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LOW TEMPERATURE BEHAVIOUR OF ISING MAGNETIC CHAINS; DECORATED SOLITONS, LOCALLY ENHANCED EXCHANGE AND DIFFUSIVE PROPAGATION

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We calculate the soliton bound lattice defect (SBLD) which arises in an Ising chain when the non-ideal rigidity of the lattice is admitted and its major consequences. Our results are (i) a correction to the soliton energy which can be 10% or larger, (ii) a positive interaction energy which falls off exponentially with soliton separation, and (iii) the existence of an energy barrier, E_b, which a moving soliton sees at each step in its progression and which can be as large as the soliton energy itself or larger. Our calculations suggest that the existance of E_b leads to diffusive propagation and a spin dynamics which agrees with recent measurements. In higher dimensions, the corresponding spin-pair bound lattice defect is a plausible mechanism for the thermoremanent magnetization of spin glasses and for the recently observed "waiting-time effect" in amorphous alloy spin glasses.

1. Introduction

Recently, many experimental investigations have been devoted to quasi one-dimensional magnetic systems[1]. Much of the work has been motivated by the wealth of (not always) intrinsically low dimensional phenomena which arise from the spin Hamiltonian[2]. An example of such phenomena which concerns us here is the occurrence of solitons (or kinks) and their dynamic behaviour. Another example is the spin-Peierls transition[3] which is a rare example of what can be predicted when the non-ideal rigidity of the underlying crystalline lattice is admitted.

In the present paper we have calculated the local lattice perturbation which can be expected to "decorate" a magnetic soliton in a strongly Ising chain. We refer to this defect as a soliton bound lattice defect (SBLD) and show that, given its magnitude, we must expect the soliton dynamics and many thermodynamic quantities such as the susceptibility to be measurably affected.

2. Static Kinks - Purely Ising Chain at Low Temperature

We first consider the lattice distortion which arises from a single static domain wall (kink or soliton) on an otherwise perfectly ordered chain of $S = \frac{1}{2}$ spins. The SBLD which we calculate is the same for solitons on ferromagnetic (F) and antiferromagnetic (AF) Ising chains. The two types of kinks are represented in Figs. 1(a) and 1(b). The SBLD arises because the chain can lower its energy by changing the separation between the two spins which bracket the soliton. The only prerequisites are (i) that the lattice is not infinitely rigid and (ii) that there is a dependence of the exchange strength on inter-spin separation.

In a first approximation which neglects the elastic coupling of the chain to the underlying solid, the lattice stiffness can be described in terms of the rigidity (or force) constant, R, which appears in the harmonic approximation for the lattice potential as:

$$U_{harm} = \tfrac{1}{2} R a_o^2 \sum_{n=1}^{N} (\delta_n - \delta_{n+1})^2 \ . \qquad (1)$$

The dimensionless deviations, δ_n, from the regular lattice are defined as $\delta_n = (x_n - na_o)/a_o$ where x_n is the position of the n^{th} ion (and spin) along the chain and a_o is the lattice spacing in the absence of kinks. A realistic value of R can be estimated quite easily. Ionic frequencies are typically $\nu_{ion} \lesssim 10^{13}$ Hz and, therefore, $R \simeq M_{ion}(10^{13}\ \mathrm{Hz})^2 \simeq 10^3\ \mathrm{K/\AA^2}$. Taking $a_o \simeq 3 - 4$ Å implies that the term Ra_o^2 in Eq. 1 is the order of $Ra_o^2 \simeq 10^4$ K. Also, the dependence of the exchange strength on separation can often be expressed as:

$$J_{ij} = J_o(a_o/|x_j - x_i|)^{\eta} \qquad (2)$$

where, for many transition metal oxides and fluorides,[4] $\eta \sim 10 - 11$. Low dimensional materials where the inter-transition metal exchange bonds arise from superexchange via O, F or Cl, can also be expected to have η's which are of this order - as is found in, for example, $(C_3H_7NH_3)_2MnCl_4$ where $\eta \simeq 12$.[5] Our main results

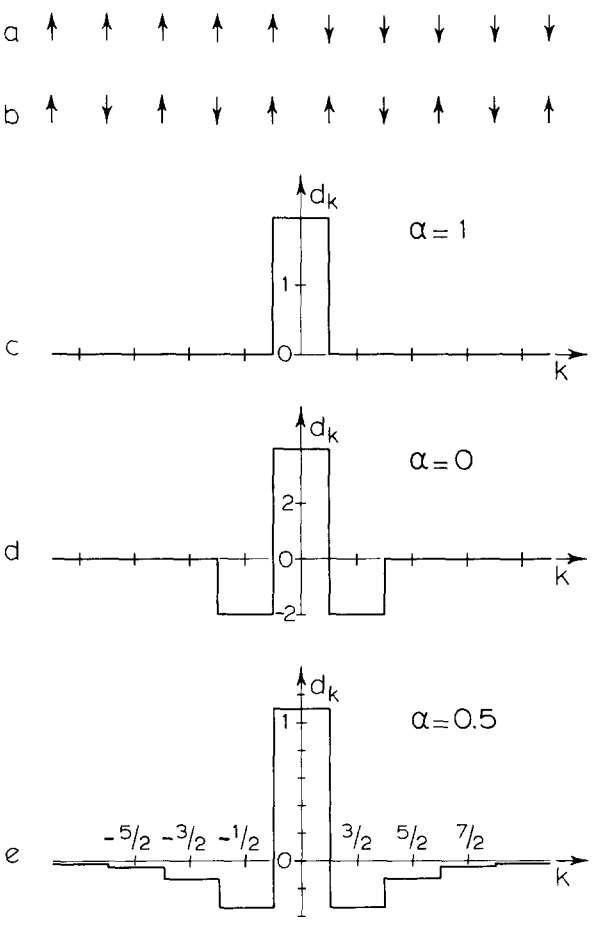

Fig. 1 The SBLD ($\{d_k\}$) is illustrated for three values of the chain to host solid coupling coefficient α. a - A ferromagnetic kink on the Ising chain. b - An antiferromagnetic kink on the Ising chain. c, d and e - Bar charts of d_k versus position index k for $\alpha = 1$, 0 and 0.5 respectively.

