Solitary Magnetic Excitations in the Low-Carrier Density, One-Dimensional $S = \frac{1}{2}$ Antiferromagnet Yb_4As_3

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We report low-temperature measurements of the specific heat, thermal expansion, and thermal conductivity on the quasi-one-dimensional, effective $S = \frac{1}{2}$ Heisenberg antiferromagnet Yb_4As_3. Distinct field-induced anomalies were found in the above quantities which are well described by the classical sine-Gordon soliton solution for an easy-plane Heisenberg antiferromagnet. Our findings strongly suggest that Yb_4As_3 represents the first example of an antiferromagnetic $S = \frac{1}{2}$ spin-chain system where this type of nonlinear excitation could be identified. [S0031-9007(99)09295-9]

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Compounds with spin chains have attracted continuous attention due to their model character as many-body systems exhibiting both quantum behavior for small spins S and classical behavior for large spins. The majority of these systems are organic and inorganic compounds with chains of 3d ions. Recently, a new class of rare-earth pnictide compounds with the cubic anti-Th_3P_4 structure like Yb_4As_3 and its Sb- and P-doped derivatives have come into focus [1]. Here the one-dimensional (1D) character is not due to the anisotropic crystal structure but the result of a more complex physical process: At high temperatures Yb_4As_3 is a homogeneous intermediate valent (IV) metal with a valence ratio of $Yb^{2+}/Yb^{3+} = 3{:}1$ where the Yb ions are residing statistically on four families of chains along the space diagonals. At $T_{co} \approx 292$ K the IV state exhibits a charge-ordering instability such that far below T_{co} the Yb^{3+} ions now occupy only one family of parallel $\langle 111 \rangle$ chains while the Yb^{2+} ions with their full $4f^{14}$ shell and zero moment occupy the other three families of cubic space diagonals. At low temperatures Yb_4As_3 is semimetallic with an extremely low carrier concentration of 10^{-3} As-$4p$ holes per formular unit [2]. Nevertheless, it exhibits typical heavy-fermion (HF) behavior with a linear specific-heat coefficient $\gamma \approx 200$ mJ/K^2 mol which is not due to the usual Kondo-lattice mechanism but has been attributed to 1D spin excitations in the Yb^{3+} chains [3]. This has been confirmed quantitatively by inelastic neutron-scattering experiments which showed that the low-temperature magnetic properties of Yb_4As_3 can be described by antiferromagnetic (AF) $S = \frac{1}{2}$ Heisenberg spin chains well isolated from each other [4,5]. However, they do not form an ideal insulating 1D Heisenberg antiferromagnet since the small number of As-$4p$ holes cause an equal number of electrons ($4f^{14}$ states) in the $4f$-hole ($4f^{13}$) chains [2]. Despite its semimetallic behavior charge-ordered Yb_4As_3 seems to be a model system for investigating the physical properties of AF $S = \frac{1}{2}$ spin chains, notably their magnetic excitations.

For large S the excitations of a spin chain can be described by spatially extended spin-wave-like excitations and localized solitonlike excitations. The latter exist, e.g., in an easy-plane geometry with external field perpendicular to the chain axis. A large body of evidence for the presence of solitons in magnetic spin chains with classical spins has been accumulated; see, e.g., [6]. However, much less is known about their presence in true quantum-spin ($S = \frac{1}{2}$) chains. So far, evidence for solitons has been reported only for a ferromagnetic $S = \frac{1}{2}$ system, the organic Cu-chain compound CHAB [7], obtained from an excess contribution to the low-temperature specific heat. This additional term was found to be surprisingly well described by the classical sine-Gordon (SG) soliton model. It was argued that quantum fluctuations effectively restrict the spins to the easy plane which renders the SG model an appropriate approach [7].

In this Letter we report on solitary excitations in Yb_4As_3 being the first example of an AF $S = \frac{1}{2}$ chain system for which they could be identified. Evidence is taken from three independent experimental observations made in finite external magnetic field: (1) A soliton-induced peak anomaly in the specific heat on top of the spin-wave-like contribution, (2) a corresponding large thermal-expansion anomaly, whose field-dependent amplitude and position are well described by the SG-soliton model, and (3) a field and temperature dependence of the thermal conductivity consistent with a resonant phonon scattering by magnetic solitons. Moreover, the field dependence of the soliton energy as derived from these experiments agrees well with the theoretical predictions for SG solitons.

