-x} bond is a deeper trap for H than Ti. A novel model has been formulated which explains the catalytic effect of Ti and the decomposition mechanism, in which hydrogen is identified as the long-range mobile species inducing the tetragonal-monoclinic phase transformation connected with decomposition [149]. Lastly, curve 7 shows that the presence of KBr does not modify the features of the low temperature peak; its lower height is due to the smaller amount of alanate in the mixed sample.

16. Energy storage—materials for the lithium batteries

Lithium cobalt oxides, $\text{Li}_{1-x}\text{Co}_x\text{O}_2$, can have an electric-energy mass density six times higher than that of lead batteries, three times that of Ni–Cd, and twice that of the nickel hydrides.

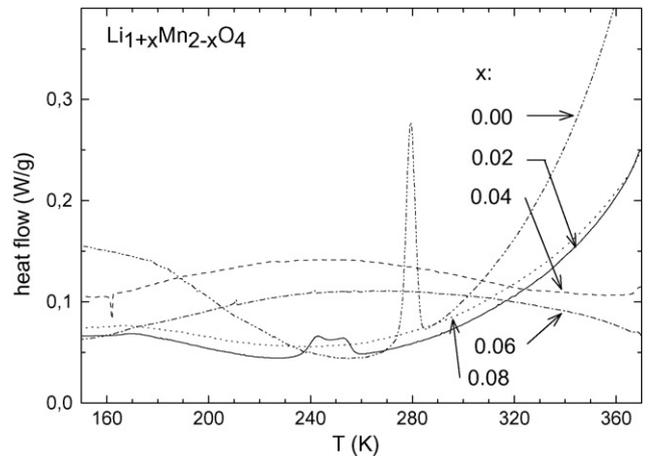


Fig. 23. Spinels for lithium ion batteries; DSC curves of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ as a function of doping measured on cooling [151].

However, because of the toxicity of cobalt, new substitutions should be synthesized. Spinels, LiMn_2O_4 , seem promising, but the occurrence of a structural phase transformation at room temperature still prevents its use in the current applications. It was reported, by measurements of differential scanning calorimetry (DSC) [150], that partial substitutions of Mn such as $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ shift the phase transformation to low temperature, out of the working temperatures of the devices. In addition, from the absence of the heat peak anomaly (at 280 K) for $x > 0.02$ (Fig. 23), it was concluded that the phase transformation is eventually suppressed [150]. On the contrary, recent measurements of elastic energy dissipation and modulus

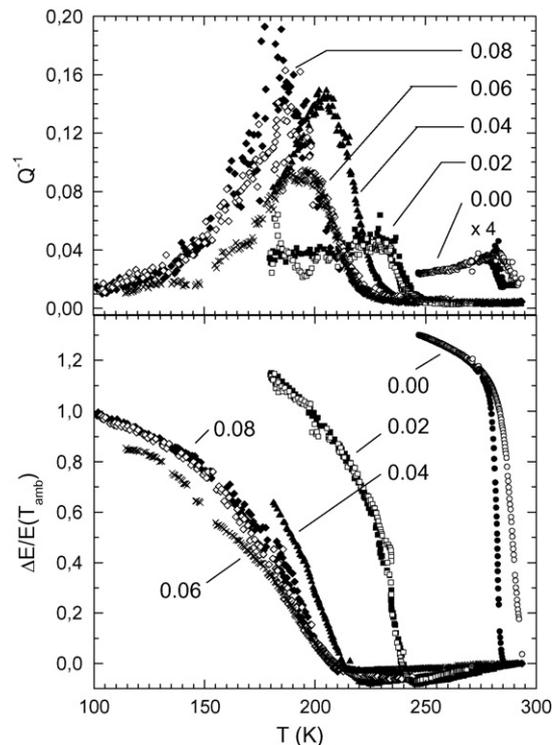


Fig. 24. Energy dissipation and relative dynamic Young's modulus vs. doping of the same $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ samples of Fig. 23 [151].

on sintered samples revealed that the phase transformation, monitored by huge Q^{-1} and f inflections (Fig. 24), persists even at the highest doping levels measured [151]. The discrepancy between the two experiments was explained [151] with a possible change of the phase transformation from the first to the second order, as doping is increased, similarly to Fe_3O_4 doped by Zn or Ti [152]; in fact, DSC does not reveal second order transformations. The results on spinels point out once more that anelastic measurements are a valuable tool for studying phase transformations.

17. Carbon nanotubes

Carbon nanotubes (CNT) are promising materials in the fields of electronics, mechanical actuators, gas sensing devices and confinement of gases and liquids in one- and two-dimensions [153–156]. The anelastic properties of bucky papers made of so called HiPco single wall carbon nanotubes were investigated for the first time. The Q^{-1} curve from 4 to 700 K displays peaks due to phase transformations, to gas absorptions, and to thermally activated processes. As a detailed paper on this subject is reported elsewhere in this Conference [157], only the main results will be summarized here.

