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Spin-Peierls transition in NaV_2O_5 in high magnetic fields

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We investigate the magnetic field dependence of the spin-Peierls transition in NaV_2O_5 in the field range 16T-30T. The transition temperature exhibits a very weak variation with the field, suggesting a novel mechanism for the formation of the spin-Peierls state. We argue that a charge ordering transition accompanied by singlet formation is consistent with our observations.

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The Peierls instability takes place in one-dimensional systems and can give rise to complex and fascinating behavior. In itinerant electronic systems the instability is driven by the coupling of electrons to the phonons of the lattice [1]. Any coupling at $T = 0$ leads to the formation of the Peierls state which is characterized by charge ordering (gap in the electronic spectrum) and a finite lattice distortion. Similar phenomena occur in purely insulating spin systems, where the spin-phonon coupling is responsible for the formation of a singlet ground state with neighboring spins pairwise bound into singlets [2]. The spin-Peierls ground state shows a characteristic gap in the excitation spectrum and has been observed in a variety of organic compounds, such as $(TTF)[CuS_4C_4(CF_3)_4]$ [2]. At high temperatures these materials behave as non-interacting Heisenberg chains, while below the transition temperature, T_c, the magnetic exchange acquires an alternating component. In 1993 the first inorganic spin-Peierls compound $CuGeO_3$ was discovered [3] with $T_c \approx 14K$. This material, like its organic predecessors, shows a characteristic 1d Heisenberg (Bonner-Fisher)-like magnetization at high T with a sharp drop at T_c, indicating a non-magnetic ground state. Very recently, a second inorganic compound, NaV_2O_5 was shown to behave as a spin-Peierls material with $T_c \approx 34$K [4]. The properties of NaV_2O_5 however have proven to be quite controversial, thus stimulating the research reported in this letter.

Magnetic susceptibility measurements of NaV_2O_5 indicate a transition to a non-magnetic phase at T_c [4,5]. This can be understood within the framework of a spin-phonon coupling driven transition on a Heisenberg chain [2]. The antiferromagnetic exchange, J, was estimated to be J≈560K. The low-temperature structure which is assumed in this interpretation of the data, is that of magnetic chains formed by the spin 1/2 V^{4+} ions along the crystalline b-axis, separated by spinless V^{5+} chains. This scenario implies a lattice distortion in one direction only. However, recent experiments have shown that the above picture is not satisfactory. X-ray diffraction measurements indicated that the system should be viewed as a quarter-filled ladder made of $V^{4.5+}$ chains [6,7], meaning that a spin of 1/2 is not attached to a single V ion, but rather to a rung of the ladder, i.e. a V-O-V orbital. Subsequent NMR [8] analysis revealed that below T_c, two inequivalent types of V sites - V^{4+} and V^{5+} appear, suggesting that charge ordering occurs in the spin-Peierls phase. Charge disproportionation leaves room for period doubling in more that one crystallographic direction, consistent with additional X-ray [9,10] and NMR [11] studies. These works suggest that lattice distortion takes place in the (a,b) plane (where b is the direction along the chains and a is perpendicular to the chains). A number of theoretical studies [12–17] have addressed the possibility of charge ordering in 1/4 filled systems, where both electron-lattice and electron-electron interactions are included. The most probable scenario at present seems to be the "zig-zag" order proposed in Ref. [12] where the charge density (i.e. the sites $V^{4.5\pm\delta}$ with deviation δ from the average valence) is distributed in a zig-zag fashion along the ladder direction. As emphasized in Ref. [12] the Coulomb repulsion in combination with the electron-lattice interaction can drive such a transition, while the formation of a spin singlet ground state "follows" the charge order. Charge modulation is consistent with the analysis of the observed magnetic excitation spectra [18], Raman spectra [19], as well as the anomalies in the thermal conductivity [20] and the dielectric constant [21] at T_c.

The present work attempts to gain further insight into the nature of the spin-Peierls transition in NaV_2O_5 by addressing the magnetic field dependence of the transition temperature in very high fields. Previous studies in fields up to 5.5T [5] have found behavior consistent with the theoretical predictions and similar to the previously known spin-Peierls compounds [2]. However, subsequent measurements in higher fields, up to 14T [22] and 16T [23], have found much weaker field dependence. These experiments were based on a determination of T_c from

the changes in the elastic constants [22] and the specific heat [23], unlike the measurement in Ref. [5] which determined T_c from the drop in the magnetization.

