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Similarities and differences between the low-temperature acoustic properties of crystalline materials and glasses

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We report on measurements of the acoustic properties of single crystals of alkali halides and aluminum, and polycrystalline copper at kHz frequencies and temperatures down to 8 mK. The goal of this study was to examine in several crystals with a small number of defects the presence and influence of two-level tunneling systems which commonly govern the low-temperature behavior of amorphous solids. The samples were investigated using vibrating reed and torsional oscillator techniques. In contrast to recent reports on glasslike behavior for a large variety of pure polycrystalline metals, our results confirm the ‘‘traditional’’ point of view that the low-temperature acoustic properties of pure monatomic crystals can be well distinguished from those of amorphous solids. [S0163-1829(97)06437-0]

I. INTRODUCTION

The low-temperature properties of amorphous materials are dominated by low-energy excitations which are believed to be caused and thus intimately related to the disordered structure. Based on 25 years of experimental and theoretical research it appears that these low-energy excitations are best described by two-level systems which have a broad spectrum of energies and relaxation times and are caused by the tunneling motion of a few atoms residing in double-well potentials.[1] Also crystals containing defects or some other sort of disorder, e.g., alloys with diffusionless phase transitions,[2] or alkali-halide mixed crystals with substitutional disorder,[3] may exhibit in certain concentration ranges low-temperature properties similar to those of glasses. In good crystals, however, no tunneling should occur due to the perfect arrangement of all atoms.

A considerable number of recent acoustic experiments by Esquinazi *et al.*,[4–7] however, indicated that the number density of tunneling systems in an arbitrarily chosen polycrystalline metal is generally of the same order of magnitude as in glasses, and that these two-level systems have a similarly broad distribution of energies and relaxation times. These observations gave rise to the statement that ‘‘there are basically no differences between the low-temperature acoustic properties of polycrystalline metals and amorphous materials.’’[5] A clear explanation for the occurrence of tunneling systems in these materials has not yet been given, though.

These puzzling results for the polycrystalline metals as well as the long-standing question of the microscopic nature of the tunneling states in amorphous solids make it worth reexamining the acoustic properties of very pure crystals as a starting point. Believing that some sort of disorder must be responsible for the existence of tunneling systems, we performed a series of vibrating reed and torsional oscillator experiments on several crystalline samples with a small and, if possible, controlled number of defects. The samples were ultrapure KCl and KCl doped with 60 ppm Li, a single crystal of Al, and polycrystalline Cu with large grains. For the copper samples we used both vibrating reed and torsional oscillator techniques to investigate the possible influence of the applied method on the experimental results and also checked the influence of annealing on the low-temperature properties. A brief account of the results for the copper samples has already been given elsewhere.[8] Although we find in most of our samples evidence for the presence of low-energy excitations, our experiments generally show that the low-temperature acoustic properties of all investigated crystalline materials can be well distinguished from those of glasses.

This paper is organized as follows. As a baseline of our discussion we will briefly recall in the next section the predictions of the tunneling model for the low-temperature acoustic properties of glasses, and review some results of previous acoustic experiments on various simple metals. Section III gives some information on the experimental technique, while Sec. IV contains the presentation and discussion of our experimental results.

II. THEORETICAL AND EXPERIMENTAL BACKGROUND

A. Acoustic properties of glasses—Predictions of the tunneling model

Here we will only briefly summarize the assumptions and predictions of the tunneling model with regard to our low-frequency acoustic experiments. More detailed discussions have been given elsewhere.[9,10] The basic assumptions of the tunneling model are: (i) In amorphous solids some atoms or small groups of atoms can move between two almost degenerate configurations. They can be modeled as particles in double well potentials with asymmetry Δ and tunnel splitting Δ_0. The resulting total energy splitting between the two lowest levels is given by $E=(\Delta^2+\Delta_0^2)^{1/2}$. (ii) Due to the irregular atomic arrangement in glasses the parameters Δ and Δ_0 are widely distributed. In general, a distribution function $P(\Delta,\Delta_0)=P/\Delta_0$ is assumed where P is a constant. (iii) Below 1 K the dominant relaxation mechanism for tunneling systems in insulating glasses is the so-called one-phonon process. The rate of this process is given by

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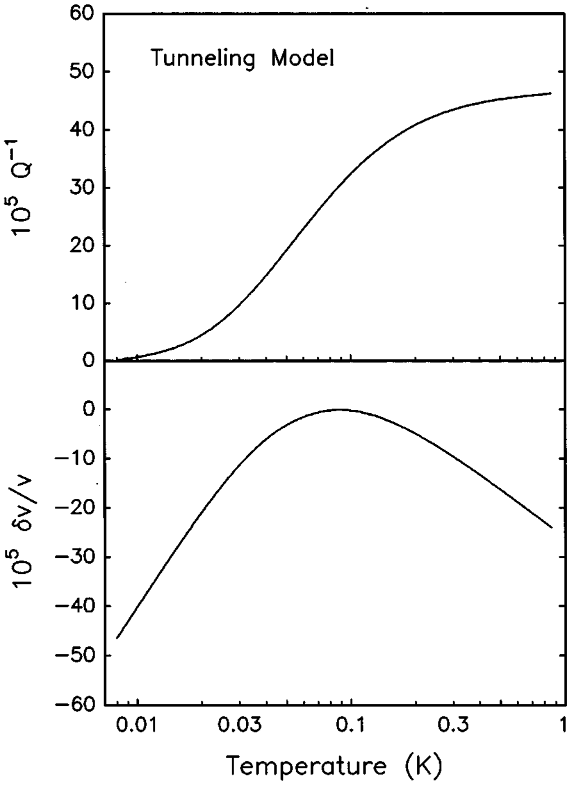

FIG. 1. Temperature dependence of the internal friction and of the relative change of sound velocity as predicted by the tunneling model for a dielectric glass. The parameters used were $A=10^8\ \mathrm{K}^{-3}$ and $C=3\times10^{-4}$. The frequency was chosen as 5 kHz.

$\tau^{-1}=A\Delta_0^2 E\ \coth(E/2k_BT)$, where the constant A is determined by the deformation potential γ, the mass density ρ, and the sound velocity v. For a given energy splitting, there is a wide distribution of relaxation times. Symmetric tunneling systems have the shortest relaxation times, denoted by $\tau_{\min}$.