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Measurements of the specific heat, $C(T)$, were performed in a ^{3}He-^{4}He dilution refrigerator utilizing a thermal-relaxation technique [8]. The coefficient of thermal expansion, $\alpha(T) = \frac{1}{l}\left(\frac{\partial l}{\partial T}\right)_p$, was determined by means of an ultrahigh-resolution capacitive dilatometer in a ^{4}He bath cryostat for $1.6 \leq T \leq 300$ K and a ^{3}He-^{4}He dilution refrigerator for $0.05 \leq T \leq 4$ K [9]. Thermal-conductivity, $\kappa(T)$, measurements were conducted in a ^{3}He-^{4}He dilution refrigerator using a conventional steady-state technique [10]. Experiments were carried out on high-quality single crystals of Yb_4As_3 prepared as described in [1].

Because of the cubic symmetry of the high-temperature phase of Yb_4As_3 with four equivalent $\langle 111 \rangle$ axes, the trigonal distortion at the charge-ordering transition is usually accompanied by the formation of a multidomain structure. By means of weak uniaxial pressure of only 80 bars applied parallel to one of the space diagonals of the cubic unit cell prior to cooling through T_{co}, Ochiai *et al.* [1] succeeded in producing a monodomain low-temperature phase. Since in our thermal-expansion experiment uniaxial pressure ranging from about 1 to 10 bars can be applied to the sample along the measuring direction, we were able to study the low-temperature expansivity for different domain-structure configurations. Figure 1a shows the relative length changes, $\Delta L/L$, measured along a space diagonal of the cubic unit cell around the charge-ordering transition for uniaxial pressures $p_1 \approx 10$ bars and $p_2 \approx 1$ bar applied at $T = 300$ K. Although the accessible pressure range does not allow production of a monodomain structure, the substantial increase in the $\Delta L/L$ discontinuities at $T_{co} \approx 292$ K upon increasing the pressure from p_2 to p_1 indicates a considerable change in the domain configuration. A quantitative comparison of the observed $\Delta L/L$ discontinuities with the structural changes, i.e., the unit-cell length and angle, as determined from x-ray scattering [11] enabled us to determine the relative volume fraction x of the sample in which the contraction of the unit-cell diagonal (i.e., the formation of the spin chains) occurs parallel to the measuring direction. In the remaining volume fraction $1 - x$, spin chains are formed along the other three space diagonals, all of which are at an angle of about 70° with respect to the measuring direction. By varying the experimental conditions we were able to study five different domain configurations with $x = 0.28, 0.35, 0.45, 0.56$, and 0.86.

Figure 1b shows low-temperature data of the linear thermal-expansion coefficient measured at varying fields for a domain configuration $x = 0.35$. Magnetic fields were applied parallel to the measuring direction. While for $B = 0$ the $\alpha(T)$ data reveal a monotonic reduction with decreasing temperature, a pronounced maximum shows up in finite fields. Upon increasing the field up to 9.5 T, the highest field accessible in our experiment, the maximum continuously grows in size and is shifted to higher temperatures. A similar feature, though less pronounced, can also be seen in the specific heat of multidomain crystals, for $0.05 \leq T \leq 2$ K and $B \leq 4$ T (Fig. 2a) (present work) as well as for $1.5 \leq T \leq 5$ K and $B \geq 3$ T (Fig. 2b) taken from [12]. Besides this anomaly Figs. 2a and 2b show a distinct suppression of the low-T term in the specific heat, γT, already at moderate fields. This has been attributed to a field-induced opening of a gap in the spin-wave-like excitations [13,14]. At present it is unclear whether or not the huge upturn in $C(T)/T$ for $T \leq 0.2$ K indicates the onset of long-range AF order.

For all domain configurations studied, i.e., $0.28 \leq x \leq 0.86$, our thermal-expansion measurements exhibit a qualitatively similar behavior: a field-induced anomaly whose magnitude and position increase linearly with the field. As demonstrated in Fig. 3 this feature adds to a structureless $B = 0$ background expansivity which is

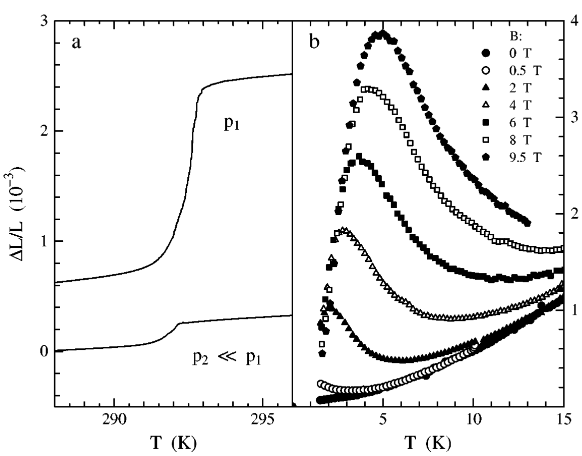

FIG. 1. (a) Relative length changes $\Delta L/L$ of Yb_4As_3 around the charge-ordering transition for uniaxial pressures $p_1 \approx 10$ bars and $p_2 \approx 1$ bar applied along the measuring direction. (b) Low-temperature thermal-expansion coefficient of Yb_4As_3 for $x = 0.35$ as defined in the text, at varying magnetic fields.

