EVIDENCE FOR ENERGETIC ANHARMONIC LATTICE EXCITATIONS AND PRACTICAL APPLICATIONS.

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Abstract. Numerical and analogue studies have been made of lattice solitons created in crystals by nuclear scattering of energetic particles. On-site potentials exclude topological solitons but allow 'optical' type. Direct evidence for these solitons is given by low energy sputtering from crystal surfaces. These solitons can have energies in the range from <1eV to >50eV. Energetic solitons are remarkably stable against random defects in the lattice and show self-focussing properties. They have potential for practical applications. In polarisable materials interaction will occur between these solitons and electrons. It has been shown that these solitons can propagate in typical high Tc superconductivity materials. Evidence is given which supports their involvement in HTSC.

1. Introduction

Very energetic particles passing through matter mainly loose energy by electronic excitation of the atoms but nuclear scattering dominates when the particles have slowed down to low velocities [1]. Large rates of energy loss can occur in electronic excitations at high energies by removing inner shell electrons from target and projectile atoms to cause ionization but little momentum is transferred to the lattice. In this regime the resulting space-charge and polarization effects in the lattice exert strong forces on the atoms, causing them to gain kinetic energy and momentum. Since little momentum is involved in the initial electronic excitations the momentum gained by the atoms must be nearly balanced by atoms moving in opposite directions. The energetic atoms resulting from this 'Coulomb explosion' create a high temperature gas or plasma which interacts with the surrounding lattice. Hence, at the microscopic level, energy and momentum is coupled to the lattice principally through nuclear, kinetic, scattering. Eventually, this energy appears in the lattice as heat from an increase in the density of lattice vibrations or phonons. Here we consider the transient motion of atoms in a lattice in response to the initial microscopic energy processes. The initial interaction between an energetic atom or ion and the lattice is essentially a two-body problem but the subsequent transient behaviour of the lattice is a many-body problem with its attendant difficulties of analysis.

This topic is important because in many practical applications energy is transferred at the microscopic level by atom to atom collisions in contrast to bulk processes arising from electric, magnetic or gravitational forces. Examples are high temperature gas atoms colliding with blades in a turbine and energetic plasma ions on the space shuttle shield. Even when the average energy of the impinging atoms or ions is relatively low there may be a high energy tail in the energy spectrum. Other examples are cavitation implosion of bubbles on ships propellers, neutron radiation damage in reactors and specialist applications such as sputtering, ion implantation and surface treatment by energetic particles.

2. Quasi-one-dimensional structures

A breakthrough came with the discovery of a new energy loss process associated with nuclear scattering. Under certain conditions transparent crystals of muscovite mica doped with impurities can record the tracks of high energy muons and positrons. The particles trigger a phase transition when the muscovite is in a meta-stable state leading to precipitation of the impurity along the track as black magnetite[2]. It was found that muons, but not positrons, could loose energy to the lattice by creating secondary tracks with unique features which showed that these secondary tracks could not be the tracks of charged particles. However, they were consistent with an interpretation based on the creation and propagation of soliton-like lattice excitations. Muscovite mica consists of complex silicate-based layers about 1nm thick separated by

mon-atomic sheets of Potassium atoms with a minimum spacing of 0.5nm within the sheets. Since the recording process was known to operate in these Potassium sheets the dynamic behaviour of these sheets was studied by numerical methods[3]. It was found that in the principal crystallographic directions chains of Potasium atoms behaved as **quasi-one-dimensional** (QOD) structures with strongly non-linear inter-particle forces. In such structures the force acting on an atom displaced in the chain direction is directed along the chain, a condition that calls for symmetry of the surrounding lattice.