In this work we have measured the magnetization of two NaV_2O_5 single crystals in magnetic fields from 16T to 30 T. The crystals were grown by high temperature solution growth from a vanadate mixture flux. The masses of the samples investigated were 1.9 and 3.1 mg respectively and they had irregular parallelepiped shapes with smooth, faceted faces. The single crystals were characterized with an Enraf-Nonius CAD4 single crystal diffractometer using Mo-radiation. The results of the structure refinement were the same as reported earlier in Ref. [7]. Magnetization was measured using a standard metal foil cantilever beam magnetometer. The "T" shaped flexible cantilever beam was made from a 7.62 μm thick heat treated MP35N alloy. The dimensions of the "T" were approximately 8 mm on a side. The gap between the "T" and the parallel fixed reference electrode was approximately 800 μm. The sample was mounted using a small amount of vacuum grease. In the presence of a DC magnetic field the interaction of the magnetic moment of the sample with the field results in a force and/or torque, deflecting the beam and changing the capacitance between electrodes. A capacitance bridge was used to monitor the changes in force (magnetization) for temperature sweeps in fixed field. Since MP35N is magnetic (typically 13.5 μemu/g at 78 K), the same bare cantilever was measured under the identical conditions (sweep direction and sweep rate) as the cantilever+sample combination to provide a background reference. The temperature dependence of the cantilever capacitance was compensated for in the same way. A room temperature measurement of the cantilever's sensitivity showed that a force of 3 nN could be resolved.

Cantilever displacement can arise from either a torque or a force on a sample with a magnetic moment. When the sample is at field center, where the field gradient is zero, then torque ($\propto \mathbf{m} \times \mathbf{B}$) will dominate. Strictly speaking, if the sample is isotropic and there are no shape factors, then there is no torque on the cantilever for fields applied along the direction of displacement (perpendicular to the sample). On the other hand, when the sample is raised (or lowered) away from field center, the force term ($F = m\ dB/dz \propto \chi\ B\ dB/dz$) will usually dominate, although torques can still be present. Figure 1 shows temperature sweeps taken for the 1.9 mg sample at the three indicated fields in the legend. The cantilever was located in a position where the field gradient was maximum. The maximum field at this position (24T) is 80% of the field center maximum (30T). The change in capacitance, ΔC, which is proportional to the change in magnetization, is calculated at each field by subtracting the background trace (cantilever alone) from the sample trace (sample+cantilever). This quantity is divided by B^2 and plotted as the ordinate in Fig. 1. As seen from the figure, the data scale reasonably well for the three different fields, confirming the B^2 dependence expected from both torque and force contributions. To accentuate the small shift in the transition temperature, we plot in the inset the derivative of $\Delta C/B^2$ with respect to the temperature. From the position of the peaks we can determine the field-dependent transition temperature.

To measure T_c at the maximum field of 30T, the sample was placed at field center (sensitive to the torque only) and the data collected and analyzed as described above. A similar scaling with B^2 was observed. Figure 2 shows the derivative of ΔC with respect to temperature at field center. Plotted in this way, the shift in T_c can be clearly seen. Data similar to those plotted in Figs. 1 and 2 were obtained for a second sample with mass 3.1 mg, and for reversed fields. In all cases the shifts in T_c were equal to or less than the shifts shown in Fig. 2. In Fig. 2 (inset) we also show the results of magnetization measurements at low fields using a commercial SQUID magnetometer (MPMS7). The singlet formation at T_c is clearly observable, but no shift of T_c can be observed within measurement accuracy in fields up to 5T, in agreement with previous work [4].