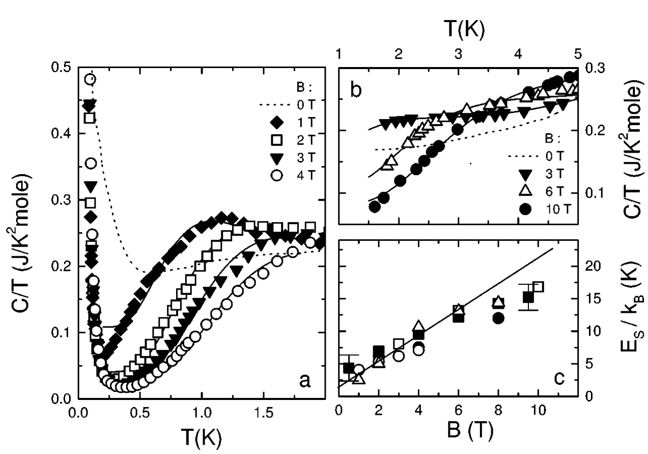

FIG. 2. Specific heat of Yb_4As_3 at varying magnetic fields from (a) the present work and (b) Ref. [12]. (c) Field dependence of the soliton energy as derived from fits shown in (a): (◯); (b) (□); and also Figs. 3a (■), 3b (●), and 4a–4d (△).

positive for $x = 0.35$ (Fig. 3a), but negative for $x = 0.86$ (Fig. 3b). From the analysis of the $B = 0$ data for the various x values investigated we infer a pronounced $\alpha(T)$ anisotropy of this (spin-wave and/or phonon) contribution yielding $\alpha_{\langle 111 \rangle} < 0$ and $\alpha_{\perp\langle 111 \rangle} > 0$. Figure 3 also demonstrates a substantial reduction in the size of the field-induced anomaly upon increasing x from 0.35 to 0.86. A detailed quantitative analysis of the data sets for the various domain configurations reveals a clear correlation between the magnitude of the anomaly, $\alpha_{\max}$, and x: With increasing x, $\alpha_{\max}$ becomes monotonically reduced and extrapolates to $\alpha_{\max} = 0$ for $x = 1$. Since the latter configuration corresponds to a monodomain structure with the field aligned parallel to the spin chains, the above correlation implies a highly anisotropic field response: The anomaly can be induced *only* for fields having a finite component perpendicular to the chains. It is clear that this orientational dependence cannot be explained by the effect of the magnetic field on the linear spin-wave-like excitations which are expected to become reduced for B both parallel and perpendicular to $\langle 111 \rangle$ [13]. Likewise, Schottky-type contributions due to isolated magnetic moments or impurities can be safely discarded as they would give rise to an anomaly whose size is nearly independent of the field.

In what follows we will argue that the above features originate in solitary excitations in the AF $S = \frac{1}{2}$ spin chains. Assuming an easy-plane (xy) exchange anisotropy the corresponding Hamiltonian in a field transverse to the chains (z direction) is given by

$$H = -J \sum_n (\vec{S}_n \vec{S}_{n+1} - \delta S_n^z S_{n+1}^z) - g_e \mu_B \sum_n S_n^x B \,, \tag{1}$$

where $J < 0$ (AF) and $\delta = (J - J_{zz})/J > 0$ for the easy-plane configuration. For classical spins and $B > 0$ it has been shown that Eq. (1) supports soliton solutions [6,15,16]. Their contribution to the free energy, f, adds to that of the linear spin-wave part, $f_{\rm sw}$, which exists already