3. The importance of on-site potentials

The studies on muscovite showed the importance of the structure surrounding a one-dimensional chain of atoms in a crystal in determining the dynamic properties of the chain. It was realised that in such quasi-one-dimensional structures the particles in the chain are subject to on-site potentials in addition to those arising from other particles in the chain. These on-site potentials restrict atoms in a chain to motions within the unit cell characterising the crystal structure and so stop pile-up of atoms along the chain characteristic of topological soliton solutions. The Hamiltonian of a quasi-one-dimensional system can be written in the form

$$H = \sum_n [M v_n^2 /2 + U(x_n , x_{n+1}) + W (x_n)] \qquad 1$$

where M is the particle mass, v_n is the particle velocity and $U(x_n , x_{n+1})$ is the inter-site potential. The last term $W (x_n)$ is the on-site potential for each particle. It is this term which leads to qodon solutions. Unfortunately, it seems that quasi-one-dimensional lattices with on-site potentials have not been studied theoretically, certainly not in detail. Consequently, to investigate the nature of disturbances that could evolve from impulses to such a structure an alternative approach was adopted based on an analogue model of the system.

3. Analogue model study

The form of the potential energy curve as a function of the displacement of an atom in a given direction in a unit cell in muscovite was found by numerical methods, from which the force-displacement curve was found. Analysis of these results gave the contribution of higher order non-linear force terms and showed that terms up to 3rd order should be included. It was realised that the force-displacement curve could be simulated with reasonable accuracy by the force between dipole magnets when the magnets are suspended by rigid struts from pivots to form a chain of particles, as indicated in Figure 1. This led to the construction of analogue models of the quasi-one-dimensional chain in which the on-site potential arose from the gravitational field. The Hamiltonian for this analogue model can be written in the form

$$H = \sum_n [M l^2 \Theta_n^2 /2 + U(\Theta_n , \Theta_{n+1}) + W (\Theta_n)] \qquad 2$$

where l is the length of the rigid strut and Θ_n is the angle of the strut to the vertical. The last term is the on-site potential caused by the gravitational field.

Two analogue models were constructed. One formed a straight chain in which the spacing between the pivots could be changed. This model was used to study starting conditions and both elastic and inelastic reflections from the ends of the chain. By rotating this analogue about the axis of the chain the strength of the on-site term could be varied, passing through zero at $\pi/2$ rotation. The other model was of circular form and so had a periodic boundary condition. Uni-directional propagation of disturbances was possible by temporarily holding one magnet fixed, applying an impulse to the next magnet and then releasing the held magnet before the evolved disturbance reached it. In this way the model behaved as an infinite chain which allowed the evolution of disturbances to be followed over considerable distances. The motion of the magnets was recorded by strobe photography followed by measurements on the photographs.

The response of the model chains to impulses of short duration was to show nearly resonant coupling between adjacent particles. Impulses rapidly evolved into compact wave-packets, as shown in Figure 2. These wave-packets resemble breather-solitons[4]. Analytical and numerical studies of a continuum approximation of the analogue models have confirmed breather-soliton envelope solutions [5].

Using appropriate starting conditions the analogues have demonstrated soliton-like behaviour of the evolved disturbances, such as the survival of oppositely moving solitons after their mutual interaction and their dispersionless propagation over long distances. These studies revealed that the internal structure of the breather-soliton moves with a phase velocity much greater than the group velocity [3]. The models also demonstrated the stability of the breather-solitons against small random defects or perturbations in the chains.

Localisation of 'qodons'

Usually, QOD structures are imbedded in a three dimensional lattice. In mica the QOD chains lie in mono-atomic sheets between complex plates. Although axial motion of atoms in a QOD chain produces no net lateral force this does not preclude the spreading of energy in the initial disturbance to adjacent chains. For example, it has been shown that a Toda-like soliton propagating in a Toda-chain in a sheet of such chains progressively spreads to adjacent chains [6]. The Toda-lattice does not contain on-site potentials. In contrast, the tracks in mica attributed to lattice-solitons do not show evidence of progressive lateral spreading but this does not rule out a stable distribution of the energy in the lattice-soliton over some adjacent QOD chains. For this reason the breather soliton-like wave-packets which evolve from impulses in QOD chains imbedded in crystals here are called '**qodons**' to emphasise the localisation of energy and their connection with QOD structures and phonons. It is conjectured that under certain conditions qodons may behave as stationary-breathers in the transverse direction and so remain localised.