should apply to such quasi-one-dimensional materials whose effective spin Hamiltonians are Ising-like at low temperatures and in which the intra-chain exchange strength varies as in Eq. 2 and irrespective of whether J_o is positive (AF) or negative (F).

Consider the derivation of $\{\delta_i\}$ for a single soliton on an infinite chain. If Eq. 2 is expanded as:

$$J_{ij} = J_o[1 - \eta(\delta_j - \delta_i) + O(\delta^2)] \qquad (3)$$

and the position index, i, is taken to be i = 0 and 1 for the spins which bracket the soliton (i.e. the soliton is at $i = \frac{1}{2}$) then the net energy difference, ΔE, between a perfectly rigid lattice containing one soliton and a non-rigid lattice also containing one soliton is expressed as:

$$\Delta E = -4\eta J_o\delta_1 + 3Ra_o^2\delta_1^2 + 2Ra_o^2\sum_{n=2}^{\infty}(\delta_n^2 - \delta_n\delta_{n-1}) \qquad (4)$$

where we have used the symmetry requirement that $\delta_p = -\delta_{-p+1}$. The minimum of ΔE represents the correction to the soliton energy, E_s, which must be made when coupling to the lattice is allowed. The minimization can be accomplished via $\partial\Delta E/\partial\delta_i = 0$ if we take the spins at $i = +N$ and $i = 1 - N$ to be pinned (for example, by two impurities which are more strongly coupled to the host solid). Then the solution is

$$\delta_i = [(2N - 2i)/(2N - 1)]\eta J_o/Ra_\delta^2 \qquad (5)$$

for $i < N$ and $\delta_i = 0$ for $i > N$. In the limit $N \to \infty$ the solution becomes
$\delta_1 = \delta_2 = \delta_3 = \ldots = \eta J_o/Ra_\delta^2$ and
$\Delta E_{min} = -2(\eta J_o)^2/Ra_\delta^2$. In words, the two chain segments on either side of the soliton are displaced by either plus or minus $\eta J_o/Ra_\delta^2$ and the only bond which is affected is the one which plays host to the soliton - its length is increased by $(2\eta J_o/Ra_\delta^2)a_o$. The net decrease in the soliton energy, ΔE_{min}, should be added to the unperturbed value of $2|J_o|$ and corresponds to ~10% for $\eta \sim 10$ and $J_o \sim 10$ K. Also, the δ's are the order of ~1 - 10% for $|J_o| \sim 10$ - 100 K. The SBLD is therefore not negligibly small and is well defined even on the scale of the root mean square ionic displacements which are generally < 1% and which also go as 1/R. Note, however, that anharmonic terms in the lattice potential will limit the δ's such that a realistic maximum is 2 - 3%.

We now describe the case where elastic coupling to the host solid is included. Such coupling adds a term $\frac{1}{2}R'a_\delta^2\sum_n\delta_n^2$ to the energy change such that the new ΔE is written:

$$\Delta E = -4\eta J_o\delta_1 + 3\alpha Fa_o^2\delta_1^2 + 2\alpha Fa_o^2\sum_{n=2}^{\infty}(\delta_n^2 - \delta_n\delta_{n-1}) + (1 - \alpha)Fa_o^2\sum_{n=1}^{\infty}\delta_n^2 \qquad (6)$$

where α and F are defined by $R = \alpha F$, $R' = (1 - \alpha)F$ and $0 \leq \alpha \leq 1$. We can expect $\alpha \simeq 1$ ($R' \ll R$) when the chains are very weakly chemically bonded to each other in the solid - such as by hydrogen bonds as in the quasi-onedimensional ferromagnet $Co[(CH_3)_3NH]Cl_3 \cdot 2H_2O$.[6] On the other hand, we expect $\alpha \simeq \frac{1}{2}$ ($R' \simeq R$) in a compound such as $CuCl_2$[7] where inter-chain bonds are comparable to the intra-chain bonds.[8] (in $CuCl_2$ the chains are magnetically isolated by frustration.[8]) For completeness, we also consider the case where $\alpha \simeq 0$ ($R' \gg R$). When $\alpha = 0$, the solution is $\delta_1 = 2\eta J_o/Fa_\delta^2$ and $\delta_i = 0$ for $i > 1$. This can also be expressed in terms of the rescaled fractional change in separation, d_k, between two ions at i and i + 1:

$$d_{i+\frac{1}{2}} \equiv (\delta_{i+1} - \delta_i)Fa_\delta^2/\eta J_o. \qquad (7)$$

