Slow Relaxation, Confinement, and Solitons

L. S. Schulman,[1,*] E. Mihóková,[2] A. Scardicchio,[3] P. Facchi,[3] M. Nikl,[2] K. Polák,[2] and B. Gaveau[4]

[1]*Physics Department, Clarkson University, Potsdam, New York 13699-5820*

[2]*Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, 162 53 Prague 6, Czech Republic*

[3]*Dipartimento di Fisica, Università di Bari, I-70126 Bari, Italy*

[4]*Université Paris 6, Case courrier 172, 4 Place Jussieu, 75252 Paris Cédex 05, France*

(Received 26 September 2001; published 16 May 2002)

Millisecond crystal relaxation has been used to explain anomalous decay in doped alkali halides. We attribute this slowness to Fermi-Pasta-Ulam solitons. Our model exhibits confinement of mechanical energy released by excitation. Extending the model to long times is justified by its relation to solitons, excitations previously proposed to occur in alkali halides. Soliton damping and observation are also discussed.

DOI: 10.1103/PhysRevLett.88.224101 PACS numbers: 05.45.Yv, 31.70.Hq, 63.20.Ry, 78.55.–m

Crystals respond in picoseconds. This is the characteristic time for lattice adjustments, for example passage to a "relaxed excited state." Nevertheless, an anomaly in the decay of luminescence in doped alkali halides has led us to conclude [1,2] that relaxation can sometimes take place on a scale of milliseconds. It is as if the tides moved like tectonic plates. Other explanations were offered for the anomalous decay in the decade since its discovery, mainly connected to lattice defects or other irregularities. But improved crystals, annealing, and experimental technique have left relaxation slowdown as the only candidate. Moreover, as detailed in [2], the slowdown hypothesis allows good data fits across a variety of compounds and temperatures. Millisecond crystal relaxation thus demands an explanation. In this article we propose that the formation and slow decay of Fermi-Pasta-Ulam (FPU) solitons (or breathers) [3,4] can account for this dramatic slowdown. The presence of FPU solitons in alkali halides has been previously proposed [5] and we believe that particular features of our system enable their production and observation.

We begin with an overview. KBr (say) is dilutely doped with Pb^{2+}. One can think of the Pb and its six surrounding Br atoms as a quasimolecule. This quasimolecule is excited by a UV flash and because of the Jahn-Teller effect distorts considerably. Absent the constraining lattice, one would expect expansion along one of the axes of perhaps 15%. The distortion is asymmetric and the Jahn-Teller interaction causes well-understood degeneracy breaking. It is the subsequent return to the ground state that provides evidence for slow lattice relaxation. The excited quasimolecule can go to a *radiative* level with a 25 ns lifetime or to a *metastable* level with an 8 ms lifetime. The luminescence decay, however, is *not* the sum of two exponentials; rather, after the initial radiative level burst, molecules in the metastable level exhibit an enhanced, but gradually declining, decay rate, which we have explained as being due to lattice-induced coupling to the fast level. This continues for milliseconds and implies that the lattice itself takes ms to accommodate to the distortion. This is the slow relaxation, and our ability to use this assumption to fit a variety of systems in a large range of temperatures is the evidence for this phenomenon.

Because the quasimolecule's distortion is asymmetric, a reasonable model [6] is a linear diatomic chain in which a particle on one end is subject to a strong push. (This is the Br adjacent to the Pb.) Nonlinearity enters because of the large displacements. To account for the three-dimensional environment we add a potential (simulating off-chain neighbors) that tends to return each ion to its normal lattice position. This model displays a remarkable property: reverberations in the chain due to the push are confined. Oscillations occur only in the 2 to 4 neighbors of the first ion. Almost no energy escapes. These assertions are based on numerical integration for $\lesssim$500 lattice time units. Accurate integration of even the 1-dimensional case for 10^9 units ($\sim$ms) appears out of reach, so if we claim this confinement underlies slow relaxation, more general arguments are needed.

