on the right side of Eq. (6), for these sites. This equation for Z_n implies a discrete diffusion equation for $u(\vec{r},n)=Z_n(\vec{r})/c^n$:

$$u(\vec{r},n+1)-u(\vec{r},n) = c^{-1}\sum_{\alpha=1}^{c}[u((\vec{r}+\vec{\alpha}),n)-u(\vec{r},n)], \qquad (7)$$

with the boundary condition that $u=0$ on perimeter sites. The left side of Eq. (7) is a discrete derivative in n and the right-hand side is the discrete Laplacian operator. The probability $v_{n+1}(\vec{x})$ that the perimeter site at $\vec{x}$ grows in the $(n+1)$th step is

$$v_{n+1}(\vec{x})=\sum_{\alpha=1}^{c}u_n(\vec{x}+\vec{\alpha})/c = c^{-1}\sum_{\alpha=1}^{c}[u((\vec{x}+\vec{\alpha}),n)-u(\vec{x},n)]. \qquad (8)$$

This is a discrete gradient at $\vec{x}$. Thus our model is a discrete version of the dendritic growth model described above.

In the study of this system by Langer and Muller-Krumbhaar,[4] they discovered that a smooth interface is unstable against wrinkling at all length scales; its growth depends on fluctuations in the diffusing field. Our findings describe the limit where these fluctuations are dominant.

The Monte Carlo study reported here may be extended to three or higher dimensions. We can study the effects of extending the size of the seed to simulate a finite tip radius of a dendrite. Realistic dendritic growth with surface tension can be simulated by making the sticking probability of particles smaller or larger for perimeter sites with fewer or more neighbors. Finally, the model can be used to predict the time-dependent growth rate of real random aggregates, as well as their mechanical and transport properties. The predicted features may appear in many processes, including gelation, condensation polymerization, and agglutination of biological molecules.

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Spontaneous Decay of High-Frequency Acoustic Phonons in CaF_2

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The decay of high-frequency acoustic phonons in CaF_2 at low crystal temperature is studied with use of an optical technique of tunable phonon detection. A strongly frequency-dependent lifetime is found for phonons at frequencies $\nu > 10^{12}$ Hz. The lifetime decreases proportionally to ν^{-5}, indicating spontaneous phonon decay by anharmonic three-phonon processes. These results suggest that nonlinear elasticity theory is applicable to describe anharmonic interactions of high-frequency acoustic phonons.

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Anharmonic lifetimes of high-frequency acoustic phonons at low crystal temperature were first studied by Slonimskii[1] using nonlinear elasticity theory. He performed calculations for an isotropic dispersionless solid, which has a longitudinal phonon branch and a degenerate transverse phonon branch. The calculations showed that longitudinal phonons can split into two phonons of lower frequency and have a lifetime decreasing as ν^{-5}. The theoretical results were confirmed by Orbach and Vredevoe[2] and by means of a simplified calculation also by Klemens.[3] Transverse acoustic phonons cannot decay by splitting processes because of energy and momentum conservation laws (assuming sufficient dispersion to forbid collinear transverse phonon decay).[2] Recently, extremely long-lived high-frequency transverse acoustic phonons have been observed in crystalline quartz[4] and in GaAs[5] by time-of-flight experiments. Various attempts have been made to detect spontaneous decay of longitudinal acoustic phonons without, however, conclusive results.[6] A study on SrF_2 (Ref. 7) seemed to indicate that the frequency dependence as well as the absolute values of experimental lifetimes disagree with the predictions of theory. We report in this Letter the first experimental evidence of strongly frequency-dependent anharmonic lifetimes of high-frequency acoustic phonons at low crystal temperature, and we show that our results, obtained for CaF_2, can be described by nonlinear elasticity theory.

We have chosen CaF_2 for our study because recently developed techniques[8] of tunable phonon detection are applicable. The acoustic dispersion curves are almost dispersionless up to large wave vectors[9] [Fig. 1(a)] and have a relatively small anisotropy. It follows from the elastic constants[10] that the velocity of sound for longitudinal phonons [L in Fig. 1(a)] varies for different crystal directions by only ±10% around an average value $c_L = 6.9 \times 10^5$ cm/s and that the velocity of transverse phonons (T) also varies by ±10%, around $c_T = 3.9 \times 10^5$ cm/s. Therefore, a comparison of experimental results with elasticity theory of the isotropic dispersionless solid is justified.