The circular analogue was used to study the longitudinal spreading of qodons as a function of the strength of the initial impulse. It was found that qodons could be easily recognised above the background noise if the initial impulsive displacement exceeded 0.3**S**, where **S** is the interparticle spacing. Numerical studies [5] have shown that well-formed qodons are produced for initial displacements ranging from 0.6**S** down to 0.03**S** or less, although at the smaller values there was significant longitudinal spreading after distances of 100**S** or more. From the potential energy vrs displacement contours for mica this gives an energy range for qodons from at least 20eV down to 1eV or less. Since some qodon tracks in mica have upwards of fifty secondary tracks, all of which must be above the recording threshold of a few eV[3], the initial energy in the most energetic qodons can apparently reach several hundred eV. Assuming an energy of 50eV for a qodon producing a single track of 500mm length then the mean rate of loss of energy of a qodon in mica is $<10^{-7}$eV per atom along the QOD chain. This is many orders of magnitude less than the classically calculated loss rates for 'focussed collision sequences'. As discussed below, sputtering experiments in elemental crystals of Au, Cu and Al show that energetic qodons can propagate in QOD chains in three-dimensional non-layered crystals over distances of hundreds of unit cells and still have sufficient energy to eject surface atoms with energies of 10eV or more. It is evident that qodons are important in spanning the energy gap between energetic two-body collisions and the eventual creation of phonons.

Creation and detection of qodons: Sputtering.

It is expected that qodons could loose energy by in-elastic scattering at a crystal suface. Direct experimental evidence for this effect is provided by the phenomenom of sputtering in which atoms are ejected from the surface of a single crystal when bombarded with energetic ions. It is well known experimentally that the ejected atoms lie within cones whose axes are parallel to atomic chains [7]. If the energy of the incident ions is high enough then the nuclear, i.e. mainly kinetic, scattering occurs deep within the crystal. The depth at which this occurs can be varied by changing the angle of incidence of the beams to the crystal surface. In this way it was shown that the energy for ejection of the sputtered atoms was coupled to the lattice within the crystal and was not due to Rutherford backscattering at the surface. Also, a remarkable study by Wehner of sputtering in a wide range of materials showed that the process depended on both the speed of sound in the materials and the momentum coupled to the target atoms from the projectile atoms [8]. This result pointed strongly at a lattice-related energy transport effect. However,

attempts to explain these results in terms of lattice-related 'focussed atomic collisions' of hard atoms were only partly successful [9]. The principal difficulty was that Wehner had shown the correlation of direction of the sputtered atoms with chain directions persisted down to low bombarding ion energies when the ions could not penetrate sufficiently into the crystal to create collision sequences [10]. Also, both analytical and numerical studies of the rate of loss of energy from atoms taking part in 'focussed collision sequences' indicated that focussed sequences would rapidly degrade by spreading laterally to adjacent chains [11]. Finally, measurements of the kinetic energy of ejected atoms when using energetic bombarding ions showed that they could have energies exceeding that for creating interstitial atoms within the crystal [12]. Hence, the collision-sequence approximation predicted an excessive rate for atomic displacements. The discovery of qodons resolved these problems.