As shown below, the confinement reflects the creation of a FPU soliton. This structure lives essentially forever. We thus go from the problem of *fast* relaxation to that of *no* relaxation. To explain the ultimate decay of the soliton we note the apparent coincidence of rates for lattice relaxation and metastable electromagnetic decay. This suggests that the electronic degrees of freedom draw energy from the soliton. This damping yields patterns of lattice relaxation that follow the time dependence used [2] in explaining the experiments. We also found (numerically) that even after quasimolecule decay the soliton remains.

This explanation introduces the question of direct observation. If indeed for $\sim$5 ms bunches of atoms vibrate at a frequency above the acoustical phonon branch, what probe could reveal this? This leads to another point. Our desire for independent probes reflects our orientation: it is the dramatic relaxation slowdown that drives our investigation; we do not claim that the model presented below is by itself of sufficient precision to offer compelling *predictive* evidence.

Details of the model.—Following the UV pulse, and faster than any scale considered here, the electronic wave

function, ψ, distorts. The quasimolecule is pushed hard along one axis and shrunk along the others. We focus on a ray of atoms along the expansion axis. The first atom is subjected to a large force which it transmits to the others. We simplify the influence of ψ by pretending there is a fictitious zeroth particle displaced by a fixed amount from its equilibrium. To allow the use of a one-dimensional chain we supply each atom on the chain with a "neighbor" force that attracts the atom to its nominal lattice location. Note that the asymmetric stresses imply lesser deformation for off-axis atoms. The interatomic potential is taken to be $V(u) = M\omega_0^2(u^2 + \lambda u^4)/2$. The Hamiltonian is

$$H = \sum_{n=1}^{N}\left\{\frac{P_n^2}{2M} + \frac{rp_n^2}{2M} + V(q_n - Q_n) + V(Q_n - q_{n-1}) + \nu[V(Q_n) + V(q_n)]\right\}, \quad (1)$$

where ν is the effective number of neighbors. Q_1 is the first atom to the right of the Pb, followed by q_1, Q_2, etc. The Q particles have mass M, the qs, M/r—but we rescale so that $M = 1$ and $\omega_0 = 1$. For KBr, $r \approx 2$. The impact of ψ is expressed by setting (the nondynamic) $q_0 \neq 0$.

The system was solved classically by numerical integration. All positions and momenta were initially zero, with q_0 providing the driving force. Figure 1 shows runs with $\nu = 0$ and 4 ($\lambda = 1$). In the first case there is wave propagation, but with $\nu = 4$ the energy is confined. A small pulse leaves the system initially, but afterward only the first atoms oscillate, mostly just the first two. Figure 2 shows the positions for $\nu = 4$, $\lambda = 0$. Evidently there is no confinement. These results are insensitive to the exact parameters, including run time and N. They become more dramatic as r moves away from unity, consistent with the trend in anomalous decay [1,2].

We next study the frequencies of the confined vibrations. To connect to solitons this will be related to lattice phonon properties. When $\nu = 4$, $r = 2$, $N = 15$, the phonon spectrum has a gap between the acoustical and optical branches running from 2.45 to 3.46 ($\omega_0 = 1$). In Fig. 3 we plot the intensity of the Fourier transform of $q_1(t)$, $0 \leq t \leq 200$, for 3 values of λ. The curve peaked near 2.45 is $\lambda = 0$. The curves for $\lambda = 0.5$ and 1 are dominated by their peaks at 2.86 and 3.27, respectively (within the gap). [The bump near 3.9 (2.86) is part of the $\lambda = 1(0.5)$ spectrum.] If q_0 is varied, peak locations change, consistent with scaling.

Besides the extreme spatial localization, another property of our confinement curves—perhaps the characteristic soliton feature in the FPU study—is the failure of energy to disperse among the normal modes. Figure 4 shows energy dispersal for various times. Unlike FPU, our initial conditions preclude concentration in one mode. Nevertheless, it is clear that while energy can shift from mode to mode (cf. time-25 in the Fig. 4), it tends to return repeatedly. Note that we show only quadratic contributions to energy, whose sum need not be conserved.