The temperature dependence, as predicted by the tunneling model, of the internal friction Q^{-1} and of the relative change of sound velocity $\delta v/v$ of an insulating glass below 1 K is shown in Fig. 1. The parameters used for the numerical calculation were $A=10^8\ \mathrm{K}^{-3}$ and $C=\overline{P}\gamma^2/\rho v^2=3\times10^{-4}$, quite typical of a glass; the frequency $f=\omega/2\pi$ was chosen as 5 kHz.

At low temperatures, when $\omega\tau_{\min}\gg1$, the internal friction increases as the third power of temperature, and the sound velocity varies logarithmically with temperature as

$$\frac{\delta v}{v}=C\ \ln\left(\frac{T}{T_0}\right), \tag{1}$$

where T_0 is an arbitrary reference temperature.

At higher temperatures, when $\omega\tau_{\min}\ll1$, the internal friction approaches the value

$$Q^{-1}=\frac{\pi}{2}C \tag{2}$$

independent of temperature and frequency. The sound velocity passes a maximum and then decreases logarithmically with increasing temperature as

$$\frac{\delta v}{v}=-\frac{C}{2}\ln\left(\frac{T}{T_0}\right). \tag{3}$$

The position $T_{\max}$ of the maximum of sound velocity shifts with frequency as $f^{1/3}$.

In metallic glasses the situation is complicated by the interaction between conduction electrons and tunneling systems that opens up an additional relaxation channel.[11] At very low temperatures the relaxation rate due to conduction electrons which is proportional to the density of states at the Fermi level can be several orders of magnitude higher than the one-phonon rate. Experimentally, evidence for a tunneling system-electron interaction comes from ultrasonic measurements of normal conducting metallic glasses[12,9] and, most clearly, of amorphous superconductors.[13,14] Since in the latter case the electrons condense into the BCS ground state the relaxation rate drops exponentially with decreasing temperature below the superconducting transition temperature and the relaxation is dominated by phonons as in dielectric materials.[6,15] In addition to the strong enhancement of the relaxation rates, conduction electrons seem to reduce the density of states of the tunneling systems.[14] More advanced theoretical treatments show that (i) the coupling of tunneling systems to conduction electrons renormalizes the tunneling energy Δ_0[16–19] which in turn may reduce, in a nontrivial way, the density of states of the tunneling systems in the normal state compared to that in the superconducting state,[20,21] (ii) it is necessary to consider incoherent tunneling which in general leads to a nonmonotonic temperature dependence of the relaxation rate,[19,22,23] and (iii) a lower bound in the distribution of Δ_0 may be introduced[20,22] which may significantly change the predictions of the temperature dependencies of Q^{-1} and $\delta v/v$.

It is worth to note that essential aspects of this more elaborate discussion of the interaction of tunneling states with conduction electrons have been verified for light interstitials in crystalline metals, particularly for hydrogen in niobium which forms tunneling systems with well-defined Δ_0 and restricted distribution in Δ: rapid freezing of the electron-induced relaxation rate on cooling below the superconducting transition,[24–26] change of Δ_0 due to the coupling to conduction electrons,[25,27] and the crossover to incoherent tunneling.[28]

Although somewhat difficult to survey, most of the experimental results can be accounted for by those more sophisticated theories. Here we want to mention only some general predictions and observations for the acoustic properties. The relaxation via conduction electrons may be relevant down to temperatures as low as 10 mK since even at very low temperatures the relaxation rates can still be comparable to the measuring frequency. In normal conductors this leads to an almost temperature-independent internal friction and to a reduction of the slope of the logarithmic increase of $\delta v/v$ [Eq. (1)] arising from the resonant interaction of tunneling systems with phonons. A modified distribution of Δ_0 allows a better description of the temperature dependence of Q^{-1} and leads to a further reduction of the slope of the increase of $\delta v/v$. At higher temperatures the relaxation via phonons becomes dominant and gives rise to a decrease of $\delta v/v$ with increasing temperature. In amorphous superconductors and at sufficiently low measuring frequency $\delta v/v$ is described by

Eqs. (1) and (3). As in dielectric glasses, $\delta v/v$ decreases much faster above approximately 1 K due to multiphonon processes.

While the situation in metallic glasses is rather complicated, acoustic experiments on dielectric glasses generally show a reasonable agreement with the predictions of the tunneling model. We want to mention only briefly some deviations which generally occur. (i) The measured temperature dependence of the internal friction does not increase with temperature as T^3 but as T^α with α between 1 and 2.[4,10,29] (ii) The sound velocity becomes strain dependent at low temperatures; it decreases with increasing strain amplitudes.[4,10] (iii) In the limit of small strains the increase of the sound velocity below the maximum is not twice as steep as the decrease above the maximum [as expected from Eqs. (1) and (3)], but the ratio of the two slopes is fairly close to $1:(-1)$.[10,29,30]

None of these observations has conclusively been explained yet. Problems such as the interaction between tunneling defects (which could lead to a linear temperature dependence of Q^{-1}) and the nonlinear response of tunneling systems to high acoustic or electric field amplitudes have recently been investigated theoretically.[31,32] For our present discussion, however, it is more important to emphasize that the tunneling model in fact gives at least a correct qualitative description of the experimental results and that the behavior of different glasses is quite universal, i.e., the parameters A and C usually vary only within one order of magnitude.

B. Previous acoustic experiments on simple metallic crystals

The low-temperature acoustic properties of pure crystals can be basically understood in terms of the Debye model and the model of the free electron gas. Within this simple approach the internal energy of a metal can be expressed as a sum of a temperature-independent term plus contributions from thermal excitations in the electron gas ($\propto T^2$) and from the lattice vibrations or phonons ($\propto T^4$). Since the elastic constants are basically the second derivatives of the internal energy with respect to deformation, the relative change of sound velocity $\delta v/v=[v(T)-v(0)]/v(T)$ is expected to vary for $T\rightarrow 0$ as

$$\frac{\delta v}{v}=-aT^2-bT^4, \tag{4}$$

where a and b are positive constants. For dielectric materials, $a=0$ and

$$\frac{\delta v}{v}=-bT^4. \tag{5}$$

The predicted behavior has been experimentally observed, e.g., for vanadium and Cu:Au(0.1%).[33] In general, however, additional contributions to $\delta v/v$ may occur, e.g., from the motion of dislocation lines under the influence of a sound field, and can give rise to a more complicated temperature dependence. A linear decrease $\delta v/v\propto -T$ was found for example for oxygen-free high-conductivity (OFHC) copper with a purity of 99.98% as well as for 99.9% pure gold and lead, while 99.999% pure copper exhibited a decrease $\delta v/v\propto -T^{1/4}$.[34] Neither of these empirical relations is theoretically understood. The occurrence of the additional contributions can be suppressed by pinning of the dislocation lines at vacancies or can be gradually reduced by successive annealing procedures.[33]