Consider a straight chain analogue which includes a fixed magnet at one end to represent the crystal surface potential barrier. When the first element in the chain is struck by a projectile it couples much of its energy to the second element and the recoil of the first element is small. However, the near-resonant interaction between the first and second elements can cause the next recoil of the first element to be larger than the initial recoil. Hence, it is the interaction with the second atom in a chain that determines the response of the struck atom. If the recoil energy of the first atom exceeds the surface potential then it can be ejected and the direction of maximum probability for ejection is defined by the chain axis. The subsequent evolution of the qodon leaves the first element with little residual energy. However, if the qodon is reflected from a crystal defect such as a dislocation then the reflected qodon can be inelastically scattered at the crystal surface, leading to ejection of the first atom. This process is remarkably efficient and, by near-resonant build-up, gives the first atom much greater energy than it achieved in the initial two recoils. Again the direction of maximum probability for ejection is defined by the chain axis. These results are in accordance with the work of Wehner who used projectile energies as low as 50eV which could hardly penetrate even the first atomic layer.

The near-resonant interaction between the first and second atoms in a chain also explains the observed enhancement of angular spread of the ejected atoms about the chain direction, caused by thermal motion, above that expected from the addition of momenta in a 'focused collision sequence'. The surface atom gains more energy as it moves inwards following its first outward swing causing closer approach to the surface atom prior to ejection. This close approach to the surface atom, which is displaced from the axis by thermal motion, magnifys the divergence from the chain axis.

The involvement of qodons with sputtering is revealed in other ways, too. Experiments show that despite bombardment with charged ions only a small fraction of sputtered atoms carry charge [7]. This implies that the ejection process is charge independent and involves interaction between atoms in the lattice. Returning to the work of Wehner, he showed that the threshold for onset of sputtering, which involves the sublimation energy for escape from the surface, correlated closely with the product of the speed of sound in the material and the momentum coupled from the projectile to the atom struck in the target. The qodon studies show that the energy finally coupled to the ejected atom propagates through the lattice at the group velocity of the qodon which is near the speed of sound. Also, the evolution of a qodon from an initial impulse conserves the momentum transferred, which agrees with Wehner's findings.

Using the straight chain analogue a quantitative study was made of the transfer of energy and momentum from a projectile to a qodon and then, after reflection, from the qodon to an ejected particle. It was found that most of the initially transferred momentum and about 70% of the energy was given to the ejected particle. The initial qodon was very apparent until it scattered inelastically after which it essentially disappeared, leaving only noise in the system.

Interactions and applications of qodons

There are four aspects to the interaction of qodons with solids: their creation, their demise by inelastic scattering and radiation, the effect of propagating qodons on the lattice and the effect of the lattice on qodon propagation.

So far only the creation of a qodon by a single impulse has been considered but the analogues show that they also can be created as the result of appropriately timed multiple smaller impulses. Hence, it is possible that low energy qodons will be created in solids from thermal noise in an analogous manner to

Toda-like solitons created from thermal noise [13]. More energetic qodons will require surface contact with high temperature gases or low energy ions in plasmas, or within the solid by energetic ions or neutrons. Of course, once formed energetic qodons will persist because of their stability against random perturbations but, as discussed above, low energy qodons will degrade as they propagate. The creation of qodons from multiple inputs of energy provides a non-equilibrium process by which energy can be concentrated and transported to grain boundaries and other lattice defects. Even if the probability for qodon production is small the accumulative effects of inelastic scattering of energetic qodons will have practical consequences which may be beneficial or harmful depending on the circumstances.

If the qodons are inelastically scattered then they can deposit relatively large amounts of energy, comparable with the atomic binding energy, at grain boundaries. If a material is highly stressed, either from internal causes or by external forces, then inelastic scattering of energetic qodons will influence grain boundary motion, with serious consequences for growth of micro-cracks. One procedure for minimising damage caused by qodons would be to impede their propagation through the material. This can be achieved by destroying the crystal structure by, for example, increasing the amorphousness of the materials or surface coatings. The creation of Beilby layers on metals to reduce wear and the use of ceramic tiles to reduce plasma-ablation are examples of. An alternative procedure would be to eliminate grain boundaries by using single crystals, doped with impurities to pin dislocations where appropriate, a procedure consistent with the latest fabrication of high performance gas turbine blades from single crystals.