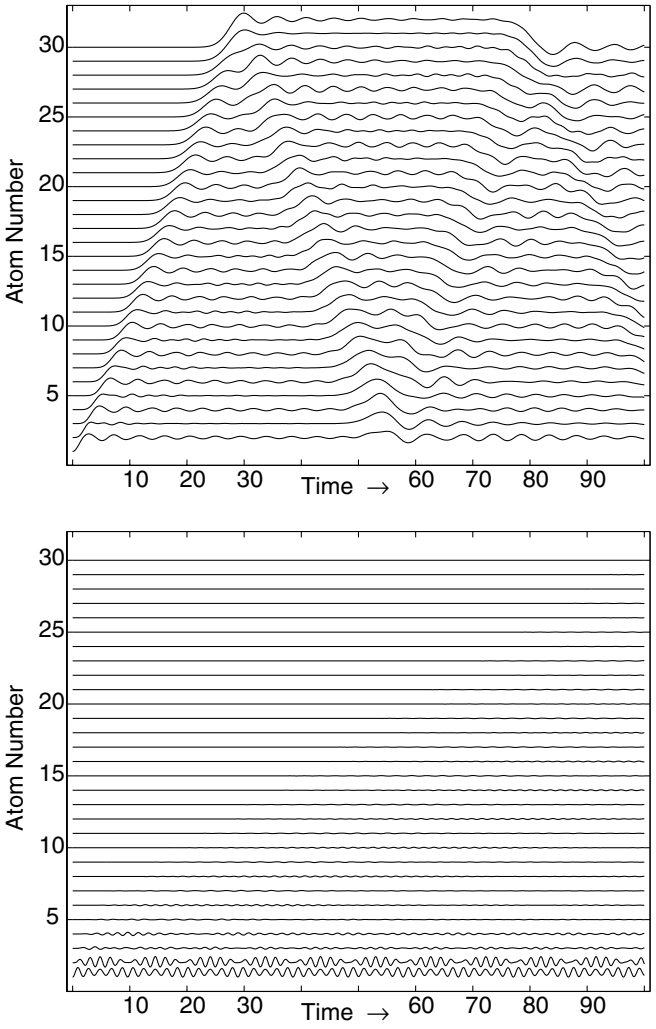

FIG. 1. Position vs time. The unconfined history has $\nu = 0$ (upper panel), no force from off-axis atoms. There is wave propagation. The reflection is an artifact of the boundary. The case $\nu = 4$ (lower panel) gives confinement (for which the boundary is irrelevant). The lowest curve is $Q_1(t)$; above it is $q_1(t)$, etc. Common parameters are $\lambda = 1$, $q_0 = 1$, $N = 15$ (30 atoms), $r = 2$.

An extensive recent literature on FPU solitons exists [5,7–10], and their presence in alkali halide crystals has been suggested [5]. Like our confinement mode, these excitations are dominated by a single frequency (although in [10] this assumption is not made). Experimental observation of breathers is reported for quasi-one-dimensional systems in [11]. In [8] the *diatomic* chain is studied, and the soliton frequency is found between the acoustical and optical phonon bands. The ability of our systems [1,2] to support solitons can be attributed to several features. (i) The distortion (à la Jahn-Teller) makes the system closer to 1D than 3D, bearing in mind [5] the lesser tendency to form solitons in 3D. (ii) Considerable enhancement of all soliton effects develops as $|r - 1| \uparrow$. (iii) Numerically we

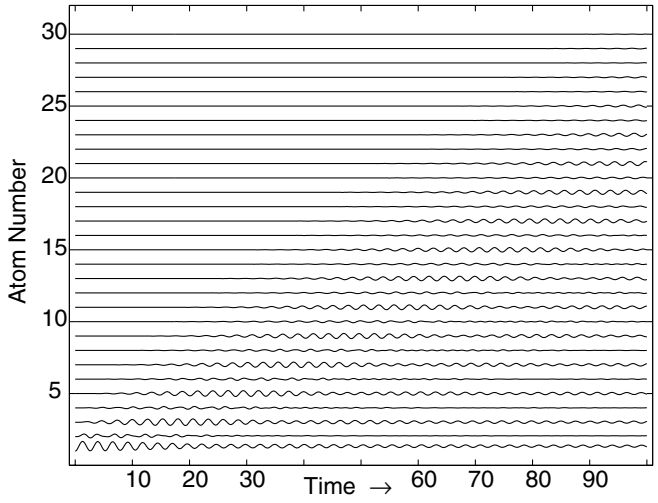

FIG. 2. Position vs time for a system that with nonlinearity would show confinement. Parameters as in Fig. 1 ($\nu = 4$), but $\lambda = 0$.

find that the boundary condition at the impurity site, based on our physical picture, enhances localization.