It has also been demonstrated by ultrasonic experiments on aluminum single crystals subjected to a bias stress that the interaction of kinks on dislocation lines can give rise to the formation of two-level tunneling systems.[35] Without applied bias stress or after careful annealing of the sample, however, no indication of the presence of two-level systems was observed. Since all crystals have some lattice defects such as vacancies, dislocations, stacking faults, or grain boundaries and contain impurities in some concentration, the observation of low-energy tunneling systems in crystals is actually not surprising.

Certainly quite unexpected, however, are the results of the vibrating reed and vibrating wire experiments by the Bayreuth group mentioned above[4–7] which indicate that the number densities and the spectra of two-level systems in polycrystalline metals are generally very similar to those found in amorphous solids. Moreover, it has been stated that neither the grain size of the polycrystals nor the impurity concentration nor the clamping of the samples (except for a temperature-independent residual absorption) have a significant influence on the experimental results.

III. EXPERIMENTAL TECHNIQUE

The vibrating reed method, which was used for measurements on aluminum and copper samples, has been described in detail in several publications.[4,10] A thin rectangular plate of the sample material is clamped at one end between two copper blocks. The reed is electrostatically driven to forced vibrations at its lowest eigenfrequency by an electrode at the free end. A second electrode on the opposite side is used for the electrostatic detection of the vibration.[36] Relative changes of the sound velocity $\delta v/v=\delta f/f$ can be measured with an accuracy better than 10^{-6} by monitoring changes of the resonance frequency f. The absolute value of the internal friction Q^{-1} can be determined with an accuracy of 3–5 % from evaluation of full resonance curves or from the exponential decay of the vibrational amplitude after turning off the driving voltage. The best resolution for the detection of relative changes of the internal friction with a typical error of 1% is achieved by monitoring $\delta A/A\simeq\delta Q/Q$, where A is the amplitude of the reed at resonance.

A setup very similar to the vibrating reed experiment was used for the torsional oscillator. Again a small plate or rod of the sample material was clamped at one end. To excite a torsional mode rather than a bending mode, two small copper bars were attached by screws to the free end of the sample, and the electrodes for excitation and detection were placed close to the end of the bars to generate a maximum torque and to detect a large amplitude, respectively. For the metal samples measured with the torsional oscillator method, there was no need to attach a bar, since they could be directly machined into a T geometry.

The actual measuring procedure of the sound velocity and internal friction was the same for the torsional oscillator as for the vibrating reed measurements.[10] However, while for the torsional vibration the measured change of sound velocity is determined by changes of the shear modulus, in a vibrating reed experiment changes of Young's modulus are observed. Another difference between the two techniques is the distribution of strains in the sample. While the torsional oscillator is subjected to a rather uniform deformation along the full length of the sample and large strain amplitudes occur over a larger portion of its volume, the maximum strain amplitudes of a vibrating reed occur at the clamping position and vanish at the free end of the sample. Hence the influence of clamping and of surface defects might be more important for a vibrating reed than for a torsional oscillator.

All of the measurements to be presented in Sec. IV were performed at such small excitation levels that the resonance curves did not exhibit any nonlinear behavior and that the measured quantities $\delta v/v$ and Q^{-1} did not significantly depend on the excitation voltage. Typical maximum strain amplitudes were on the order of 1×10^{-7}.

The investigated samples were a nominally pure KCl single crystal and a KCl single crystal containing 60 ppm ^{7}Li, both cut along ⟨100⟩, an aluminum single crystal, and polycrystalline OFHC copper with grain sizes of approximately 1 mm. The impurity content of the metallic samples is not precisely known. However, all Cu samples were prepared from the same piece of copper and should therefore contain almost the same amount of impurities. One copper torsional oscillator was annealed at approximately 1000 °C under argon atmosphere for almost 1 h. Afterwards the sample was cleaned in a solution of nitric and hydrochloric acid. No mechanical stress was applied to the sample after annealing.

Typical sample dimensions were 10 mm length, 3 mm width, and 0.3 mm thickness for the reeds. For the torsional oscillators, the width was slightly reduced ($\simeq 2$ mm) and the thickness enhanced ($\simeq 1$ mm). The resonance frequencies of all samples ranged between 1 and 10 kHz.

IV. RESULTS AND DISCUSSION

A. Pure and Li-doped KCl crystals

Figure 2 shows the temperature dependence of the internal friction and of the relative change of sound velocity for the pure KCl crystal and for the KCl sample doped with 60 ppm ^{7}Li. The frequencies of the torsional oscillators were 1.4 and 1.1 kHz, respectively. Within the experimental resolution of 2×10^{-7} the sound velocity of the pure crystal (open circles) is independent of temperature below 150 mK and decreases monotonically above that temperature. The decrease is much stronger than expected for just the Debye phonon contribution Eq. (5). Presumably, crystal defects such as dislocations influence the sound velocity in this temperature range.

Comparing these data with the results for the Li-doped crystal we find striking differences. At low temperatures the sound velocity of the doped sample (full circles) is strongly reduced compared to the pure crystal and shows a nonmonotonic temperature dependence. This can be understood by the tunneling of the Li$^+$-defect ions in KCl. It is known for over thirty years that Li$^+$, which substitutes for K$^+$ in KCl, experiences a potential with eight minima towards ⟨111⟩ crystal directions. At low temperatures tunneling between these eight positions occurs and gives rise to a tunnel splitting Δ_0. The energy spectrum of this eight state system consists of four levels, the middle two of which are threefold degenerated. Note that Li-doped KCl is a well studied model system for the tunneling of defect ions in alkali-halide crystals. For details we refer to the overview articles Refs. 37 and 38.