The growth of micro-cracks is an accumulative process in terms of the energy deposited and so could be slowed by reducing the power dumped by qodons. This can be done by increasing the volume density of lattice discontinuities for constant rate of qodon production by, for example, creating smaller grain sizes by cold working. This action would be beneficial when the qodons are created at random within the material, such as by neutron scattering. This suggests a reduction in grain size in welds in nuclear reactors would be beneficial.

In considering the effect on a crystal of qodons in flight it is noted that the energy of a well-formed qodon is typically 10eV or more and since most of the energy resides with about 10 atoms in the chain the average energy per atom in a qodon is of the order of several eV, equivalent to temperatures >10,000K. Consequently, it is not surprising that the large amplitudes of atomic motions in an energetic qodon will encourage the lattice locally to relax to a lower energy state, as in thermal annealing, or trigger the release of energy from a meta-stable material leading to separation of phases, as shown by the formation of tracks in mica. This process could be especially useful for reducing strain at interfaces between substrates and surface coatings and invites practical application. This also could be of importance in the treatment of surfaces of cast alloys, especially as energetic qodons can be created by relatively cheap means at any temperature of the bulk material. If, however, the lattice contains random displacement defects, such as produced during ion implantation of micro-electronic devices, then the passage of qodons would encourage repair of this damage. This is because energetic qodons are not inelastically scattered by small random defects in a lattice.

The effect of the lattice on qodon propagation will show up mainly in terms of the qodon mean free path (mfp), expressed here in terms of the atomic spacing S. In amorphous materials and liquids the mfp will be determined by the length of the chains and so will be very short, of order 10S. Sputtering experiments show that in single crystals of Al, Cu, Ag and Au, all of which have a FCC structure, the mfp can be 100S or more. Both dislocations, which limit chain lengths, and lateral instability will limit the mpf. In crystals with an appropriate layered structure, however, qodons may be stable laterally and the mfp then can be very long as observed in mica.

Electron-qodon interactions.

Just as electron interactions with phonons are of basic importance in the solid state it is anticipated that electron-qodon interactions also are important, especially in layered crystals containing QOD structures. The trapping of charge by lattice-solitons has been studied for various types of soliton, such as the Davydov soliton [14], kink soliton [15] and for stationary-breathers [16]. In each case it has been shown that trapping can occur under certain conditions. The lack of an analytical form for a qodon makes

extension of these studies to qodons difficult at present but some progress is possible in the following way. In the stationary-breather case it has been shown that a bound electron-breather state can exist at least over half of the breather period of oscillation but is lost during the remaining part of the oscillation. To a first approximation a qodon can be considered as a coherent alternation of a small number of 'quasi'-breathers with adjacent quasi-breathers out of phase. In a moving qodon, however, the internal motion sweeps these quasi-breathers forward so that, in effect, they do not oscillate. A charge trapped in the potential well of a quasi-breather born at the rear of a qodon can remain trapped in that potential well until the quasi-breather fades as it is swept to the front of the qodon. Since the analogue studies show that qodons can have two such potential wells separated by a potential hill this suggests that a single qodon could trap a pair of charges for a limited period of time after which it would break up. After break up a new bound pair could form by capture of a charge into the newly formed potential well at the rear of the qodon. The average propagation distance before such bound pairs break up can be estimated from the ratio of phase to group velocities of a qodon and its longitudinal extent; present estimates indicate it is of the order of 1nm.