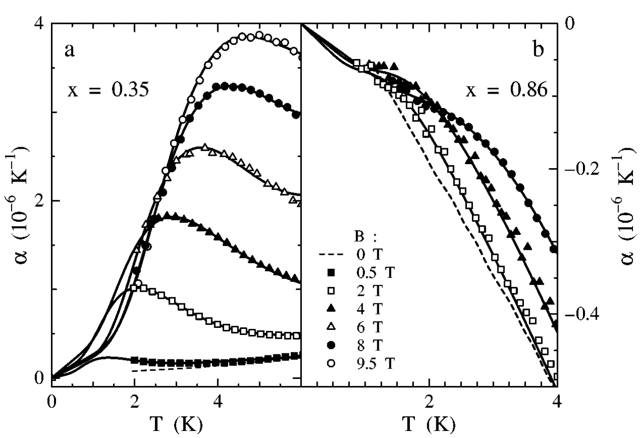

FIG. 3. Thermal expansion of Yb_4As_3 for two different domain configurations (defined in the text) $x = 0.35$ (a) and $x = 0.86$ (b). Solid lines are fits according to Eq. (4).

at zero field:

$$\begin{aligned} f &= f_{\rm sw} - \beta^{-1} n_s \,, \\ n_s(T) &= m(\tfrac{2}{\pi})^{1/2} (\beta E_s)^{1/2} \exp(-\beta E_s) \,, \end{aligned} \tag{2}$$

where $n_S(T)$ is the density of solitons per site, $\beta = 1/T$ ($k_B = 1$), $E_s = g_e \mu_B S B$ is the soliton energy in the AF case, and $m = g_e \mu_B B / 2|J|S$ is the soliton mass. The effective g factor g_e of the $S = \frac{1}{2}$ pseudospin is given by $g_e = \sqrt{7}\, g_{7/2} \sin 2\theta$ where $g_{7/2} = \frac{8}{7}$ and θ is an unknown crystal-electric-field (CEF) mixing angle. For Yb_4As_3 we assume that the Kramers doublet of the ground state appropriate for the present C_{3h} symmetry is given by $|\pm\rangle = \cos\theta |\pm \frac{7}{2}\rangle + \sin\theta |\mp \frac{5}{2}\rangle$ and not by one of the possible pure states $|\pm \frac{1}{2}\rangle$ or $|\pm \frac{3}{2}\rangle$. The latter would lead to a very anisotropic pseudospin Hamiltonian which is incompatible with neutron-scattering results [4,5]. These results, however, do not exclude a small easy-plane anisotropy as assumed in Eq. (1).

From Eqs. (1) and (2) it follows that solitons exist only for fields perpendicular to the spin chains in accordance with our experimental observations. Furthermore, the presence of solitons manifests itself in a humplike contribution $C_s(T)$ to the specific heat which adds to the linear spin-wave-like term $C_{\rm sw}(T) = \gamma T$ and the cubic lattice term cT^3. For $\beta E_s \ll 1$, the soliton density is low and the total specific heat is given by

$$C(T) = \gamma T + cT^3 + C_s(T)$$

with (3)

$$C_s(T) = n_s(T) \, [(\beta E_s)^2 - \beta E_s - \tfrac{1}{4}] \,.$$

Although the existence of solitary excitations for $S = \frac{1}{2}$ systems is not clear *a priori*, we apply Eq. (3) to the specific-heat results in Figs. 2a and 2b using E_s and g_e as fit parameters for the soliton contribution as well as $\gamma = \gamma(B)$ for the spin-wave-like part, cf. [14]. As can clearly be seen from these fits, Eq. (3) provides a good description of the finite-field data. The so-derived soliton energy E_s is plotted as a function of B in Fig. 2c. Finally, we note that the imperfections, i.e., the additional very few electrons in the hole chains ($4f^{13}$), should have only little effect on the soliton energy E_s and, consequently, C_s. This has been explicitly shown for spin chains with static imperfections [17]. An even weaker damping effect can be anticipated, however, when the "defects" are mobile as has been proposed for Yb_4As_3 [2].

Contrary to the specific heat it is not immediately obvious how magnetic solitons contribute to the linear thermal-expansion coefficient. Since here we are mainly interested in the temperature dependence of the soliton contribution, α_s, we refrain from including directional-dependent effects. Then, by definition, $\alpha_S = \frac{1}{3}(V_c c_B)^{-1} (\partial S_s / \partial \epsilon_V)$ where $S_s = (\beta E_s + \frac{1}{2}) n_s$ is the soliton entropy, $\epsilon_V = \Delta V / V$ the volume strain, c_B the bulk modulus, and V_c the volume per Yb atom. We find

$$\begin{aligned}\alpha_s &\approx \tfrac{1}{3}(V_c c_B)^{-1}\Gamma(C_s - S_s)\\ &= \tfrac{1}{3}[\Gamma/(V_c c_B)]n_s[(\beta E_s - 1)^2 - \tfrac{7}{4}],\end{aligned} \quad (4)$$

with a Grüneisen parameter $\Gamma = -(\frac{\partial E_s}{\partial \epsilon_V})\frac{1}{E_s}$ [18].