The result for $\alpha = 0$ is then $d_{\frac{1}{2}} = +4$, $d_{3/2} = -2$ and $d_{k>3/2} = 0$. Similarly, the result for $\alpha = 1$ is re-expressed as $d_{\frac{1}{2}} = +2$ and $d_{k>\frac{1}{2}} = 0$. The solutions $\{d_k\}$ for $\alpha = 0$ and 1 are shown graphically in Figs. 1(d) and 1(c) respectively. The special case of $\alpha = \frac{1}{2}$ is illustrated in Fig. 1(e) and some relevant quantities for $\alpha = 0$, $\frac{1}{2}$, and 1 are given in Table 1. The SBLD can be obtained for arbitrary α by minimizing

Table 1 Pertinent quantities associated with a SBLD.

quantity	units	bound chain $\alpha = 0$	intermediate $\alpha = 0.5$	free chain $\alpha = 1$
δ_1	$\eta J_o/Fa_\delta^2$	+2.0	+1.1055	+1.0
δ_2	"	0.0	+0.4223	+1.0
δ_3	"	0.0	+0.1613	+1.0
$d_{\frac{1}{2}}$	——	+4.0	+2.2111	+2.0
$d_{3/2}$	——	-2.0	-0.6832	0.0
$d_{5/2}$	——	0.0	-0.2610	0.0
ε_1	$(\eta J_o)^2/Fa_\delta^2$	2.0	1.1055	1.0
ε_2	"	1.0	0.3416	0.0
ε_3	"	0.0	0.1305	0.0
ΔE_{min}	"	-4.0	-2.2111	-2.0
E_b^o	"	+12.0	+5.7884	+4.0

Note that, quite generally $E_b^o = \eta|J_o|(6\delta_1 - 2\delta_2)$ and $\Delta E_{min} = -2\eta|J_o|\delta_1$.

Eq. 6 and is expressed as

$$\delta_i = C_o(\eta J_o/Fa_\delta^2)\exp[i/r_o] \qquad (8)$$

where the dimensionless constants r_o and C_o depend on α as given in Fig. 2. Note that $\{\delta_i\}$, as given by Eq. 8 and when $\alpha \neq 1$, satisfies the relation $d_{\frac{1}{2}} = -2\sum_{n\frac{1}{2}} d_n$ which follows from the boundary condition $d_{\pm\infty} = 0$. It also follows that $\Delta E_{min}/\eta J_o = 2\delta_1$ which is plotted as a function of α in Fig. 2 (dashed line).

As expected, the SBLD is, in most cases, well localized - falling off exponentially with coordinate index from the soliton at $i = \frac{1}{2}$. Such defects give rise to a local decrease in the magnetic exchange which is the order of $(\eta J_o)^2 d_{\frac{1}{2}}/Fa_\delta^2$ - that is, typically 10% for $\eta \simeq 10 - 12$ and $|J_o| \simeq 10$ K or greater. We now ask which properties are most sensitively affected by this.

It is easy to see that many of the thermodynamic properties of the chain are affected by the SBLD. In the context of static solitons we assume the lattice response time, τ_L, to be zero - which is true to the extend that $1/\nu_{ion}$ is much smaller than the spin autocorrelation time, τ_{ac}. As a first approximation we also take $\{d_k\}$ to be of the form given in Fig. 1(c). We write half of the local change in J_{ij} as $\varepsilon_1 J_o = (\eta J_o)^2 d_{\frac{1}{2}}/2Fa_\delta^2$ and the effective spin Hamiltonian can be expressed as:

$$\mathcal{H}_1 = \sum_{ij}^{N} [J_o(1 - \alpha_{ij}) + J_o(1 - 2\varepsilon_1)\alpha_{ij}]S_i^z S_j^z \qquad (9)$$

where the sum is over near neighbour spins, $S_i^z = \pm 1$ and α_{ij}, for the AF case, is equal to 1 when sign (S_i^z) = sign (S_j^z) and zero otherwise. Using $\alpha_{ij}^{AF} = \frac{1}{2}(1 - S_i^z S_j^z)$, Eq. 9 reduces to:

$$\mathcal{H}_1^{AF} = \sum_{ij}^{N} [J_o(1 - \varepsilon_1)S_i^z S_j^z] + NJ_o\varepsilon_1 \qquad (10)$$

in which the zero of energy is shifted by $\varepsilon_1 NJ_o$ and the exchange constant is replaced by an effective exchange of $J_o(1 - \varepsilon_1)$. This means, for example, that the broad maximum in the zero field susceptibility of the AF Ising chain is shifted towards lower temperatures by an amount $\varepsilon_1|J_o|$ whereas its functional form is unaffected to this "first order". Consequently, if one derives the soliton energy from the position of this maximum in a real system, one arrives at an already corrected E_s of $2|J_o(1 - \varepsilon_1)|$. Similarly, all of the equilibrium thermodynamic quantities such as specific heat and soliton density are redefined by the substitution $J_o \to J_o(1 - \varepsilon_1)$. Note that Eq. 10 is exact, within the $\tau_L = 0$ assumption when $\alpha = 1.0$ and that, to this first order, the true soliton energy $(2|J_o| + \Delta E_{min})$ is correctly given by the effective J value.