Decay of the soliton.—Given the confinement-soliton connection, why does the crystal relax at all? In fact the FPU soliton may not live forever. Reference [4] shows that FPU dynamics is equivalent to Henon-Heiles chaos. For our parameters, however, as for FPU, the excitation is extremely long-lived, disappearing only in case of Arnold diffusion. However, even if for KBr:Pb^{2+} that diffusion time would be ms, its sensitivity would leave unexplained the coincidence of relaxation and metastable decay times in other doped alkali halides. Note too that the soliton is robust. Defects may shift its properties but not the fact of its existence. Moreover, anomalous decay has been seen with various levels of crystal defects. For these reasons we turn to other degrees of freedom, and in view of the coincidence of time scales, it is the electronic coupling that we argue provides decay.

The decay of the metastable A_{1u} level (ψ_u) to the A_{1g} ground state (ψ_g) is electromagnetically forbidden, and the decay occurs by coupling ψ_u to vibronic modes. Calling H the Hamiltonian of the quasimolecule, metastable decay involves $\langle\psi_u|H|\text{vib.}\rangle\langle\text{vib.}|H|\psi_g\rangle$. For soliton decay we invoke almost the same matrix elements, but in a different order: $\langle\text{vib.}|H|\psi_u\rangle\langle\psi_u|H|\text{vib.}\rangle$: the soliton disturbs the electron, which in turn interacts with the surrounding ions. Density of states factors may differ. Nevertheless, it is plausible that the rates are comparable, and this is our assumption.

To incorporate this in our classical model we view the coupling as a damping: soliton energy is converted to undifferentiated vibrational energy via electronic coupling. This affects primarily the Br in the quasimolecule, so that classically we included $-\gamma\dot{Q}_1$. In Fig. 5 we show a smoothing (average) of the oscillations of Q_1 over an extended time period with damping. This is also superimposed on $1 - \exp(-\Gamma t)$, with $\gamma \approx \Gamma$. This comparison is essential to the main goal of this article. The lattice relaxation pattern $1 - \exp(-\Gamma t)$ is adopted in [2] in the slow-relaxation explanation of anomalous decay. Its recovery from the soliton theory is vital to connecting the original experimental observations to the soliton explanation.

Remarks.—(i) We expect the quantum version of our theory to give similar results. The quantization of the soliton should be doable by path integral, WKB (EBK), and numerical methods [12]. Semiclassical quantization is

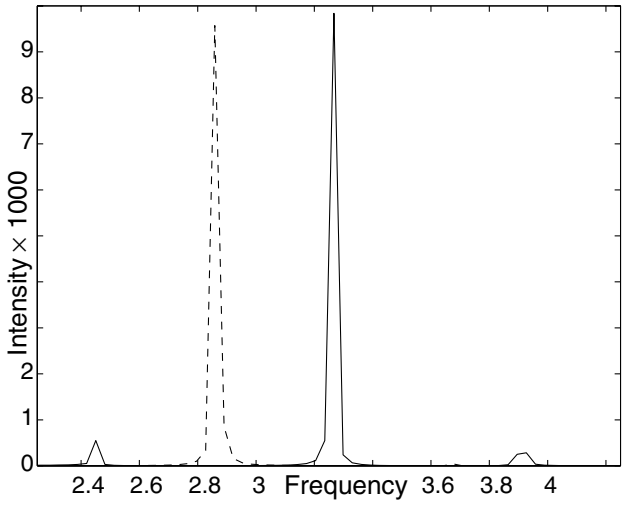

FIG. 3. Fourier transform (intensity) of $Q_1(t)$ with varying nonlinearity. The dashed curve is $\lambda = 0.5$. The two solid-line curves do not overlap, with amplitude to the left of 2.45 corresponding to $\lambda = 0$ and to the right of 3, to $\lambda = 1$. For $\lambda = 0$, the peak is just within the acoustical band. With $\lambda = 0.5$ (dashed line) almost all energy is in the peak, now well within the gap. Finally, with $\lambda = 1$ (solid line, again) the peak has almost reached the optical branch and a second small peak beyond the optical spectrum is more pronounced.