Three relaxation peaks are observed: peak A at 25 K ($f \sim 400$ Hz), peak B at 150 K, and peak E at 550 K (Fig. 25). The first peak cannot be explained in classical terms and its features recall the tunnelling of atomic hydrogen in transition metals [158].

Peak B practically disappears when heating the sample to 700 K and reappears after exposing to a hydrogen atmosphere at 80 K. Therefore it is suspected to be due to the hydrogen molecule. The presence of a dissipation peak is indicative that the hexagonal lattice of the CNT is not neutral, but is distorted by its interaction with the H_2 molecule. A model has been proposed in which this distortion is assumed to be produced by the fraction of molecular hydrogen in the ortho state, giving rise to three distinct defect orientations.

Peak E above room temperature slowly decreases in height after repeated thermal treatments in a vacuum at 700 K, and was associated with the dynamics of the carboxylic groups or other molecular clusters attached on the surface.

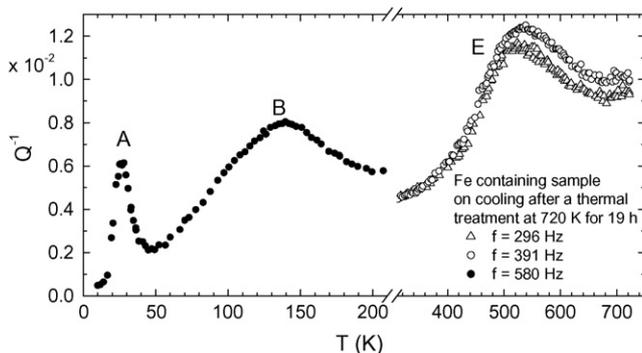


Fig. 25. Anelastic relaxation processes in bucky papers of single-wall carbon nanotubes [157].

18. Ferroelectric materials

The relaxor ferroelectrics are a class of materials, which is receiving considerable attention, owing to the high values that their electromechanical coupling parameters and dielectric permittivity may reach. These materials are mainly perovskites with strong cationic disorder that prevents the formation of long-range polar order, e.g. $(\text{Pb/La})(\text{Zr/Ti})\text{O}_3$ (PLZT). Instead of ferroelectric domains they develop polar nanoclusters whose fluctuations freeze below some temperature T_g , signaled by a broad frequency dependent maximum in the dielectric susceptibility. Similarly to other glassy systems, the relaxor ferroelectrics exhibit ageing (decrease of dielectric susceptibility and elastic compliance $s(\omega, T)$ during a stay at fixed temperature), rejuvenation (on further cooling, the reference curve measured on continuous cooling is rejoined, as if no ageing occurred), and memory (on subsequent heating, the ageing holes in $s(\omega, T)$ are partially retraced). Also the memory of multiple ageing stages may be retained, as observed below T_g in some spin glasses, but it has been found that PLZT exhibits such phenomena typical of the frozen glassy state even above T_g , as shown in Fig. 26 [159], which poses questions on the nature of its glassy state. Anelastic spectroscopy experiments combined with NMR relaxation and dielectric susceptibility on PLZT [160] have also revealed the existence of non-polar relaxation modes, likely related to rotations of the oxygen octahedra, that are faster and weakly coupled to the freezing polar fluctuations.

19. Manganites

Manganites (formula units of type $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$) remarkably vary their electrical resistivity upon application of an external magnetic field. Moreover, at about 260 K they display a phase transition from the paramagnetic-insulating to the ferromagnetic-metallic state. The latter phase, which appears

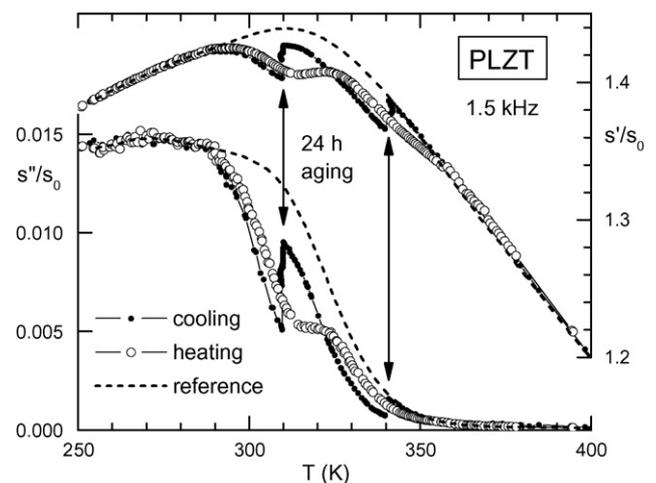


Fig. 26. Real and imaginary parts of the elastic compliance of PLZT with 9%La and 65%Zr, normalized to its value s_0 at high temperature. During cooling two ageing stages are made, whose memory is retained upon heating [159] (written permission of the author).