In the next order calculation we take $\{d_k\}$ to be of the form shown in Fig. 1(d) and define ε_2 by $\varepsilon_2 J_o = (\eta J_o)^2 d_{3/2}/2Fa_\delta^2$. The effective spin Hamiltonian is then written as:

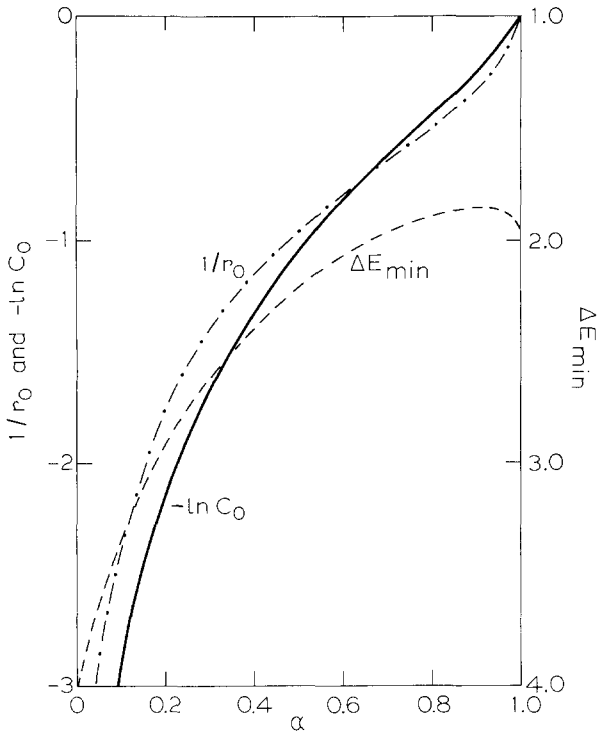

Fig. 2 $1/r_o$ and $-\log_e C_o$ as functions of α. $|r_o|$ is the range of the SBLD in number of lattice units and C_o is a dimensionless constants which also depends only on α and scales the magnitude of δ_i - see Eq. 8. The correction, ΔE_{min}, to the soliton energy is also plotted as a function of α and in units of $(\eta J_o)^2/Fa_o^2$ (right hand scale - dashed line).

$$\mathcal{H}_2 = \sum_{ij}^{N} J_o\left[1 - 2\varepsilon_1\alpha_{ij} + 2\varepsilon_2(\alpha_{i-1,i} + \alpha_{j,j+1})\right]S_i^z S_j^z \tag{11}$$

which reduces to

$$\mathcal{H}_2^{AF} = \varepsilon_1 N J_o + J_o\sum_{ij}^{N}\left[(1 - \varepsilon_1 + 2\varepsilon_2)S_i^z S_j^z - \varepsilon_2(S_{i-1}^z S_j^z + S_i^z S_{j+1}^z)\right] \tag{12}$$

where it is understood that only terms with $|i - j| = 1$ contribute to the sum. From Eq. 12 we see that to "second order" it is not sufficient to have an effective exchange but that longer range spin correlations enter the picture. The second term in the sum of Eq. 12 gives rise to a short range repulsion between solitons since it makes it energetically unfavourable for two solitons to be separated by only one spin. This repulsion must however be corrected because the lattice defects which arise from two solitons are not additive such that, even for $\alpha = 0$, Eq. 12 is only a good approximation within the zero lattice response time assumption. In section 4 we shall show that to "infinite order" (i.e. allowing $\{d_k\}$ to have a long range extension for general $\alpha \neq 0$ or 1) the SBLD's lead to a repulsive potential which falls off exponentially with inter-soliton separation and whose range and strength are functions of α.

Concerning soliton interactions, we point out that dipole-dipole forces can play an important role in the ferromagnetic case at low temperatures. For an isolated $S = \frac{1}{2}$ Ising chain with $J_o < 0$ the domain size, ξ, at $T = 0$ K can be shown to be given by:

$$\xi/a_o \simeq (|J_o|\, a_o^3/\mu_B^2)^{\frac{1}{2}} \tag{13}$$

where μ_B is the Bhor magneton. With $|J_o| = 10$ K and $a_o = 3$ Å, this corresponds to roughly thirty lattice units. On the other hand, the purely Ising Hamiltonian predicts that the density of domain walls should be zero at $T = 0$ K - clearly the dipole-dipole interactions will perturbe the Ising thermodynamics considerably at temperatures which are small compared to $|J_o|$.

In the next section we argue that, whereas the Hamiltonians $\mathcal{H}_1$ (Eq. 10), $\mathcal{H}_2$ (Eq. 12), etc. adequately describe the equilibrium properties of a non-rigid Ising chain at low temperatures, they do not lead to the correct soliton dynamics when the usual transverse exchange terms are added to allow such dynamics.

3. Soliton Dynamics: Quasi-Ising Chain at Low Temperature

It is now well known that soliton dynamics arise in both the F and AF rigid Ising chains when a transverse exchange term is added to the Hamiltonian - see, for example, the recent review by de Groot et al.[9] Villain has shown[10] that, in the AF case, a transverse term of the form $\gamma J_o(S_i^x S_j^x + S_i^y S_j^y)$ with $|\gamma| \ll 1$ is sufficient to give dynamics. In analogy with Villain's work, if we add a term $\gamma J_o(1 - 2\varepsilon_1\alpha_{ij})(S_i^x S_j^x + S_i^y S_j^y)$ to our Hamiltonian of Eq. 9 we arrive at a corrected dynamics where the soliton velocity is given by:

$$v_s(k) = 4\gamma J_o(1 - 2\varepsilon_1)\sin 2k \tag{14}$$

and k is the soliton wavevector. This picture ignores the soliton interactions (which is justifiable to this first order at low temperatures) but, most importantly, it neglects the fact that τ_L is not zero. This is a major flaw which makes the relation (14) inapropriate for any real system at any temperature.

