Specific Heat of $CsNiF_3$: Evidence for Spin Solitons

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The specific heat of the linear-chain magnet $CsNiF_3$ has been measured at temperatures between 4 and 18 K, in magnetic fields up to 8 kG (0.8 T). A rounded peak is observed in both the temperature and field dependence. The peak positions in the field dependence are in qualitative agreement with classical soliton theory and they are also consistent with neutron-scattering estimates of the soliton rest energy. Quantitative comparisons indicate the need for extensions of the theory.

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Systems with nonlinear integrable equations of motion have been studied intensely over the past decade. They are of interest for statistical mechanics because they can support new types of simple excitations which are nonlinear and of large amplitude yet just as elementary as the more usual small-amplitude linear modes. Much of the theoretical attention has focused on the sine-Gordon equation, whose excitations include breathers and solitons as well as linear waves.[1] Experimental realizations of such systems are rare because they must be effectively one dimensional and their microscopic interactions must obey conditions which are strictly not obtainable. However, Mikeska has shown[2] that an easy-plane linear-chain magnet such as $CsNiF_3$ can, under certain conditions, be approximated by the sine-Gordon Hamiltonian, and neutron scattering experiments by Kjems and Steiner[3] have been interpreted successfully in terms of soliton excitations. It is clear, however, that $CsNiF_3$ cannot be described completely by the classical sine-Gordon model and several calculations show that the actual situation is much more complex and that multiple linear excitations and quantum effects may also be important.[4,5] In an effort to improve the understanding of the thermodynamic properties of this interesting one-dimensional system, we have now measured the specific heat of $CsNiF_3$ in a transverse field.

Currie, Krumhansl, Bishop, and Trullinger[6] (CKBT) have developed the statistical mechanics of the classical sine-Gordon system and find a distinct nonnegligible soliton contribution to the free energy. A novel feature of their theory is a soliton-induced rounded peak in the *field dependence* of the specific heat. In the present work, we have specifically looked for this structure to see how well $CsNiF_3$ can be interpreted in terms of a simple sine-Gordon model.

In $CsNiF_3$, the Ni^{2+} ions form linear chains with interchain and intrachain Ni-Ni distances equal to 6.23 and 2.61 Å, respectively. The interactions between spins along the chains are dominant and above the Néel point, $T_N = 2.8$ K, the system behaves like an assembly of uncoupled one-dimensional ferromagnetic chains of spins. The spin Hamiltonian has been determined by Steiner, Villain, and Windsor[7]:

$$H = -J \sum_i \vec{S}_i \cdot \vec{S}_{i+1} + A \sum_i (S_i^z)^2 + g\mu_B \sum_i \vec{B} \cdot \vec{S}_i , \qquad (1)$$

where $J/k_B = 23.6$ K, $A/k_B = 9$ K, $g = 2.4$, $S = 1$, and z denotes the chain axis. Zero-field specific-heat,[8] susceptibility,[9] and neutron-scattering[7] measurements support the picture of an easy-plane system for $T \ll (AJ)^{1/2}/k_B \approx 15$ K. To look for soliton effects, we have therefore concentrated on the temperature region $4 < T < 8$ K, with additional measurements up to 18 K.

Specific-heat measurements were made by the conventional heat-pulse method, using a calorimeter described previously.[10] A number of minor modifications were made. The temperature was measured with a Lake Shore Cryotronics Carbon Glass thermometer (CGR-1-1000), which has a negligible magnetoresistance[11] in the range of the present experiments ($0 \leq B \leq 8$ kG). The thermometer resistance was measured with a computer-controlled ac Wheatstone bridge described elsewhere.[12] The sample consisted of six crystals roughly 3 cm long parallel to the chain axis and varying in thickness between 0.1 and 1 cm. The sample was previously used in neutron-scattering experiments[3] and had been grown by Crystal Tec (Grenoble). The crystals were wrapped in copper coil-foil and thermally connected with Apiezon-N grease.[12]

The largest experimental uncertainties arose from radiative heat losses and the resulting thermal gradients in the sample, and to compensate for these we used two electric heaters, one to provide a small constant background and the other to provide the heat pulses. This arrangement could introduce small systematic errors, but these should not be important for the field dependence of the specific heat at constant temperature, the quantity of primary interest in this study. For the field dependence we estimate a relative accuracy of <0.5% and for the overall accuracy 1% to 2% at the lowest and highest temperatures studied. The magnetic field, applied perpendicular to the chain axis, was provided by a large electromagnet and it was measured with a calibrated Hall-effect gaussmeter. We found that corrections to the microscopic field due to magnetic dipole interactions and demagnetizing effects were <5% and therefore we have plotted all results as a function of applied field.

The temperature dependence of the specific heat in fields of 0, 4, and 8 kG (0.8 T) is shown in Fig. 1.[13] From these results it is clear that there is a nontrivial *field dependence* of the specific heat, which varies markedly with temperature. To study this dependence we made additional measurements at selected temperatures in various fields and we show the results in Fig. 2. The striking feature of these curves is the marked peak which is observed as the field is varied.