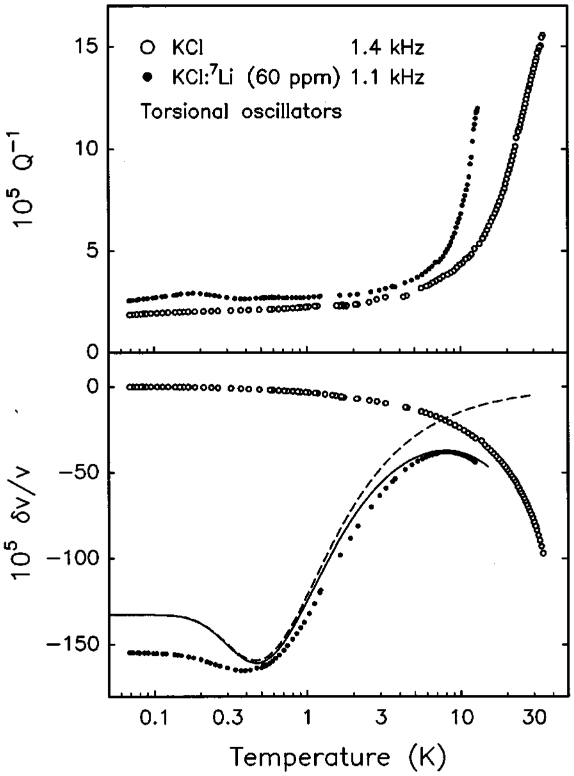

FIG. 2. Internal friction and relative change of sound velocity as a function of temperature for pure KCl (open circles), and KCl doped with 60 ppm ^{7}Li (full circles). For both samples the torsional oscillator method was used. The dashed line in the lower panel is a calculation according to Eq. (6) while the solid line is the same fit where, however, the temperature dependence of $\delta v/v$ of the pure KCl crystal was added. For the parameters used see text.

The misfit in size of the Li ions leads to a distortion of the host lattice around the defect. The resulting elastic quadrupole moment can make the system couple to internal and external strain fields. In addition, the Li$^+$ carries a rather large electrical dipole moment. At sufficiently low Li concentrations the tunneling states can be considered as being isolated. For the geometry of our torsional oscillator experiment and for low frequencies (static limit) the temperature dependence of the sound velocity determined by the Li$^+$ defects is in this case given by[39]

$$\frac{\delta v}{v}=-\frac{2n\gamma^2}{\rho v^2\Delta_0}\tanh\left(\frac{\Delta_0}{2k_BT}\right)-\frac{n\gamma^2}{\rho v^2k_BT}\operatorname{sech}^2\left(\frac{\Delta_0}{2k_BT}\right), \tag{6}$$

where n is the number density of tunneling systems. The first term represents the so-called resonant contribution and scales with the occupation number difference. The origin of the second part of Eq. (6) is particularly interesting because this relaxational contribution arises from the linear coupling of the external strain fields to some of the eight energy levels.

Note that this is a special property of this kind of eight state system and would not occur for a symmetric two-level system. In Eq. (6) we have assumed that the one-phonon relaxation rate $\tau^{-1}=A\Delta_0{}^3 \coth(\Delta_0/2k_BT)$ is much larger than the frequency of our experiments so that the Debye factor $1/(1+\omega^2\tau^2)$ can be omitted (static limit). This is justified by the observed absence of a relaxation peak in the internal friction at $T\simeq\Delta_0/2k_B=550$ mK, see upper part of Fig. 2. The maximum of Q^{-1} around 180 mK has a different origin that will be discussed below.

Qualitatively, the two contributions in Eq. (6) account well for the observed temperature dependence of $\delta v/v$. The resonant part determines the large reduction of the sound velocity below 10 K while the relaxational part leads to the local minimum at 400 mK. In the lower panel of Fig. 2 we show a calculation according to Eq. (6) as dashed line where $n\gamma^2/(\rho v^2 k_B)=7.3\times10^{-4}$ K and $\Delta_0/k_B=1.1$ K. The solid line in Fig. 2 is the same fit where we have added, however, the temperature dependence of $\delta v/v$ of the pure KCl crystal. This is based on the assumption that in the doped crystal the same effects (in a similar magnitude) as in the pure sample are leading to the reduction of the sound velocity at high temperatures. From our data we cannot conclusively decide to which extent this assumption is justified since there are no data for the Li-doped crystal above 13 K.

Despite the reasonable overall agreement between data and fits there occur some obvious quantitative discrepancies at low temperatures. The reason is that at a concentration of 60 ppm the Li^+ defects cannot be considered as being completely isolated.[40–42] This has several consequences: (i) The prefactor of the resonant part of the sound velocity in Eq. (6) is somewhat reduced. (ii) An additional relaxation contribution due to the collective motion of the Li ions occurs which leads to a reduction of the sound velocity at low temperatures. (iii) The tunnel splitting Δ_0 is modified by the interaction energies between the defects. This leads to a distribution of effective tunnel splittings and hence to a broadening and to a small shift towards lower temperatures of the minimum of sound velocity.

A complete discussion of these effects is beyond the scope of this paper.[39] The main aspect here is that the presence of just 60 ppm Li strongly modifies the temperature dependence of the sound velocity below 10 K and, in particular, leads to a reduction of $\delta v/v$.

The internal friction data for the two samples are shown in the upper part of Fig. 2. Both samples exhibit a very similar temperature dependence and absolute value of the internal friction. Up to about 5 K we find a weak increase of Q^{-1} with increasing temperature. At higher temperatures this increase is much stronger. The important point is that we observe a nearly temperature independent absorption at low temperatures with absolute values of Q^{-1} between 2×10^{-5} and 3×10^{-5}, which is most likely due to the residual absorption of our experiment and does barely reflect the intrinsic properties of the samples. An interesting feature of the doped sample is the small maximum around 180 mK caused by the additional relaxational contribution which, as mentioned above, arises from the interaction between the defect ions. Since the relaxation rates for this process are comparable to our measuring frequency we happen to observe this contribution in our experiment.