A typical soliton velocity, as can be estimated from the transverse exchange in a quasi-onedimensional antiferromagnetic compound such as $RbFeCl_3.2H_2O$[9] and assuming perfect rigidity, is $v_s \sim 1 - 10$ m/s. This is by far slow enough, compared to ionic frequencies, to consider that the SBLD is unaltered in shape by the soliton motion and that it effectively follows the soliton without lag. Although $\tau_{ac}^Q \equiv a_o/v_s \gg \tau_L$, the relaxation time, τ_L, for the SBLD to reestablish itself on the new soliton position is not zero and this means that, when the soliton jumps, the energy of the chain is raised by an amount the order of $(3\eta^2 J_o/Ra_o^2)E_s$ and for a time τ_L. This amounts to a barrier in energy which the soliton must overcome at each step in its progression. The barrier height, E_b^Q, can be taken to be the change in energy which is pro-

duced in moving the soliton by one lattice unit without altering the SBLD and the barrier width is the order of $(\tau_L/\tau g_c)a_o$. The ratio of E_b^o to the SBLD-corrected soliton energy E_s is shown as a function of $|J_o|$ in Fig. 3. The anharmonic effects were assumed to enter and be effective in limiting δ_1 when $\delta_1 \gtrsim 1\%$. Surprisingly, E_b^o is comparable to or larger than E_s for $|J_o| \gtrsim 10$ K and is notably much larger than the transverse exchange terms (γJ_o) which are assumed to be responsible for the dynamics in the real systems.

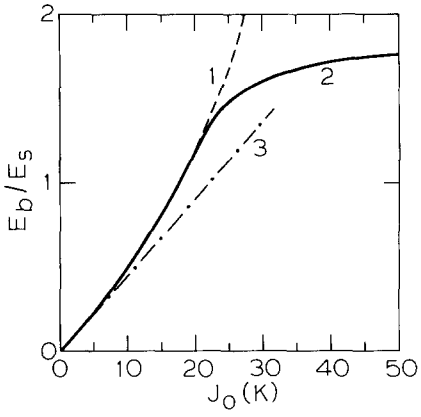

Fig. 3 Ratio of barrier energy, E_b^o, to SBLD corrected soliton energy, E_s, as a function of $|J_o|$ for $\alpha \simeq 0.5$. Curve 1 ignores anharmonic limitations and corresponds to $E_b^o/E_s \simeq \theta|J_o|/(1 - \theta|J_o|/\phi)$ with $\theta \simeq 3\eta^2/Fa_\delta^2 \simeq 0.04$ K^{-1} and $\phi \simeq 3$. Curve 2 includes anharmonic effects which are chosen to limit $\delta_1 \sim 2 - 3\%$ and curve 3 is the low $|J_o|$ limit of $E_b^o/E_s \simeq \theta|J_o|$.

In order to calculate the soliton dynamics properly we should start from a Hamiltonian which contains the phonon degrees of freedom however this is impractical. We follow the phenomenological approach[11] and take the soliton to be a particle of rest mass $M_s = E_s/c_o^2$ where c_o is the maximum soliton velocity as obtained, for example, from the dispersion relation (14) where $c_o = 4|\gamma J_o|(1 - 2\varepsilon_1)$. The soliton kinetic energy is taken to be $E_{sk} = \frac{1}{2}M_s v_s^2$ which has a thermal average of $(4/\pi^2)E_s$ at $k_BT \gg 2\gamma J_o$. This euristic approach suggests what the effect of E_b^o might be on the soliton dynamics. For small barriers ($J_o \lesssim 1$ K) the soliton will have a mean free path of many lattice units before it is self scattered in the opposite direction. For large barriers ($J_o \gtrsim 25$ K) the soltion is self-trapped and must tunnel out of its own barrier - in which case we can expect its progression to be truly random walk-like with equal probabilities at each step to jump forward or backwards. In either case, these considerations suggest that in many real systems the soliton propagation should be diffusive.

In the next section we suggest that a very effective mechanism which drives dynamic solitons apart arises from the effect which nearby solitons have on the two barrier heights (E_b^+ and E_b^-) for the motion of a given soliton towards (E_b^+) and away from (E_b^-) the nearest neighbouring soliton. E_b^+ is found to always be larger than E_b^-.

4. SBLD Interactions

It is straightforward to calculate the SBLD ($\{\delta_i\}$) which arises from two static kinks some number, d/a_o, of lattice units apart. The corresponding energy perturbation, ΔE_d, is less negative than the total, $2\Delta E_{min}$, for two kinks infinitely far apart and, clearly:

$$\lim_{d\to\infty} \Delta E_d \simeq 2\Delta E_{min}(\alpha,F,\eta,J_o,a_o) \ .$$

The interaction potential between two static kinks in a non-rigid chain can therefore be written as $V(d) = \Delta E_d - 2\Delta E_{min}$ and turns out to be:

$$V(d) = V_o((\eta J_o)^2/Fa_\delta^2)\exp[d/Da_o] \qquad (15)$$

where the dimensionless constants V_o and D depend only on α in the manner shown in Fig. 4.