The principle of our experiment is shown in Fig. 1(b). Uniaxial stress is applied to a CaF_2 crystal doped with Eu^{2+} ions. The lowest excited state level of Eu^{2+} (a $4f^6 5d$ level, 24.200 cm^{-1} above the $4f^7$ ground state) is split to a doublet by uniaxial stress. The energy splitting $h\nu$ (h = Planck's constant) increases linearly with stress applied parallel to the [001] axis of CaF_2.[8,11] This system is used for tunable phonon detection up to a frequency ν of 3.2 THz which is reached at a stress of 8 kbar. The crystal is optically excited with laser radiation absorbed in broad absorption bands of Eu^{2+}. Nonradiative transitions [dashed lines in Fig. 1(b)] lead to population of the doublet levels and also to phonon generation. In the nonradiative transitions to the stress-split energy levels mainly optical phonons are created, which decay very fast into acoustic phonons. Additional phonon generation is due to one-phonon spin-lattice relaxation in the doublet levels. Since the spin-lattice relaxation is very

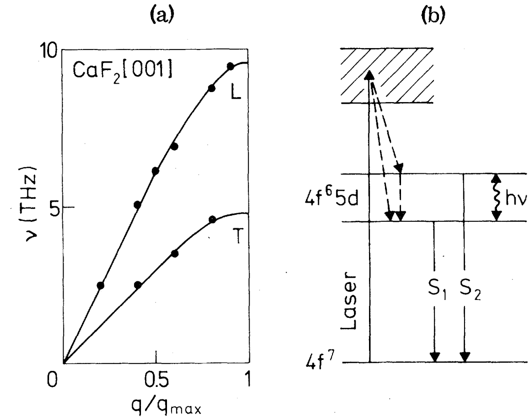

FIG. 1. (a) Dispersion curves for acoustic phonons in CaF_2 from neutron data (Ref. 9) and (b) principle of phonon generation and detection in CaF_2:Eu^{2+} (see text). S_2 fluorescence occurs at a wavelength of 413 nm.

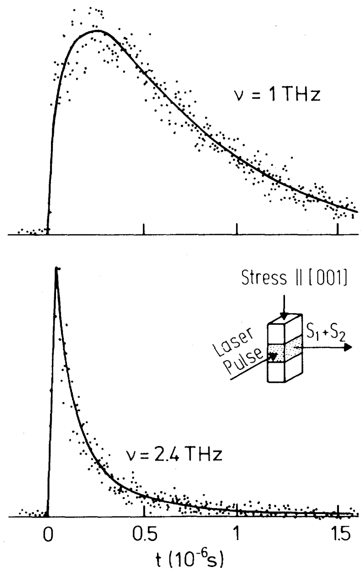

FIG. 2. Phonon-induced S_2 fluorescence signals after optical excitation at time $t = 0$ for two different detector frequencies. The inset shows the optical configuration.

fast ($<10^{-9}$ s, as concluded from an optical experiment), the relative population of the doublet levels is in equilibrium with phonons at the resonance frequency ν and is a measure of the phonon occupation number. By observing S_1 and S_2 fluorescence [Fig. 1(b)] the relative population of the doublet levels and therefore the phonon occupation number can be determined. Phonon lifetimes are obtained from the decay of the S_2 fluorescence after optical excitation.

The optical configuration is shown in the inset of Fig. 2. Uniaxial stress is applied to a CaF_2 crystal (doped with 0.003 mole% Eu^{2+}, size 3.4×10 mm^3). The crystal is surrounded by liquid helium at 2 K. A large part of the crystal is optically excited by radiation from a nitrogen laser (wavelength 337 nm, pulse length 1 ns, pulse energy typically 10^{-5} J). S_1 and S_2 fluorescence radiation is separated by a double grating monochromator and detected with a photomultiplier. The photomultiplier pulses are analyzed by photon counting technique using a Biomation transient recorder (time resolution 5 ns).

Phonon-induced signals are shown in Fig. 2. For a detector frequency of 1 THz the S_2 signal (upper curve) decreases with a time constant (550 ns) which is only slightly shorter than the time constant (670 ns) of the S_1 fluorescence decay. For a detector frequency of 2.4 THz, however, the S_2 signal (lower curve) decreases much faster. This indicates that phonons at 2.4 THz have a much shorter lifetime than phonons at 1 THz. The signal for 1-THz phonons shows in addition to a fast increase also a slow increase (for about 200 ns). We think that the slowly increasing signal is caused by phonons created by the decay of acoustic phonons at higher frequencies. The signal curve for 2.4-THz phonons indicates that these phonons are generated immediately after the optical excitation. We have also detected phonons by the method of vibronic sideband spectroscopy.[7] Phonon-induced signals observed in the anti-Stokes sideband of the $4f^65d \rightarrow 4f^7$ fluorescence line at zero stress were one to two orders of magnitude smaller, but showed the same slope of the signal curves. This indicates that the stress applied to the crystal has no influence on the phonon lifetimes. Furthermore, we found that an increase in the concentration of Eu^{2+} ions by an order of magnitude has no influence on the decay.