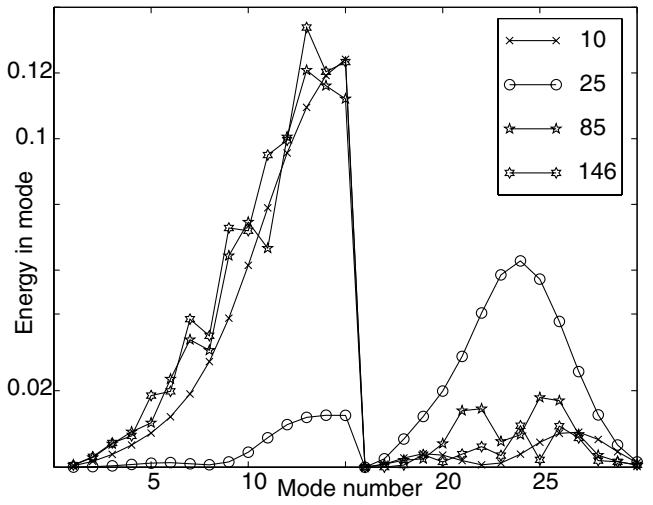

FIG. 4. Energy per normal mode at various times. Parameters as in Fig. 1, $\nu = 4$.

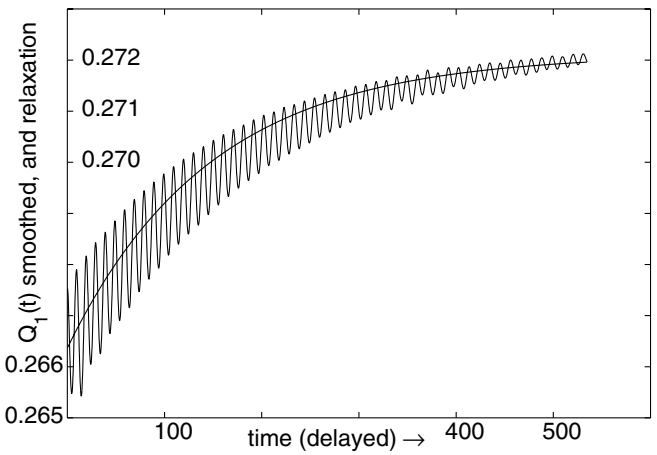

FIG. 5. The function $Q_1(t)$, partially smoothed, calculated with damping (γ). Also shown is $1 - \exp(-\Gamma t)$ for $\Gamma \approx \gamma \approx 0.01$. $Q_1(t)$ is from the confinement run of Fig. 1.

aided by the fact that the phase space trajectory of this soliton is a torus. Weak phonon coupling provides damping, as in [13], and a lifetime. (ii) For nonzero temperature other mechanisms of soliton decay enter and indeed our data fits [2] indicate increased "Γ" with temperature. Mechanisms such as those studied in [14] should play a role, although as observed there, the effect may be sensitive to system details.

Detection of solitons.—Our explanation of slow relaxation implies that for periods ~5 ms subsequent to a UV pulse, small bunches of atoms (perhaps 5 on a side) oscillate at frequencies above the acoustical phonon band. For KBr this is at roughly $\nu_a = 3 \times 10^{12}$ s^{-1} [15]. A direct way to see these would be by off-resonant Raman scattering, to avoid the difficulties of strong luminescence. The crystal would simultaneously be illuminated with a Raman laser and, for soliton creation, UV light (e.g., a hydrogen lamp). One would then look for new peaks, in addition to the characteristic peaks of $PbBr_6$ and the second order Raman spectrum of KBr. At liquid He temperatures we expect Raman lines above the acoustical branch and therefore any new peak is expected to be near the laser excitation line. When the UV light is switched off (terminating A-band excitation of Pb^{2+}) these Raman lines should disappear. We also anticipate requiring a higher Pb concentration than is now used in decay experiments.