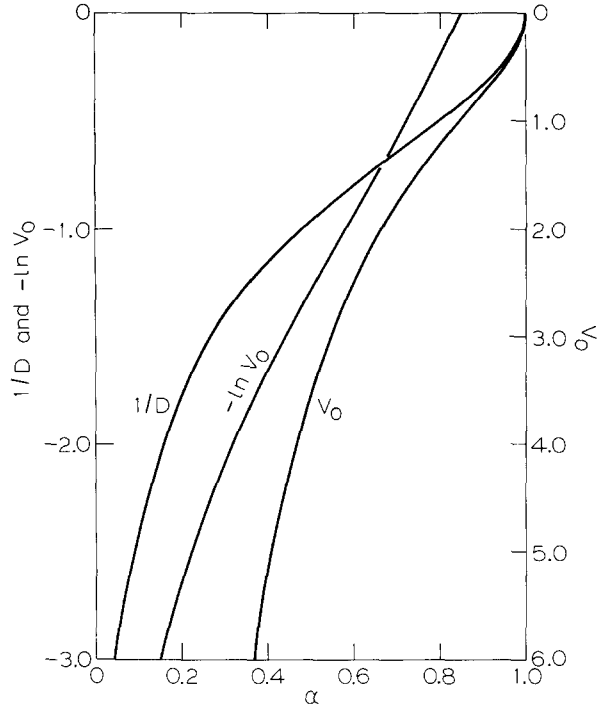

Fig. 4 1/D and $-\log_e V_o$ as functions of α (left hand scale). $|D|$ is the range of the soliton interaction energy and V_o appears in its magnitude - see Eq. 15. V_o is also plotted directly (right hand scale).

In the limit that the ionic positions in the chain are strongly related to a specific set of regularly spaced host solid coordinates ($\alpha \to 0$), the potential becomes very short ranged and very strong. If the chain is progressively freed from the host solid elastic constraints ($\alpha \to 1$), then

the range, $|D|$, of the repulsive potential grows monotonically until $|D| = \infty$ at $\alpha = 1$ and its strength, V_o, simultaneously decreases until $V_o = 0$ at $\alpha = 1$. At $\alpha = 0.5$, we see that the energy involved, $V_o(\eta J_o)^2/Fa_\delta^2$, becomes comparable to or larger than $|J_o|$ for $|J_o| \gtrsim 25$ K. In real systems, therefore, one can only hope to observe free soliton gas behaviour if $\eta^2|J_o| \ll Fa_\delta^2$ which typically means $|J_o| \ll 25$ K. For larger J_o values there will be a strong tendency, energetically, for the solitons to be regularly spaced apart. This tendency is reenforced by the dipole-dipole forces in the F case.

The above energy considerations imply that, in equilibrium, the distribution of near neighbour soliton separations is narrowly peaked about the average value of $1/n_s$ where n_s is the number of kinks per unit length. If the solitons possess dynamics by virtue of a small transverse exchange term, then a similar distribution must still result from many "snap shots" of the chain. There must therefore exist a "dynamic repulsion" which does not arise directly from V(d) since V(d) simply describes the energetics of the chain without corresponding to a true repulsive force between solitons. The required mechanism arises from the barriers E_b^+ and E_b^- which must exist since in any real lattice $\tau_L \neq 0$. We calculate the barrier heights in the manner described in section 3 and our results for $\alpha = 0.1$ and $\alpha = 0.5$ are plotted in Fig. 5.

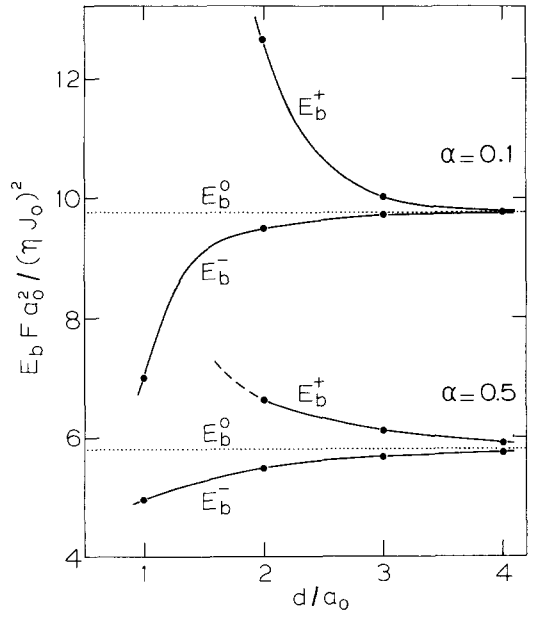

Fig. 5 The two barrier energies E_b^+ and E_b^- for two values of α and as a function of inter-soliton separation d/a_o. The solid lines are merely meant as an aid to the eye. The value, E_b^o, for a solitary kink is also shown by a dotted line for each of the two α values.

The relation to V(d) becomes clear if we write the difference between barrier heights as $\Delta \equiv (E_b^+ - E_b^-)/(E_b^+ + E_b^-)$. The functional dependence of Δ on near neighbour soliton seperation, d/a_o, (assuming only two solitons on the chain) is then found to be:

$$\Delta(d) = \Delta_o \exp[d/Da_o] \tag{16}$$

where D is the same as defined in Eq. 15 and plotted in Fig. 4. $\Delta(d)$ and V(d) therefore both fall off exponentially as $\exp(-d/|D|a_o)$. Δ_o increases monotonically from being zero at $\alpha = 1.0$ through $\Delta_o = 0.117$, 1.382 and 13.330 at $\alpha = 0.1$, 0.5 and 0.9 respectively.