One obvious possible explanation of the peaks is that they might be Schottky anomalies due to impurities, but this can be rejected since the effects would require relatively large concentrations (~5%) with large magnetic moments ($g\mu_B S \sim 30\mu_B$). Moreover, the temperature dependence of the peak field is not linear (see below), as it would have to be for an impurity with a dominant Zeeman splitting. On the other hand, large effective moments, such as these, immediately suggest the possibility of solitons, which in a system like $CsNiF_3$ may be pictured as 2π twists in the spin orientation along the length of the chain.

To compare the experimental results with the theory of CKBT we use Mikeska's relation between the microscopic spin Hamiltonian, Eq. (1), and the classical sine-Gordon Hamiltonian. This gives for the soliton rest energy

$$E_s^{(0)} = 8(Jg\mu_B BS^3)^{1/2} \tag{2}$$

and for the soliton width

$$d = [JS/g\mu_B B]^{1/2} a, \tag{3}$$

where a is the intrachain Ni-Ni distance. These values may be substituted in the expression for the specific heat (per unit length) derived by CKBT:

$$C_H = \frac{k_B}{a} + k_B\left[\left(\frac{E_s^{(0)}}{k_B T} - \frac{1}{2}\right)^2 - \frac{1}{2}\right] n_s^{\text{tot}}, \tag{4}$$

where n_s^{tot} is the total density of solitons and

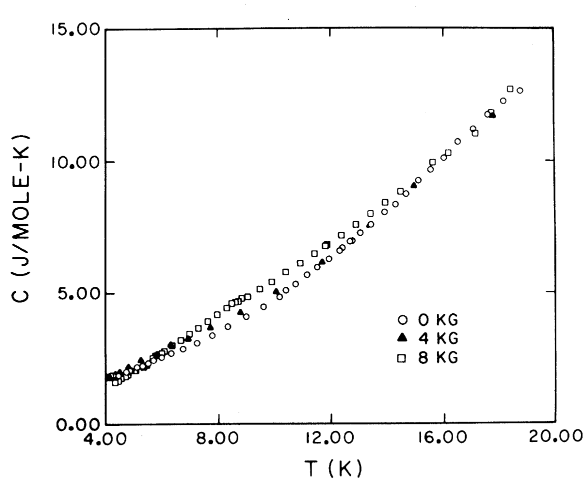

FIG. 1. Specific heat of $CsNiF_3$ as a function of temperature in applied magnetic fields of 0, 4, and 8 kG.

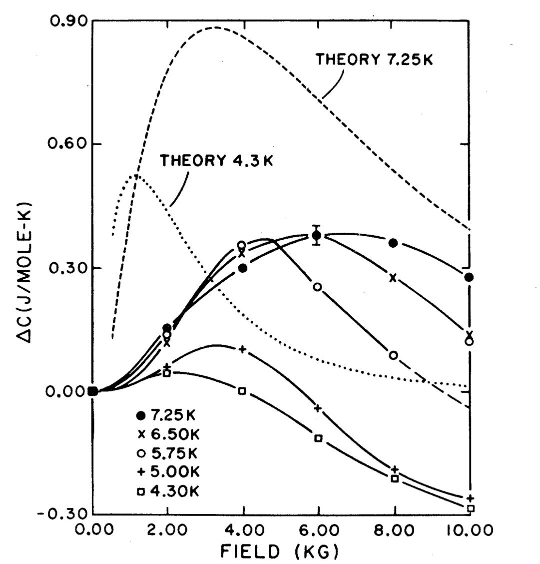

FIG. 2. Specific-heat difference $\Delta C = C_H - C_{H=0}$ as a function of applied magnetic field at temperatures of 4.3, 5.0, 5.75, 6.5, and 7.25 K. The solid lines are drawn as guides to the eye. The dashed lines are calculated from the theory of CKBT [Eq. (4)] in the range of validity.

antisolitons (assumed to be small):

$$n_s^{\mathrm{tot}} = \left(\frac{8}{\pi}\right)^{1/2} \frac{1}{d} \left(\frac{E_s^{(0)}}{k_B T}\right)^{1/2} \exp\left(\frac{-E_s^{(0)}}{k_B T}\right). \quad (5)$$

The first term in Eq. (4) is the analog of the Dulong-Petit specific heat for spin waves, a feature of the classical approximation which must clearly be modified for a real quantum system. To reduce the effect of this term we can examine the difference $\Delta C = C_H - C_{H=0}$. The results for two different temperatures are plotted in Fig. 2.

It can be seen that the quantitative agreement is not very good, which perhaps is not surprising in view of the various approximations implicit in the comparisons. On the other hand, the theory clearly predicts the temperature-dependent peaks which are observed in the experiments and, in particular, it predicts quite well the temperature variation of the fields, B_p, at which the peaks occur. By maximizing Eq. (4) with respect to $E_s^{(0)}$ we find for the specific-heat peak

$$(E_s^{(0)}/k_B T)_{\mathrm{peak}} = 3.9, \quad (6)$$

which together with Eq. (2) gives

$$B_p = 62.4T^2. \quad (7)$$

This is shown as the dashed line in Fig. 3. Since there are no adjustable constants in this comparison, the agreement with the experimental points is quite reasonable. The agreement is improved even further if, in place of the soliton creation energy in Eq. (2), we use a renormalized value of $0.7E_s^{(0)}$. This gives the dotted line shown in Fig. 3. Renormalization of $E_s^{(0)}$ also improves the agreement for the temperature dependence of the peak heights, although the discrepancy in the absolute values remains large. This is probably due to the classical approximation.