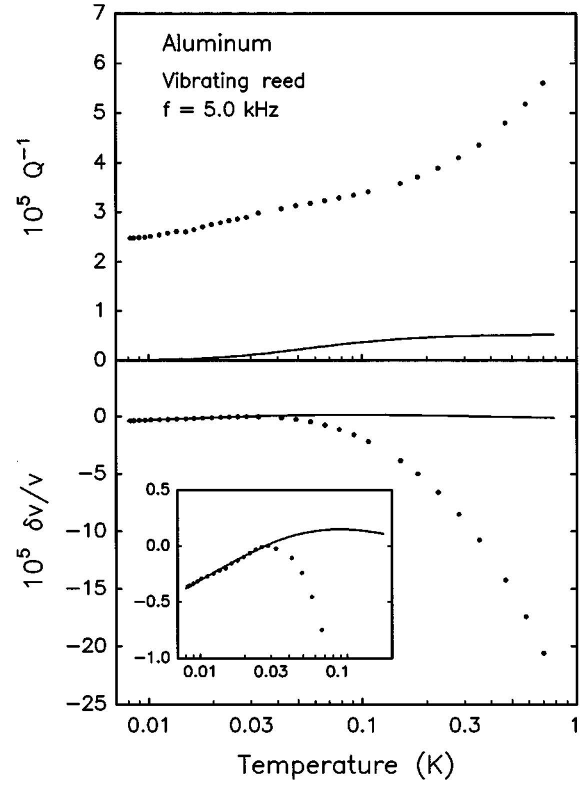

FIG. 3. Internal friction and relative change of sound velocity as a function of temperature for a reed of aluminum single crystal. As in the following figures, the inset shows the sound velocity at low temperatures on a strongly expanded scale. The tunneling model (solid lines) with parameters $C=3.4\times10^{-6}$ and $A=10^8\ \mathrm{K}^{-3}$ completely fails to describe the data.

B. Crystalline metals

Figure 3 shows the temperature dependence of the internal friction and the relative change of sound velocity for the aluminum single crystal reed at 5 kHz. Up to 30 mK $\delta v/v$ slightly increases and rapidly decreases above that temperature. Since the increase is nearly logarithmic in temperature it is tempting to interpret this as glasslike behavior and to use Eq. (1) to extract the parameter C from the slope which would yield $C=3.4\times10^{-6}$. It is rather questionable, however, whether this interpretation is adequate since all the other features typical of a glass (see Sec. II A) do not occur: The decrease of the sound velocity above 30 mK is much steeper than the increase below the maximum, whereas in glasses both slopes are of similar magnitude. Moreover, the decrease is not logarithmic in temperature but rather shows a $-T^{0.8}$ dependence. Finally, the internal friction rises only slightly up to 0.2 K and increases more rapidly above that temperature, which is in marked contrast to the prediction of the tunneling model even if we allow for an arbitrary background loss due to clamping of the sample.

The maximum of sound velocity occurs in a temperature range well below the superconducting transition temperature $T_c\simeq1.2$ K of Al where almost all conduction electrons are condensed into the BCS ground state. Hence, at least up to 200 mK the interaction between tunneling systems and electrons can be also ruled out as a possible explanation for the observed features in $\delta v/v$ and Q^{-1}.

Only for illustration purposes, we have drawn as solid lines in Fig. 3 a ''fit'' to the experimental data using the standard tunneling model, where relaxation occurs only via one-phonon-processes, with the parameters $C=3.4\times10^{-6}$ and $A=10^{8}\ \mathrm{K}^{-3}$. The parameters were chosen mainly to reproduce the logarithmic increase of $\delta v/v$ below the maximum. Other sets of parameters cannot significantly improve the quality of the fit: For example, by using a larger value of A it is possible to shift the maximum of sound velocity to lower temperatures (in better agreement with experiment), but in this case the theoretical curve would exhibit a significant curvature in the region below the maximum where the experimental data are linear in log(T). Moreover, the ratio of slopes below and above the maximum of $\delta v/v$ cannot be changed at all by the choice of the fitting parameters. As expected from the above discussion, the tunneling model is completely inappropriate to describe the experimental data.

Our results for the Al crystal are markedly different from those reported by König *et al.*[7] for polycrystalline aluminum wires where acoustic properties quite similar to those of glasses were observed. In these measurements the slope of the logarithmic increase of sound velocity at low temperatures is more than one order of magnitude larger than in Fig. 3, and the maximum of sound velocity occurred, depending on the frequency, around 200 mK. The most plausible explanations for the dissimilarities between the two measurements are differences between the experimental methods (which will be briefly discussed at the end of this paper) or differences between the number of defects in the samples, e.g., due to grain boundaries or dislocations. Our results for copper polycrystals presented in the following paragraphs will demonstrate that the presence of a small number of grain boundaries does not lead to glasslike properties of polycrystalline metals. Supposing that the differences between the results are not entirely due to the experimental techniques we are led to conclude that the number of tunneling states and the glasslike properties of polycrystalline metals are strongly correlated either with the grain size or with the density of dislocation lines.

Data quite similar to those for the Al crystal were obtained for a large-grained copper reed at 2.8 kHz (Fig. 4). In this measurement the noise level was unusually high but the main features of the measured quantities can still be resolved. Again the sound velocity increases logarithmically at very low temperatures (with a slope 30% larger than for the Al sample) and decreases rapidly (approximately linearly in T) after passing a maximum at 0.1 K, while the internal friction smoothly increases with increasing temperature.

It is interesting to compare the results of the vibrating reed experiment at 2.8 kHz in Fig. 4 with those of a torsional oscillator measurement at 9.7 kHz in Fig. 5. Both samples were cut from the same piece of copper. The internal friction shows a very similar temperature dependence for both samples although the absolute value is lower (presumably only due to a smaller residual absorption) for the torsional oscillator. As for the vibrating reed a maximum of the sound velocity occurs for the torsional oscillator. However, the slope of the increase of $\delta v/v$ below the maximum is reduced by a factor of five compared with the copper reed, and the position of the maximum is shifted to much lower temperatures (from 100 to about 25 mK). With an insulating amorphous sample, a small shift of the maximum to higher temperatures is expected due to the higher measuring frequency whereas the change of the oscillator mode should have no influence on the position of the maximum. The observed differences between the vibrating and the torsional modes provide additional clear evidence for nonglassy behavior.