Finally we observe that the soliton frequency corresponds to an energy, $\hbar\omega \sim 10$ meV. The energy dumped into the soliton vibrational modes is uncertain and bounded from above by 650 meV. If as much as 50 meV is available for the soliton, the semiclassical approach taken here should be qualitatively reliable.

We thank V. Čápek, R. Englman, S. Pascazio, and A. Soffer. This work was supported by NSF Grants No. PHY 97 21459 and No. PHY 00 99471, and by Czech Grant No. ME382.

*Email address: schulman@clarkson.edu

[1] K. Polák, M. Nikl, and E. Mihóková, J. Lumin. **54**, 189 (1992).

[2] B. Gaveau, E. Mihóková, M. Nikl, K. Polák, and L. S. Schulman, Phys. Rev. B **58**, 6938 (1998); J. Lumin. **92**, 311 (2001); E. Mihóková, L. S. Schulman, M. Nikl, B. Gaveau, K. Polák, K. Nitsch, and D. Zimmerman, "Temperature Dependence of Anomalous Luminescence Decay: Theory and Experiment."

[3] E. Fermi, J. Pasta, and S. Ulam, in *Enrico Fermi, Collected Papers* (University of Chicago Press, Chicago, 1965), Vol. II, p. 978. Note that FPU solitons are different from those of the KdV equation, described, e.g., in M. Tabor, *Chaos and Integrability in Nonlinear Dynamics* (Wiley, New York, 1989).

[4] J. Ford, Phys. Rep. **213**, 271 (1992).

[5] A. J. Sievers and S. Takeno, Phys. Rev. Lett. **61**, 970 (1988); S. R. Bickham and A. J. Sievers, Phys. Rev. B **43**, 2339 (1991).

[6] We do not model early events within the quasimolecule and energy that may be carried off isotropically as a result. See R. Englman, Chem. Phys. **58**, 227 (1981).

[7] O. A. Chubykalo, A. S. Kovalev, and O. V. Usatenko, Phys. Lett. A **178**, 129 (1993).

[8] V. M. Burlakov, S. A. Kiselev, and V. N. Pyrkov, Phys. Rev. B **42**, 4921 (1990); S. A. Kiselev, S. R. Bickham, and A. J. Sievers, Phys. Rev. B **50**, 9135 (1994).

[9] R. Dusi, R. Viliani, and M. Wagner, Phys. Rev. B **54**, 9809 (1996); R. Dusi and M. Wagner, Phys. Rev. B **51**, 15 847 (1995); J. B. Page, Phys. Rev. B **41**, 7835 (1990); S. Takeno and A. J. Sievers, Solid State Commun. **67**, 1023 (1988).

[10] Y. Zolotaryuk, S. Flach, and V. Fleurov, Phys. Rev. B **63**, 214 422 (2001).

[11] B. I. Swanson, J. A. Brozik, S. P. Love, G. F. Strouse, A. P. Shreve, A. R. Bishop, W.-Z. Wang, and M. I. Salkola, Phys. Rev. Lett. **82**, 3288 (1999).

[12] L. S. Schulman, *Techniques and Applications of Path Integration* (Wiley, New York, 1996); J. B. Keller, Ann. Phys. (New York) **4**, 180 (1958); W. Z. Wang and J. Tinka Gammel, A. R. Bishop, and M. I. Salkola, Phys. Rev. Lett. **76**, 3598 (1996).

[13] A. O. Caldeira and A. J. Leggett, Phys. Rev. Lett. **46**, 211 (1981).

[14] R. Reigada, A. Sarmiento, and K. Lindenberg, Phys. Rev. E **64**, 066608 (2001).

[15] A. M. Karo and J. R. Hardy, Phys. Rev. **129**, 2024 (1963).