It is well known that high Tc superconductors (HTSC) have layered structures. To investigate the possibility that qodons might propagate in such structures a study [17] was made of YBaCuO and LaCuO which showed that these materials do contain QOD structures. In particular, it was found that QOD structures exist in the CuO sheets believed to be associated with charge transport. If qodons are involved in HTSC then the presence of QOD chains would be a necessary condition for superconductivity in these materials. This aspect has been examined in the family of layered materials based on the $Ni_2B_2(LuC,LaN)_n$ structure. The compounds with n = 1 or 3 contain QOD chains and have been shown to be superconductors [18]. For the n = 2 case, however, the lack of symmetry excludes QOD chains and this material is known to be a non-superconductor [19]. This structural dependence is indicated in Figure 3. This finding supports the hypothesis that qodons are involved in HTSC but does not clarify their role. The qodons might be exchanged between bound charges or could bind the charges within the qodons. It is noted, however, that binding of charges within a qodon would assist movement of charges through the structure.

Conclusion.

The realisation that on-site potentials due to the surrounding lattice must be included in the Hamiltonian describing atomic motions in quasi-one-dimensional (QOD) chains in crystals led to the discovery of qodons. The reality of energetic qodons is demonstrated by sputtering experiments. Since at present there is no known analytical expression for qodons they have been investigated by means of analogue models and by numerical methods. Although it can not be proven that qodons are true solitons they have been shown to exhibit many of the properties of solitons. Numerical and experimental studies show that qodons span the energy gap between phonons and high energy two-body collisions. Since energetic qodons can release excess energy stored in a lattice they should find practical applications.

It is expected that qodons will interact with electrons (holes) in polarisable materials in a similar manner to phonons. To first order this interaction can be studied by synthesising a qodon from several breather-solitons of known analytical form and it is already known that an electron can be bound in the potential well of a breather. Since a qodon typically contains two such potential wells it should be possible to form qodon-bound pairs of charges. This invites application to HTSC since it has already been shown that YBCO and LCO contain QOD chains. The hypothesis that HTSC involves qodons has been tested in a family of related compounds by correctly predicting which are superconductors based on the presence of QOD chains.

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References.

1. A Dunlop and D Lesueur, Materials Science Forum Vols. 97-99, p553-576 (1992)
2. F M Russell and J W Steeds, Nucl. Tracks Radiat. Meas., 22, 1-4, 65-70 (1993)
3. F M Russell and D R Collins, Nucl. Radiation Measurements, 25, 1-4, 67-70 (1995)
4. J C Eilbeck, Solitons and condensed matter -. Ed. Bishop & Schneider, Springer-Verlag,28-43 (1978)
5. Y Zolotaryuk, F M Russell, T Dauxois and J C Eilbeck, Breather in a chain of magnetic dipoles. to be published; preprint available (1995)
6. V Martynenko and P G Moscovkin, Radiation Effects and Defects in Solids, 117, 321-328 (1991)
7. R S Nelson, M W Thompson and H Montgomery, Phil. Mag., 7, 1385-1405 (1962)
8. G K Wehner, Phys. Rev., 102, 3, 690-704 (1956)
9. R H Silsbee, J. of Applied Phys., 28, 11, 1246-1250 (1957)
10. P Sigmund, Phys. Rev., 184, 2, 383-416 (1969)
11. R Behrisch, Ed., Sputtering by particle bombardment I, Springer-Verlag, Ch.2, (1981)
12. M W Thompson and R S Nelson, Phil. Mag., 7, 1425-1428 (1962)
13. N Theodorakopoulous and N C Bacalis, Phys. Rev. B, 46, 17, 10706-10709 (1992)
14. A S Davydov, Solitons in Molecular Systems, Reidel, Dordrecht (1985)
15. A Zolotaryuk et al., Phys. Rev. Letts., 67, 6, 707-710 (1991)
16. S Flach and K Kladko, submitted to Phys. Rev. B (1995)
17. F M Russell and D R Collins, Anharmonic excitation in high Tc materials. to be published; preprint available (1995)