In order to calculate the dynamics which might arise from Eq. 16, we assume the heuristic model described in section 3 where the soliton is taken to be a particle which must tunnel through a square potential barrier with height comparable to E_s (as shown in Fig. 3) and width $\sim(\tau_L/\tau_{ac}^o)a_o$. The two barriers E_b^+ and E_b^- then give rise to two transmission coefficients T^+ and T^- which of course are functions of the inter-soliton separation. We expand $T(E_b^o; d/a_o)$ about $E_b^o = E_b'$ and write

$$[T^+(d/a_o) - T^-(d/a_o)] = \frac{\partial T}{\partial E_b^o}\Big)_{E_b'} E_b^o \Delta \tag{17}$$

or

$$(T^- - T^+) \simeq 2A\Delta/(1 + A)^2 \tag{18}$$

where we have taken $E_b' \simeq E_b^o$ such that $A = 2(E_b^o)^2(E_s/E_{sk})(a_o\tau_L/c_o\hbar\tau_{ac}^o)^2$. It is then possible to calculate the time, t(n), it takes for two solitons which are initially only one lattice unit apart (as when, by thermal activation, a single spin is overturned on an otherwise ordered part of the chain) to become separated by n lattice units. t(n) is simply:

$$t(n) \simeq \frac{a_o}{c_o}\int_o^n [T^-(d/a_o) - T^+(d/a_o)]^{-1}\partial(d/a_o)$$

$$= \frac{a_o}{c_o}\frac{(1 + A)^2}{2A}\Delta_o|D|[\exp(+n/|D|) - 1] \tag{19}$$

For $k_BT \gg \gamma J_o$, the thermally averaged soliton kinetic energy can be written $E_{sk} \simeq (4/\pi^2)E_s$ and a reasonable estimate of the ratio τ_L/τ_{ac}^o is $\sim 10^{-2}$. It then follows that for $E_b^o \simeq 15$ K and $a_o/c_o \simeq 3 \times 10^{-11}$ s, t(n) is approximately given by $t(n) \simeq (6 \times 10^{-11}\text{ s})\Delta_o|D|[\exp(n/|D|) - 1]$. This suggests that for a large range of α, t(n ~ 10-100) can be much smaller than the ^{57}Fe Mössbauer measurement time of $t_m \sim 10^{-7}$ sec. The consequences of this on the Mössbauer spectrum of a quasi-onedimensional Ising-like magnet are discussed in the next section. Note that, if $\gamma = 0$ and only thermal "walking" is allowed then the above constant 6×10^{-11} s must be replaced by a thermal hopping time which is expected to be larger at these low temperatures but which is still fast compared to, for example, the measurement time of AC susceptibility.

5. Spin Autocorrelation Times from the Mössbauer Effect

It has recently been pointed out that the Mössbauer technique is a useful tool for the study of soliton dynamics in quasi-onedimensional magnets.[12] For a review of the subsequent experimental work see ref. 9. From that work it is clear that the spin dynamics cannot be understood from the free soliton gas behaviour since,

as de Groot et al.[9] have pointed out, this would yield an excess linebroadening which would go as the soliton density, that is, as $\exp(-2|J_o|/kT)$ instead of the observed temperature dependence of $\exp(-4|J_o|/kT)$. The observed $4J_o$ dependence has not been explained. De Groot et al. have noted[9], however, that a "soliton-lattice structure", which would arise if a strong enough soliton repulsive interaction existed, could explain the $4J_o$ dependence. This is consistent with our present picture where (i) a regular array-like structure of solitons does arise from V(d), (ii) the local jumping of a soliton about its "equilibrium" position is the order of $c_o T^{\pm}/a_o$ and is therefore too fast compared to $1/t_m$ to cause a linebroadening and (iii) the spin fluctuations which can cause the broadening arise from the rapid running apart (in a time t(n)) of a thermally created soliton/antisoliton pair. The frequency of fluctuations $(1/\tau_{ac})$ then goes as the frequency of pair creation events which, as in any activation process, goes as $\sim 4|J_o|$ - the creation energy for a soliton pair. Note that, to 1st order, the correction to E_s discussed in section 2 usually does not apply to the above discussion since J_o is most often estimated experimentally from the susceptibility. Such estimates of J_o are, in any case, not usually more reliable than ~10%.

6. Conclusion

This paper presents two components. One is to show that in any real Ising-like chain a SBLD must arise and has various non-negligible consequences. The other is to suggest, by an heuristic and largely phenomenological calculation, that the SBLD will quench out the dynamics and may at best allow a diffusive propagation of solitons.

Our main rigorous results can be stated as follows. A SBLD which, although it is of the same order as the root mean square ionic displacements, involves a large energy because of the strong dependence of superexchange on inter-spin separation. A correction to the soliton energy which can be larger than 10%. A series of effective spin Hamiltonians $\mathcal{H}_1, \mathcal{H}_2, \ldots$ which are exact to first order and represent successively better approximations within the zero lattice response time assumption. A positive soliton interaction energy, V(d), which falls off exponentially with soliton separation and whose range can be as large as the mean soliton separation at temperatures of interest. A perturbed soliton dynamics (Eq. 14) which is exact in the limit of low soliton densities and when $\tau_L = 0$ but which is not conceivably useful for most real systems since we expect $\tau_L/\tau_{ac}^0 > 0.001$. And, most importantly with regards to the dynamics, the existence of a barrier energy, E_b^0, when $\tau_L \neq 0$. Such a barrier must certainly affect the dynamics since it can be comparable to the soliton energy itself and is much larger than the transverse exchange terms which are usually assumed to cause the dynamics at low temperatures.