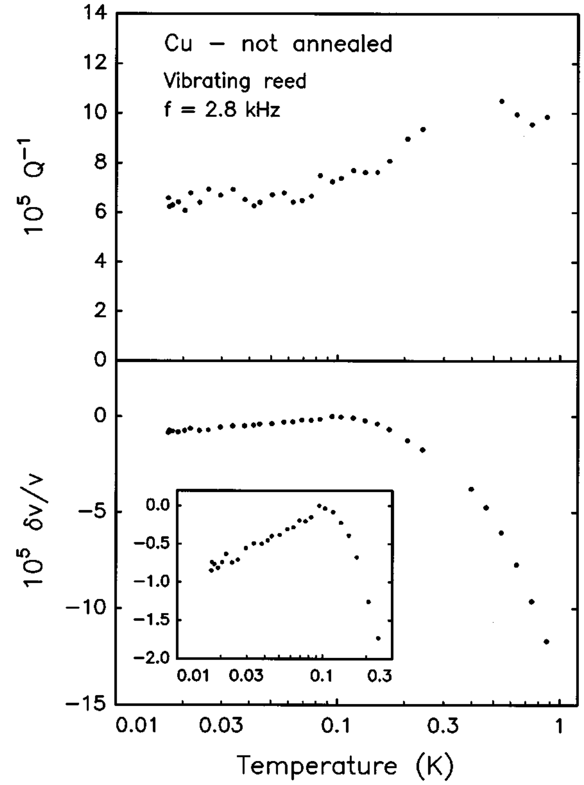

FIG. 4. Internal friction and relative change of sound velocity as a function of temperature for a polycrystalline copper reed.

Figure 6 shows another torsional oscillator experiment on a well-annealed sample of the same polycrystalline copper. The internal friction is a little higher but has a weaker temperature dependence compared with the results of Fig. 5. In the relative change of sound velocity the log(T) increase and the maximum have completely disappeared. Instead, a monotonic decrease of $\delta v/v$ is observed which above 50 mK is well described by a $-T^{0.5}$ dependence.

The very small increase with increasing T of the sound velocity in Figs. 3–5 is obscured already at fairly low temperatures by a contribution which leads to a strong decrease of $\delta v/v$ with increasing temperature. The effect is especially large for the annealed Cu torsional oscillator in Fig. 6. Several possibilities for the origin of this contribution have to be considered: (i) From the above discussion, it is clear that the observed behavior cannot be described in accordance with the tunneling model by the interaction of tunneling systems with acoustic phonons. (ii) At least for copper the possible influence of the interaction of conduction electrons with tunneling systems has to be taken into account. However, in contrast to what is expected for an amorphous metal in the normalconducting state, the sound velocity shows a very sharp maximum rather than a broad transition ranging over one order of magnitude in temperature, and the changes of $\delta v/v$ below and above the maximum differ by at least one

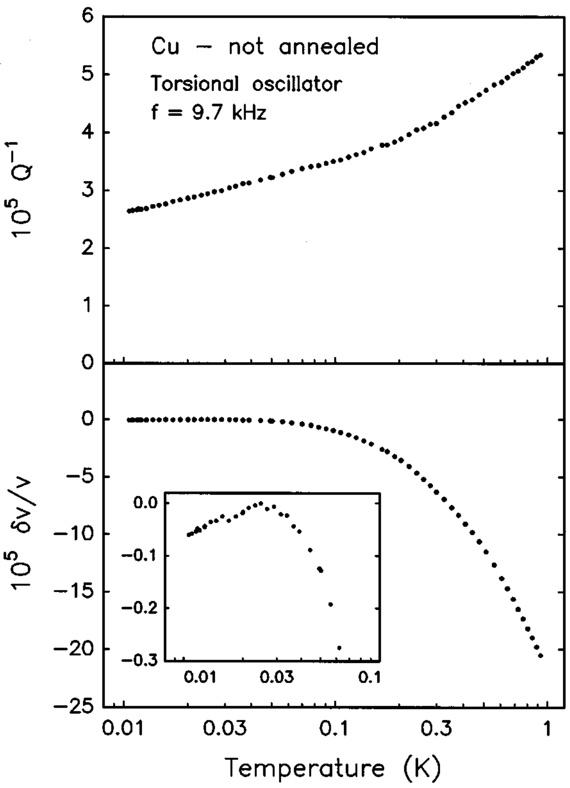

FIG. 5. Internal friction and relative change of sound velocity as a function of temperature for a polycrystalline copper torsional oscillator. The sample came from the same piece of material as for the vibrating reed mesurement shown in Fig. 4. For the torsional oscillator method the slope of the increase of $\delta v/v$ at very low temperatures is much smaller compared to the vibrating reed.

order of magnitude rather than being comparable in size. Moreover, the similarity between the data for Al (Fig. 3), where electrons cannot contribute to relaxation processes, and Cu (Figs. 4 and 5) make us believe that the interaction between electrons and tunneling states, although possibly present, must be very small and is definitely not the dominating effect. (iii) Elementary excitations such as electrons and phonons should give rise to a quadratic or quartic temperature dependence of the sound velocity [Eqs. (4) and (5)], in clear disagreement with the phenomenological relation $\delta v/v \propto -T^{\alpha}$ with α between 0.5 and 1 that has been observed for all of the investigated samples. (iv) The observed temperature dependence is rather similar to the behavior reported by Alers *et al.* for different polycrystalline metals.[34] As in these earlier experiments, the motion of dislocation lines may play an important role for our measurements. The strong influence of dislocation motion on the low-temperature properties of crystalline metals has been very clearly demonstrated for instance by measurements of the thermal conductivity of plastically deformed niobium and tantalum single crystals.[43,44] Although a quantitative understanding of the observed temperature dependencies of the sound velocity and internal friction due to the motion of dislocation lines is still lacking, we may draw an interesting conclusion from this interpretation: The increase of sound velocity with increasing T at very low temperatures in Figs. 3–5, which probably arises from resonant tunneling systems, and the decrease at higher temperatures are very likely entirely uncorrelated, and the position of the maximum of $\delta v/v$ results from the respective magnitude of the two underlying competing effects. It is noteworthy that, consistently, the maximum occurs at the highest temperature $T_{\mathrm{max}} \simeq 100$ mK for the copper reed where the total decrease of the sound velocity up to 1 K $(\delta v/v)_{\mathrm{tot}} \simeq 1.3\times 10^{-4}$ is the smallest of all metallic samples, whereas $T_{\mathrm{max}} \simeq 30$ mK is much lower for the Al reed and the nonannealed Cu torsional oscillator where the total change of sound velocity $(\delta v/v)_{\mathrm{tot}} > 2\times 10^{-4}$ is considerably larger. Finally, for the annealed Cu oscillator with the largest total change of sound velocity $(\delta v/v)_{\mathrm{tot}} > 4\times 10^{-4}$ no maximum is found at all.