From the decay times τ_2 of S_2 signals (Fig. 2) phonon lifetimes τ are obtained using the relation $\tau_2^{-1} = \tau^{-1} + \tau_1^{-1}$, where τ_1 is the (stress-independent) decay time of the S_1 fluorescence. Experimental results obtained for different detector frequencies are shown in Fig. 3 (points). We find that τ is only weakly frequency dependent at small frequencies, but shows a strong decrease for $\nu > 1.5$ THz. At the smaller frequencies τ is an order of magnitude longer than the ballistic time of flight of the phonons out of the crystal (Fig. 3). We find that the experimental lifetimes at $\nu > 1.5$ THz are independent of the size of the optically excited volume (for diameters of the excited volume larger than 0.5 mm). This indicates that the phonons are not able to escape spatially, but are diffusion trapped. We think that the diffusion is mainly caused by elastic impurity scattering and we estimate that the scattering time is less than 10^{-8} s. This is qualitatively confirmed by heat-pulse experiments in which we found also a strong impurity scattering for phonons at lower frequencies. We therefore conclude that the observed phonon decay at high frequencies is mainly caused by frequency-conversion processes. The experimental data of the phonon lifetimes at $\nu > 1.5$ THz can be described by a ν^{-n} dependence where a best fit gives $n = 5.1 \pm 0.4$. The data are therefore consistent with a ν^{-5} dependence (solid line

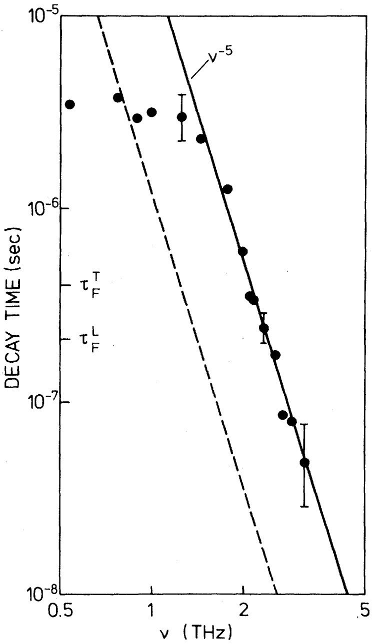

FIG. 3. Lifetimes of acoustic phonons in CaF_2 at low crystal temperature. $\tau_F{}^L$ is the (average) time of flight of longitudinal and $\tau_F{}^T$ that of transverse phonons out of the excited volume. The curves are discussed in the text.

in Fig. 3), which gives strong evidence that the phonon decay at high frequencies is due to phonon splitting by anharmonic three-phonon processes. The reason for the almost frequency-independent phonon decay at lower frequencies ($\nu < 1.5$ THz) is not known. The decay may be due to inelastic phonon scattering at impurities.

We point out that mode mixing can occur because of the fast elastic impurity scattering. We assume that the mode mixing is sufficiently rapid to equilibrate the various phonon modes at fixed frequency. For a comparison with theory[1-3] we attribute the observed phonon decay of the phonon mixture to the decay of the longitudinal phonons and we assume that decay of transverse phonons can be neglected. By a detailed balance it follows that the total phonon population decays with the time constant $\tau(\nu) = [1 + D_T(\nu)/D_L(\nu)]\,\tau_L(\nu)$, where $D_T(\nu) = 8\pi\nu^2/c_T^3$ and $D_L(\nu) = 4\pi\nu^2/c_L^3$ are the densities of states of transverse and longitudinal phonons, respectively. According to the average sound velocities, we obtain $D_T(\nu)/D_L(\nu) \simeq 13$ and $\tau_L(\nu) \simeq (1/14)\tau(\nu)$. This analysis leads to a frequency-dependent lifetime $\tau_L(\nu)$ of longitudinal phonons, which is also proportional to ν^{-5} (dashed line in Fig. 3).

We compare our result with the predictions of elasticity theory for the isotropic dispersionless solid. Accordingly, the lifetime of longitudinal phonons is given by the expression[1-3] $\tau_L^{-1}(\nu) \simeq (h/32\pi^2\rho)\varphi^2 q^5$. In this expression (in cgs units) $\rho = 3.21$ g/cm^3 is the mass density of CaF$_2$, $q = 2\pi\nu/c_L$ is the (average) wave vector of the longitudinal phonons and φ is a dimensionless anharmonicity parameter which is a measure of the strength of the anharmonic three-phonon interaction. By comparing the experimental curve for $\tau_L(\nu)$ (dashed in Fig. 3) with the theoretical expression, we obtain $\varphi = 1.3$. The theory shows that φ can be expressed by a quantity depending on second- and third-order elastic constants and on the sound velocities.[1,2] It follows from theory that φ has the same order of magnitude as the mode Grüneisen parameters for acoustic phonons, which, however, are expressed by different combinations of second- and third-order elastic constants.[12] In CaF$_2$ an average value of the low-temperature Grüneisen parameter is $\gamma = 1.2$.[13] Our experiment therefore gives direct evidence that the anharmonicity parameter φ is close to γ, as predicted by theory.[14]