Equation (4) is used to fit the field-induced anomalies in $\alpha(T,B)$ for the various domain configurations (cf. solid lines in Figs. 3a and 3b for $x = 0.35$ and 0.86). The field dependence of E_s derived from these fits agrees very well with that obtained from the $C(T,B)$ data; see Fig. 2c. Note that the fitting procedure has been performed in the temperature range $\beta E_s \leq 0.3$ where the soliton density is sufficiently low.

Further evidence for the presence of magnetic solitons in Yb_4As_3 can be derived from the temperature and field dependences of the thermal conductivity $\kappa_B(T)$. In Figs. 4a–4d we display the normalized quantities $\kappa_B(T)/\kappa_0(T)$ vs T at various fields. The zero-field data for $T \leq 6$ K (not shown) can be well described by $\kappa_0(T) = a_1T + a_2T^2$ with $a_1 = 0.518$ mW/K^2 cm and $a_2 = 0.359$ mW/K^3 cm. We ascribe the linear term to a contribution of 1D spin-wave-like excitations and/or hole carriers to the thermal transport and the quadratic term to a contribution of the Debye phonons scattered off those spin-wave-like excitations/holes.

The most prominent feature of the curves shown in Fig. 4 is the occurrence of a flat minimum whose position shifts upwards with increasing field, in good agreement with the temperatures of the $C(T,B)$ and $\alpha(T,B)$ maxima. This strongly suggests that the $\kappa_B(T)$ structure is related to the maxima of the latter. Therefore, we attribute the minimum of $\kappa_B(T)/\kappa_0(T)$ to the scattering of the main heat carriers, i.e., the three-dimensional phonons, by solitons. This mechanism was previously proposed for the same purpose in the $S = \frac{5}{2}$ spin-chain systems TMMC and DMMC [19]. The solid curves in Figs. 4a–4d are fits using the expression for $\kappa_B(T)$ given in [19] which is based on a phenomenological relaxation time for a resonant phonon-soliton interaction. Here E_s and the relative strength of this scattering process were used as fit parameters. The experimental results are well described by these curves, especially for high fields. The field dependence of $E_s(B)$ derived in this way is in good agreement with that obtained from fitting the $C(T,B)$ and $\alpha(T,B)$ data, as shown in Fig. 2c. It demonstrates that for small fields $E_s(B)$ increases nearly linearly with B, in accordance with the SG soliton solutions [6]. The deviations at higher fields may originate in a crossover from xy solitons at small fields to yz solitons for large fields. At present it is not clear, whether $E_s(B)$ extrapolates to zero for $B \rightarrow 0$ or to a finite value (as suggested by the solid line in Fig. 2c). The latter would indicate a broken xy-symmetry state even in the absence of an external field.

In conclusion, experimental evidence is provided for field-induced magnetic excitations in the AF $S = \frac{1}{2}$ chains of Yb_4As_3 that add to the spin-wave-like excitations which exist at $B = 0$. These additional features show the characteristics of classical sine-Gordon solitons in an easy-plane 1D-Heisenberg antiferromagnet. We propose that Yb_4As_3 represents the first AF $S = \frac{1}{2}$ system which shows this type of nonlinear excitations.

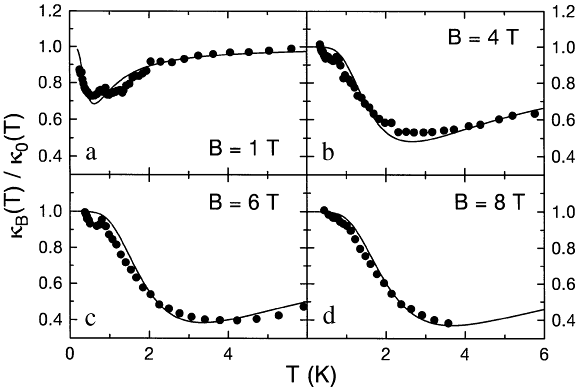

FIG. 4. Thermal conductivity of Yb_4As_3 at varying magnetic fields, $\kappa_B(T)$, normalized to that at $B = 0$, $\kappa_0(T)$. Solid lines are fits for a resonant phonon-soliton scattering following [19].

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