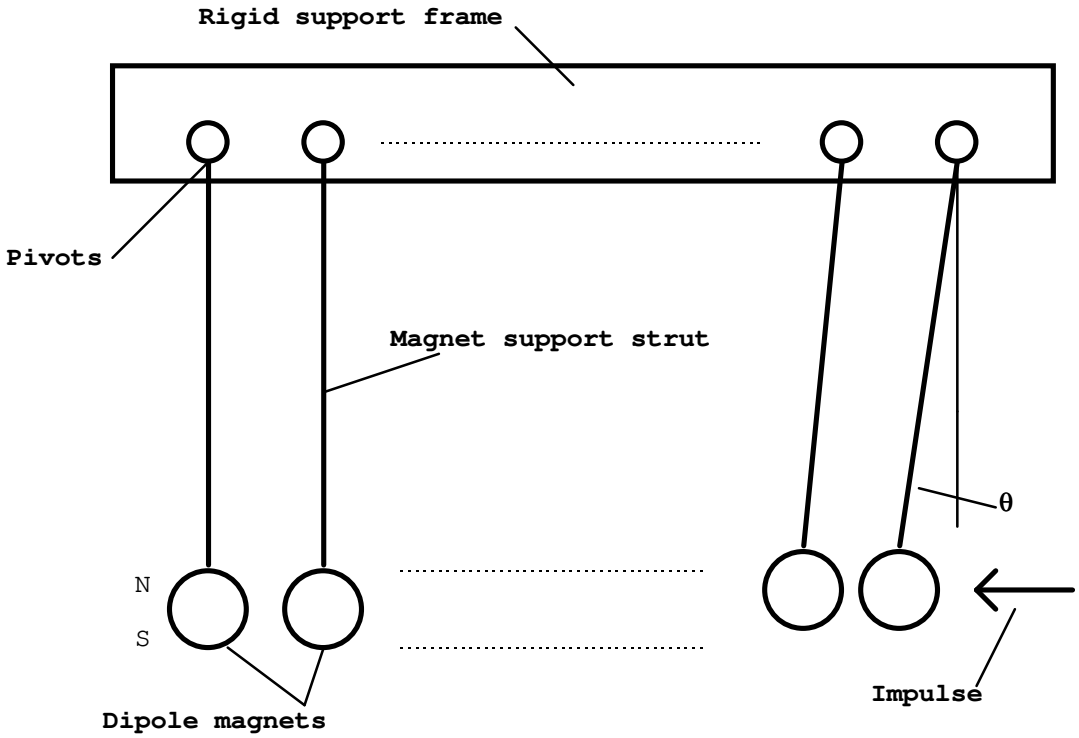


Figure 1. Diagram of the straight chain magnet analogue model. The inter-particle potentials arise from the dioples and the on-site potential from gravity. Qodons evolve from impulses which are of short duration compared to the period of oscillation of the magnet pendulum. Additional fixed magnets can be placed at the ends of the chain to produce potential energy barriers representing the free surface of a crystal or a reflecting dislocation in the crystal.