We note that we have also performed experiments on SrF$_2$ (doped with 0.003 mole% Eu^{2+}). Due to an additional fluorescence signal of unknown origin the experiments were more difficult to perform. The results indicate, however, a similar behavior of the phonon lifetime as for CaF$_2$. The lifetime is also independent of frequency for $\nu < 1.5$ THz and decreases strongly at larger frequencies. The frequency-dependent lifetimes are smaller by about a factor of 2 than for CaF$_2$. This is in agreement with theory, because the density ρ is larger by 30% and the sound velocities are smaller by about 15% than for CaF$_2$. We suggest that in the recent experiment on SrF$_2$,[7] where only a weak frequency dependence of the phonon lifetime was found, mutual interaction of the phonons may have influenced the phonon decay. In this experiment phonons of a relatively high density were generated at a crystal surface by the heat-pulse method. Our experiment was performed with small phonon energy densities. We estimate that by the laser excitation a total phonon energy density of 3×10^{-5} J/cm^3 is generated. According to specific-heat data[15] this leads, in case of fast thermalization, to a temperature increase to only 3 K in the crystal. The nonthermal phonon occupation numbers determined from the ratio of S_2 and S_1 fluorescence intensities[16] immediately after laser pulse excitation were of the order of 10^{-5} (at 3 THz) to 10^{-3} (at 0.5 THz). We found by experiments with higher laser pulse energies that the phonon occupation numbers increased linearly with the energy density and that the phonon decay times (at $\nu > 1.5$ THz) were independent of the energy density which we varied by a factor of 30 (up to 10^{-3} J/cm^3). We conclude therefore, that phonon combination processes played no role in our experiment. We point out that, because of the weak optical excitation, resonance trapping of the phonons due to scattering at excited Eu^{2+} ions was negligible in our experiment.

In summary, we have observed for the first time evidence of a strongly frequency-dependent lifetime for the spontaneous decay of high-frequency acoustic phonons in the regime $h\nu \gg kT$. Our analysis suggests that nonlinear elasticity theory is applicable for the description of the anharmonic interaction of high-frequency acoustic phonons. We have shown that experimental lifetimes in CaF$_2$ at low crystal temperature are in close agreement with predictions of elasticity theory for an isotropic dispersionless solid. A more quantitative theory for the spontaneous decay of a phonon mixture as observed in our experiment should, however, include the decay of transverse acoustic phonons, because in an anisotropic crystal such as CaF$_2$ the phonons of the upper transverse-acoustic-phonon branch are also allowed to decay spontaneously.

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Evidence for Discommensurations in Graphite Intercalation Compounds

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New x-ray diffuse scattering results are presented that show that the layer structure in stage-2 alkali-metal graphite intercalation compounds is almost commensurate with a $(\sqrt{7}\times\sqrt{7})R19.11°$ superlattice. Through model calculations, features of the in-plane diffraction patterns are associated with a hexagonal array of discommensurations oriented parallel to the real-space graphite [110] directions. The array appears to be disordered down to at least $T = 10$ K. Several previously unexplained results are understood through our model.

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The physics of systems with competing periodicities is currently a very active research area. Of particular interest is the transition, or sequence of transitions, from commensurate to incommensurate structures.[1] Studies of monolayers of adsorbed gases[2] and of charge density waves in layered chalcogenides[3] have proven especially interesting in that much direct information can be obtained by various diffraction techniques. However, in spite of several recent theoretical predictions[1,4] relating to the commensurate-incommensurate transition (CIT), experimental tests are very limited at this time.

In this paper we describe x-ray diffuse scattering experiments on a set of materials, related to adsorbates but not previously discussed in this context, in which monolayers of alkali metal (AM) ions are intercalated into the graphite structure.[5] We find that in some cases such materials are *weakly incommensurate* and, in single-crystal form, may provide important testing grounds for theories of the CIT. Our findings suggest a new structural interpretation of dilute AM graphite intercalation compounds (GIC's) which can explain several controversial and poorly understood aspects such as the origin of structural modulations and the interpretation of unusual diffraction effects.

The incommensurability of stages $n \geqslant 2$ of the Cs, Rb, and K GIC's has been recognized for