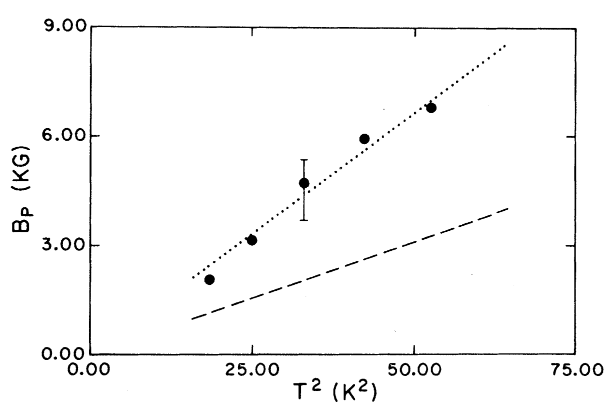

FIG. 3. Positions of the peaks for the five isotherms in Fig. 2. The dashed line is the theoretically predicted variation, Eq. (7), without any adjustment of the constants. The dotted line shows the theoretical variation with the renormalized soliton energy $0.7E_s^{(0)}$. The error bar is weighted to show the possible demagnetization correction.

It is interesting to note that a similar change in the value of $E_s^{(0)}$ was found by Kjems and Steiner[3] when they compared the integrated neutron scattering intensity of the central peak with soliton theory. For a field of 5 kG they found a fit for $E_s^{(0)}/k_B = 27$ K, compared to the theoretical value of 34 K, corresponding to a reduction factor 0.8. A similar reduction was also found by Goto and Yamaguchi[14] who recently measured the nuclear-spin-lattice relaxation time and were able to fit their data with a process involving solitons with $E_s^{(0)}/k_B = 23$ K at 5 kG.

The mapping of the spin Hamiltonian to the sine-Gordon Hamiltonian is clearly questionable. The most serious objection concerns the assumption of classical behavior. The argument has been made[15] that the necessary approximations are mutually exclusive, in the sense that, since $S = 1$ for $CsNiF_3$, the assumption of a classical equipartition is only valid at high temperatures where the out-of-plane tipping, assumed to be negligible in the sine-Gordon model, is large. On the other hand, a proper quantum-mechanical treatment of this problem is very difficult because the system possesses no spontaneous magnetization and free spin-wave theory becomes seriously deficient in the field and temperature region of most interest. If one simply uses free spin-wave theory with the dispersion relation given by Reiter,[4] one finds a monotonically decreasing contribution to the specific heat.[12] It would be of interest to see if spin-wave interaction effects give any indication of the onset of a peak in $C_H(H)$, as found in our experiments, or whether the results can only be explained in terms of solitons.

In any case, it seems clear that the present experimental results call for further developments of the theory.

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Note added.—Specific-heat experiments qualitatively similar to ours have recently been reported by Borsa[16] for the linear chain antiferromagnet TMMC [$(CH_3)_4NMnCl_3$]. To look for soliton contributions, Borsa has analyzed the *temperature dependence* of the specific heat in magnetic fields parallel and perpendicular to the anisotropy axis. Good agreement with the simple sine-Gordon theory was found, but no attempt was made to verify the characteristic field dependence predicted by the model.

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Dynamical Group SO(6) and Coexistence: Superconductivity and Charge-Density Waves

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SO(6) is identified as the dynamical group of a mean-field Hamiltonian for the coexistence of superconductivity and charge-density waves. The energy spectrum is given in terms of the Casimir invariants. The explicit rotation of the Hamiltonian to canonical Cartan (diagonal) form is found, and expressions for the superconductivity and charge-density-wave order parameters are given in terms of the rotation angles. The descent from the SO(6) to the decoupled BCS-SO(3) and charge-density-wave–U(2) algebras is exhibited.

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Superconductivity[1] can be understood as a spontaneously broken gauge-group [U(1)] symmetry,[2] or by use of a pseudospin SU(2) group with tensor order parameter.[3] A charge-density wave[4] in an isotropic electron Fermi sea can be viewed as spontaneously breaking an SO(3) invariance. Other cooperative many-body effects such as spin-density waves, ferromagnetism, and ferroelectricity also can be investigated as broken symmetries.[5] Complementing the idea of broken symmetry, dynamical groups, or spectrum-generating algebras,[6] have been used, e.g., to investigate properties and phases of superfluid Helium.[7] The recent reports of coexisting cooperative effects such as superconductivity and charge-density waves (SC-CDW),[8] or superconductivity and magnetism,[9] raise the question whether the coexistence or competition of such many-body effects can be profitably investigated in a dynamical group framework. We believe that