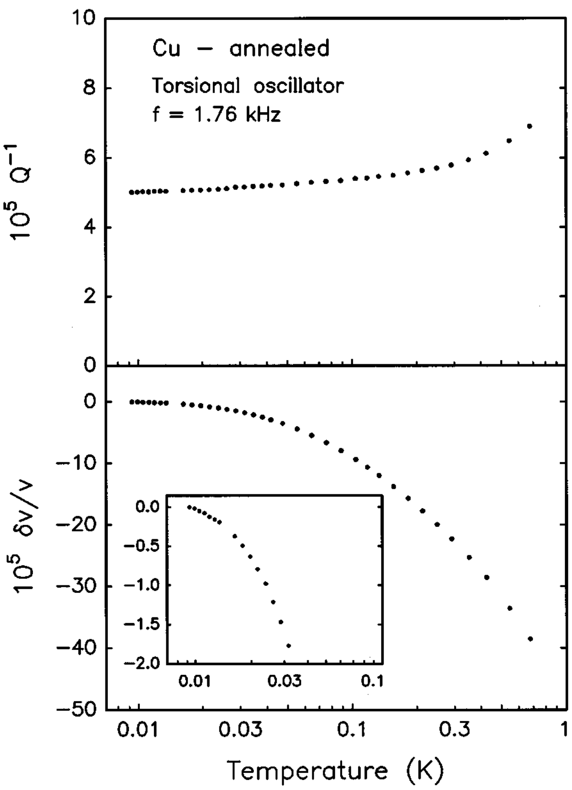

FIG. 6. Internal friction and relative change of sound velocity as a function of temperature for a polycrystalline copper torsional oscillator after annealing. Down to the lowest temperatures the sound velocity slightly increases with decreasing temperature.

The fact that all our samples do not show glassy behavior does of course not necessarily mean that they do not contain two-level tunneling systems. The weak increase of sound velocity with increasing temperature observed for the Al samples and the nonannealed Cu samples (Figs. 3–5) is most likely due the resonant interaction between tunneling systems and acoustic phonons. It is not possible, however, to draw unambiguous conclusions on the density of states of tunneling systems from our measurements. Note that the resonant interaction even for a well defined defect with a singular density of states, such as the Li atom in the KCl matrix in Fig. 2, causes a change of sound velocity which looks nearly logarithmic in a sufficiently narrow temperature window, e.g., between 0.8 and 3 K. A fairly narrow distribution of energy splittings may thus account for our results on the metallic samples as well as a glasslike, i.e., constant density of states. Measurements extending over several orders of magnitude in temperature as in Ref. 4 were necessary to allow more reliable conclusions on the distribution of energy splittings.

Our measurements do, on the other hand, allow us to state that the total number of tunneling systems in our samples must be very small. The resonant effect in the metallic samples in Figs. 3–5 is between two and three orders of magnitude smaller than for the KCl sample doped with only 60 ppm ^{7}Li in Fig. 2. This is especially remarkable since the deformation potential $\gamma = 0.04$ eV of the Li defects is extremly small, i.e., their coupling to external strain fields is very weak.[39] Hence even a concentration of tunneling defects well below 1 ppm in an otherwise perfect crystal may give rise to changes of the sound velocity comparable to those observed in our experiments on Al and Cu. Obviously, the limits of crystal preparation are coming into play here, and we may speculate that we will find even in the best crystals some very small decrease of $\delta v/v$ with decreasing temperature if we get down to sufficiently low temperatures and have a very high experimental resolution.

Finally, we want to discuss the influence of the experimental technique on the observed low-temperature acoustic properties. Our studies with different oscillator modes on two copper samples (Figs. 4 and 5) show that not only the background losses but also the temperature dependence of $\delta v/v$ can change significantly with the applied method. As already mentioned in Sec. III, it is highly conceivable that the clamping of the sample in a vibrating reed experiment has a considerably larger influence on the measured quantities than for a torsional oscillator where the strain amplitudes are distributed more uniformly and over a larger portion of the volume. Hence surface defects, e.g., in the oxidized surface layer, or volume defects created by the deformations occurring from the clamping might play a more significant role. Our observations may be relevant, of course, also with respect to other experimental techniques. In view of the strain distribution in a vibrating wire (the maximum deformations occur, as for the vibrating reed, at the clamping position) and its small diameter of typically 25 μm it is possible that for this experimental technique the clamping of the sample as well as surface defects may influence the behavior even stronger than for other low-frequency acoustic experiments. In our opinion, it will be difficult to find a conclusive explanation for the obvious discrepancies between the results presented here and those recently reported on the glasslike acoustic properties of polycrystalline metals[4–7] if they cannot partly be accounted for by differences of the experimental techniques.

V. SUMMARY

We have investigated the temperature dependence of the internal friction and the sound velocity of different crystalline materials at low frequencies and low temperatures using vibrating reed and torsional oscillator techniques. The results for the Li-doped KCl sample in comparison to pure KCl demonstrate how large the influence even of a fairly small number of well-defined tunneling defects on the acoustic properties can be. For the Al single crystal and for the nonannealed Cu polycrystals, but not for pure KCl and annealed Cu, we found at the lowest temperatures a weak increase with increasing temperature of the sound velocity. This behavior arises most likely from the resonant interaction of the sound wave with a small number of low-energy two-level systems. We have shown, however, that one cannot interpret this behavior in a simple manner in the framework of the tunneling model since all the other observed features do not only quantitatively but also qualitatively differ from the acoustic properties of amorphous materials: Above 0.1 K the sound velocity decreases with increasing temperature as $\delta v/v \propto -T^{\alpha}$ (with the exponent α between 0.5 and 1), and the internal friction smoothly increases with increasing temperature over the full temperature range. At present, there is no conclusive and quantitative explanation for this behavior which is not what is expected for an ideal crystal, but clearly not glasslike either. It is very likely that the motion of dislocation lines plays an important role though. An influence of the experimental method on the acoustic properties has been demonstrated for the copper samples. These measurements indicate that defects at the surface or arising from the clamping of the samples can be of great significance for the results of low-frequency acoustic experiments. Overall, our experiments lead back to the ‘‘traditional’’ view that there can be and usually are clear differences between the low-temperature acoustic properties of pure monatomic crystals and dielectric glasses.