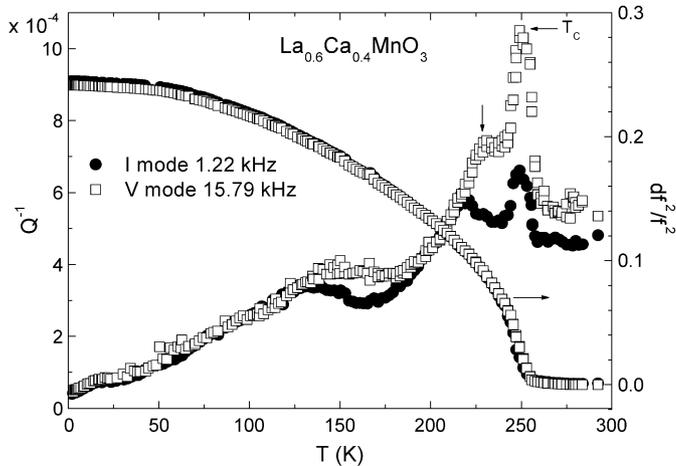


Fig. 27. Elastic modulus and energy dissipation of the manganite $\text{La}_{0.60}\text{Ca}_{0.40}\text{MnO}_3$ [162,163].

at low temperature, presents an inhomogeneous distribution of insulating and metallic domains on a nanometric scale. The strong magneto-conductive coupling induces an overall spin alignment occurring on a nanometric scale, and this confers to those materials a possible interest in spintronics. The occurrence of the magneto-conductive coupling was explained by Zener in 1951 [161] by a double exchange mechanism.

This magnetic phase transition was revealed [162,163] both by the elastic modulus and the energy loss (Fig. 27). The Q^{-1} curve shows a main peak at the Curie transition temperature; in addition, a side peak was found slightly below T_C , whose temperature and frequency behaviour is typical of the dielectric and magnetic susceptibilities of spin glasses and inhomogeneous frustrated systems. These features were interpreted by a strong magnetoelastic coupling associated to the formation of magnetic clusters in the low temperature inhomogeneous phase [162,163].

20. Biological matter

Gene therapy is a therapeutic approach aimed at correcting genetic defects by replacing the disease-causing gene, adopting a procedure by which a correct copy of the gene itself is transferred into the cells of the patient [164]. Of particular interest are the studies focused on non-viral and non-infecting transfection vectors such as lipid membranes.

The highest transfection efficiency was found to occur in the neutral lipid DOPC (dioleoyl phosphatidylcholine), and in mixtures of a cationic and a neutral lipid [164]. Elastic modulus and energy loss measurements in samples obtained by depositing the biologic gel on well characterized silicon substrates, revealed a main relaxation process at about 200 K (Fig. 28), which is weakly thermally activated and is not described by a single Debye curve. The peak is present only in the lipid systems displaying the higher transfection efficiency [165], and is likely to be caused by the formation of a new phase constituted by mobile domains, for instance by cationic lipid domains intercalated by the neutral ones, having a collective dynamics based on short-range lateral diffusion in the membrane plane. The study of a possible correlation between the presence of the dissipation

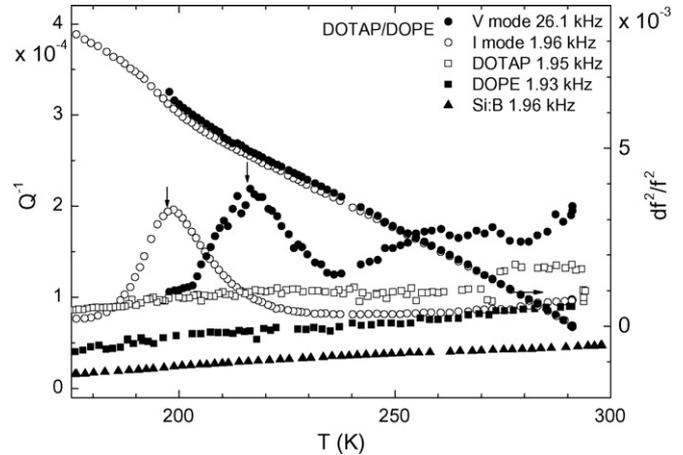


Fig. 28. Q^{-1} curves of the DOTAP/DOPE (dioleoyl trimethylammonium propane/dioleoyl phosphatidylethanolamine) mixture at two frequencies, of pure cationic DOTAP, of neutral DOPE, and of the pure Si:B (1 0 0) substrate for background reference. The relative changes of the dynamic Young's modulus of the DOTAP/DOPE mixture are also reported [165].

peak and the gene transfection mechanism would be of remarkable interest.

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