The existence of V(d) and E_b^0 make any free soliton gas approach to the dynamics questionable. We argue that, depending on its height and width, the barrier will lead to something between "self trapping" of solitons (for large barriers) to "self scattering" with finite scattering lengths (for smaller barriers). Also, the SBLD for two solitons gives rise to two different barrier heights for motion away from or towards the other soliton. We argue that this leads to a fast running apart, within a time t(n), of two solitons which are thermally created but that, otherwise, there is a strong tendency for the solitons to be regularly spaced apart. This picture is consistent with the temperature dependence of the spin autocorrelation times which are obtained by the Mössbauer effect.[9]

Finally, we would like to point out that such localized lattice defects of magnetic origine should also be present in two and three-dimensional magnets whenever strong uniaxial spin anisotropies exist and $\tau_{ac} \gg \tau_L$. It is well known, as can be shown by structural considerations[13], that many amorphous alloys and spin glasses have a uniaxial anisotropy term which is large compared to the exchange term in the Hamiltonian. It has also been shown recently[14,15], that such materials often have spin fluctuations with $\tau_{ac} \sim 10^{-9} - 10^{-10}$ sec. in a large temperature range below their magnetic ordering temperatures and that, therefore, $\tau_{ac} \gg \tau_L$. In such cases, the local defects might more appropriately be termed "spin-pair (or cluster-pair) bound lattice defects" and represent a mechanism, for thermoremanent magnetization (TRM) in frustrated magnetic systems, which is quite independent of domain wall considerations. For example, consider the frustrated system which consists of an ensemble of isolated Ising trimers with AF spin-spin coupling. If zero field cooled to saturation at time $t = 0$, then the TRM evolves as

$$\mathrm{TRM}(t) = \frac{N}{3} g\mu_B \exp[-2t/\tau] \tag{20}$$

where $1/\tau$ is the soliton jump rate. If the jumps are taken to be thermally activated over the barrier E_b then,

$$\frac{1}{\tau} = \nu_o \exp[-E_b/kT] \tag{21}$$

where, as before, $E_b \sim 6\pi^2 J_\delta^2/Ra_\delta^2$. Although they are an oversimplification, Eqs. 20 and 21 do qualitatively describe the TRM of real spin glasses. In addition, our spin-pair bound lattice defects offer a simple explanation for the observed "waiting-time" effect[16] which consists in τ having a dependence on the time the system is kept in the zero field cooled state before the field is turned off to measure the TRM. This arises naturally, since the local defects represent a diving force for structural rearrangement of the amorphous hard sphere structure. The system relaxes during the waiting time to a structure which, in the cooling field, is more energetically favourable. Such slight structural changes are quite conceivable since, for a given packing fraction, there are many amorphous structural configurations which, in the absence of spins, have equivalent energies. And of course the lower the temperature, the longer one must wait for the same change in τ, as is observed experimentally. This picture also predicts that there should be no such waiting time effect in a topologically frustrated spin-glass such as C_5NiFeF_6 - this, to our knowledge, has

not yet been tested experimentally.

Finally, Eqs. 20 and 21 may be useful in that they suggest an experiment, on a strongly anisotropic trimer compound, which would unambiguously show the existence of the barrier E_b that must arise from our SBLD.

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References

1. L.J. de Jongh and A.R. Miedema, Adv. Phys. 23, 1 (1974), review
2. e.g. Physics in One-Dimension, editors J. Bernasconi and T. Schneider, Springer Verlag, 1981.
3. J.W. Bray, L.V. Interrante, I.S. Jacobs, and J.C. Bonner, Extended Linear Chain Compounds, ed. J.C. Millder, Plenum, (1982) 353.
4. R.M. White and T.H. Geballe, Long Range Order in Solids, Academic Press, (1979).
5. H.A. Groenendijk, thesis, Kamerlingh Onnes Laboratorium, Leiden, (1981).
6. J.N. McElearney, G.E. Shankle, D.B. Losee, S. Merchant and R.L. Carlin, ACS Symposium series, no. 5, ACS, Washington D.C., (1974).
7. J.W. Stout and R.C. Chisholm, J. Chem. Phys, 36, 979 (1962).
8. D.G. Rancourt, C. Meschi, and S. Flandrois, Phys. Rev. B33, 347 (1986).
9. H.J.M. de Groot, L.J. de Jongh, M. ElMassalami, H.H.A. Smit, and R.C. Thiel, I.C.A.M.E. 1985, Hyp. Int. (review), and references therein.
10. J. Villain, Physica 79B, 1 (1975).
11. J.F. Curie, J.A. Krumhansl, A.R. Bishop, and S.E. Trullinger, Phys. Rev. B22, 477 (1980).
12. R.C. Thiel, H. de Graaf, and L.J. de Jongh, Phys. Rev. Letters 47, 1415 (1981).
13. R.W. Cohrane, R. Harris and M. Plischke, J. Non-Cryst. Sol. 15, 239 (1974).
14. D.G. Rancourt, S.R. Julian and J.M. Daniels, J. Magn. Magn. Matter. 51, 83 (1985).
15. D.G. Rancourt, unpublished.
16. R.V. Chamberlin, Phys. Rev. B30, 5393 (1984).