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[1] See, for example, *Amorphous Solids—Low Temperature Properties*, edited by W. A. Phillips (Springer, Berlin, 1981).

[2] J. E. Van Cleve, A. K. Raychaudhuri, and R. O. Pohl, Z. Phys. B **93**, 479 (1994).

[3] S. K. Watson and R. O. Pohl, Phys. Rev. B **51**, 8086 (1995).

[4] P. Esquinazi, R. König, and F. Pobell, Z. Phys. B **87**, 305 (1992).

[5] R. König, P. Esquinazi, and F. Pobell, Physica B **194–196**, 417 (1994).

[6] P. Esquinazi, R. König, D. Valentin, and F. Pobell, J. Alloys Compd. **211–212**, 27 (1994).

[7] R. König, P. Esquinazi, and B. Neppert, Phys. Rev. B **51**, 11 424 (1995).

[8] G. Weiss, M. Hübner, J. Classen, C. Enss, and S. Hunklinger, Physica B **219&220**, 305 (1996).

[9] S. Hunklinger and A. K. Raychaudhuri, in *Progress in Low Temperature Physics*, edited by D. F. Brewer (Elsevier, New York, 1986), Vol. 9, p. 265.

[10] J. Classen, C. Enss, C. Bechinger, G. Weiss, and S. Hunklinger, Ann. Phys. (Leipzig) **3**, 315 (1994).

[11] J. L. Black, in *Glassy Metals. Topics in Applied Physics*, edited by H. J. Güntherodt and H. Beck (Springer, Berlin, 1981), Vol. 46, p. 167.

[12] B. Golding, J. E. Graebner, A. B. Kane, and J. L. Black, Phys. Rev. Lett. **41**, 1487 (1978).

[13] G. Weiss, S. Hunklinger, and H. v. Löhneysen, Physica B **109&110**, 1946 (1982).

[14] P. Esquinazi, H. M. Ritter, H. Neckel, G. Weiss, and S. Hunklinger, Z. Phys. B **64**, 81 (1986).

[15] G. Weiss and B. Golding, Phys. Rev. Lett. **60**, 2547 (1988).

[16] For a recent review see, U. Weiss, *Quantum Dissipative Systems*, Series in Modern Condensed Matter Physics Vol. 2 (World Scientific, Singapore, 1993).

[17] J. Kondo, Physica B **84**, 40 (1976).

[18] K. Vladar and A. Zawadowski, Phys. Rev. B **28**, 1564 (1983); **28**, 1582 (1983); **28**, 1596 (1983).

[19] Yu. Kagan and N. V. Prokof'ev, Zh. Eksp. Teor. Fiz. **97**, 1698 (1990) [Sov. Phys. JETP **70**, 957 (1990)].

[20] Yu. Kagan and N. V. Prokof'ev, Solid State Commun. **65**, 1385 (1988).

[21] G. Weiss, Mater. Sci. Eng. A **133**, 45 (1991).

[22] J. Stockburger, M. Grifoni, M. Sasseti, and U. Weiss, Z. Phys. B **94**, 447 (1994).

[23] S. N. Coppersmith and B. Golding, Phys. Rev. B **47**, 4922 (1993).

[24] J. L. Wang, G. Weiss, H. Wipf, and A. Magerl, in *Phonon Scattering in Condensed Matter*, edited by W. Eisenmenger, K. Lassmann, and S. Döttinger (Springer, Berlin, 1984), p. 64.

[25] H. Wipf *et al.*, Europhys. Lett. **4**, 1379 (1987).

[26] W. Morr, A. Müller, G. Weiss, H. Wipf, and B. Golding, Phys. Rev. Lett. **63**, 2084 (1989).

[27] W. Morr, G. Weiss, and H. Wipf, in *Quantum Aspects of Molecular Motions in Solids*, edited by A. Heidemann, A. Magerl, M. Prager, D. Richter, and T. Springer, Springer Proceedings in Physics Vol. 17 (Springer, Berlin, 1987).

[28] D. Steinbinder *et al.*, Europhys. Lett. **6**, 535 (1988).

[29] S. Rau, C. Enss, S. Hunklinger, P. Neu, and A. Würger, Phys. Rev. B **52**, 7179 (1995).

[30] J. E. Van Cleve, Ph.D. thesis, Cornell University, 1991.

[31] A. L. Burin and Yu. Kagan, Zh. Eksp. Teor. Fiz. **107**, 633 (1995) [J. Exp. Theor. Phys. **80**, 761 (1995)]; A. L. Burin, J. Low Temp. Phys. **100**, 309 (1995).

[32] D. A. Parshin, Z. Phys. B **91**, 367 (1993).

[33] G. A. Alers, in *Physical Acoustics: Principles and Methods*, edited by W. P. Mason (Academic Press, New York, 1966), Vol. 4A, p. 277.

[34] G. A. Alers and J. E. Zimmerman, Phys. Rev. **139**, A414 (1965).

[35] A. Hikata and C. Elbaum, Phys. Rev. Lett. **54**, 2418 (1985).

[36] The KCl-samples were covered with a 30 nm gold layer to make them electrically conducting.

[37] V. Narayanamurti and R. O. Pohl, Rev. Mod. Phys. **42**, 201 (1970).

[38] F. Bridges, Crit. Rev. Solid State Sci. **5**, 1 (1975).

[39] M. Hübner, Diploma thesis, Universität Heidelberg, 1994; M. Hübner, C. Enss, and G. Weiss (unpublished).

[40] R. Weis, C. Enss, B. Leinböck, G. Weiss, and S. Hunklinger, Phys. Rev. Lett. **75**, 2220 (1995).

[41] R. Weis and C. Enss, Czech. J. Phys. **46**, 2557 (1996).

[42] C. Enss, Physica B **219&220**, 239 (1996).

[43] W. Wasserbäch, Philos. Mag. A **38**, 401 (1978).

[44] W. Wasserbäch, Phys. Status Solidi A **128**, 55 (1991).