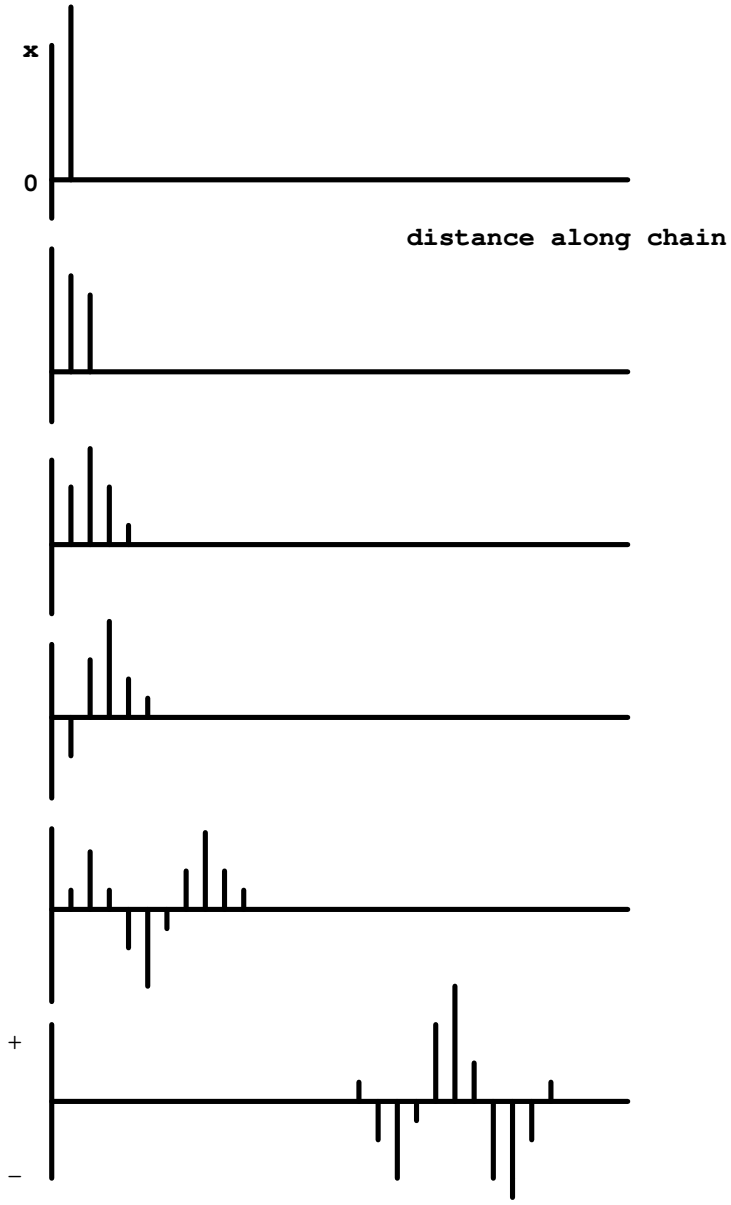
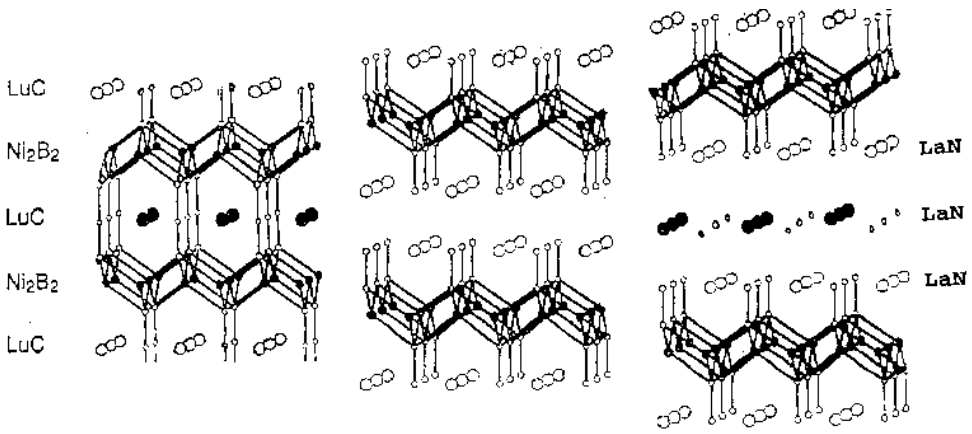


Figure 2. Sketch of the evolution in time of an impulse into a qodon. The vertical lines represent the displacement of particles in the chain direction from their equilibrium positions.



$LuC(Ni_2B_2)$ $Lu_2C_2(Ni_2B_2)$ $La_3N_3(Ni_2B_2)$

Figure 3. Three closely related compounds containing 1, 2 or 3 planar sheets between puckered NiB layers which act as charge reservoirs. The compounds with 1 and 3 sheets both contain QOD chains and are known to be superconductors. The addition of the second sheet excludes QOD chains and experiments show this compound is a non-superconductor.