In Fig. 3 we present our high field data for the variation of T_c in terms of $\Delta T_c/T_c(0) = T_c(H)/T_c(0) - 1$ and the square of the scaled magnetic field $h = g\mu_B H/2kT_c(0)$ [24]. This scaling is expected in spin-Peierls systems, and for small fields $h \ll 1$, the relative variation of T_c should be quadratic [2]:

$$\Delta T_c/T_c(0) = -\alpha h^2. \quad (1)$$

The data of Fig. 2 follows this dependence quite well, and we estimate $\alpha_{exp} \approx 0.072(8)$. The value $T_c(0)$ was not measured directly but was estimated from an extrapolation to zero field of the quadratic dependence of T_c vs. H to be $T_c(0) = 34.2K$. This value is close to published values and to the $T_c(0)$ measured by us using SQUID magnetometer measurements of the magnetization of a 40mg polycrystalline sample. The combination of our high field data and the lower field data of previous measurements gives the variation of T_c over a large range of magnetic field and shows a very weak dependence. In contrast, the "conventional" inorganic spin-Peierls compound $CuGeO_3$ exhibits a much stronger field dependence with $\alpha = 0.39$ [25], in good agreement with the theory. The theoretical values of α_{SP} predicted for the spin-Peierls transition are $\alpha_{SP} = 0.44$ or 0.36, depending on the way interaction effects are taken into account [2]. The first, larger number corresponds to the Hartree approximation for the interactions between the Jordan-Wigner fermions, representing the localized spins [26]. The value 0.36 is obtained by exact treatment of the correlation effects [27], which is possible in the Luttinger liquid framework in one dimension [28]. In both cases the characteristic scaling $H/T_c(0)$ which appears in

Eq.(1) is due to the commensurate nature of the dimerized phase. For large fields, corresponding to a reduction of T_c by a factor of $T_c/T_c(0) = 0.77$, a transition into an incommensurate phase is expected to take place [27]. Such a transition is less sensitive to magnetic field and has been observed in a variety of spin-Peierls materials [2,25]. In NaV_2O_5 however, a transition into such a modulated phase does not seem to take place, since even in the highest field (30T), $T_c(30T)/T_c(0) = 0.97$, which is very far from the expected incommensurate boundary. Notice that even in a field as high as $30T$ the scaled ratio $h = 0.59$ is quite small due to the large $T_c(0)$.

We now discuss the possible sources for the difference between the measured value α_{exp} and the theoretically predicted one $\alpha_{SP} = 0.36 \approx 5\alpha_{exp}$ for spin-Peierls systems. In addition to this discrepancy, any theory of NaV_2O_5 should also be able to explain the large value of the ratio $2\Delta/T_c(0) \approx 6$ ($\Delta \approx 100K$ [8] being the spin gap), where a mean-field value of 3.52 might be expected.

As discussed in the introduction, a transition into a charge ordered state in a 1/4-filled system is consistent with a number of recent experiments. Although it is not clear whether the charge density wave (CDW) precedes or forms simultaneously with the magnetically dimerized spin-Peierls state, it seems certain that the physics of charge ordering must be taken into account. Recent numerical work has shown [16,17] that CDW and spin-Peierls order can co-exist in quasi one-dimensional 1/4-filled electronic systems. If we assume that the CDW formation is the driving force behind the opening of a spin gap, as argued in Ref. [12], then the "charge" part of the transition will be mainly responsible for the $T_c(H)$ dependence. In a system of non-interacting electrons, undergoing a Peierls transition into a (commensurate) CDW state, the decrease of T_c for small magnetic field (coupled to the electron spin via a Zeeman term) is also described by Eq.(1), but with $\alpha_{CDW} = 0.21$ [29].

Two effects, orbital coupling and electron-electron interactions, could further modify this result. Orbital effects are known to be present when nesting is imperfect, and generally compete with the Pauli terms, producing a flatter dependence of T_c on H, i.e. a further reduction of α_{CDW} [30]. However spin-orbit interactions lead to anisotropic variation of T_c with respect to the magnetic field direction. In NaV_2O_5 this variation has been found to be extremely weak [4,5,22,23], which is also confirmed in this work, and consequently the orbital effects can be ruled out as a source of the weak $T_c(H)$ dependence. On the other hand, electron-electron interaction effects do not reflect anisotropies and are important in the formation and stabilization of a CDW state [12,16]. In general, the stability of the CDW depends on the strength of the electron-phonon coupling (which drives the transition) and on the on-site and nearest-neighbor Coulomb correlations [16].

To demonstrate this latter point concerning strong correlation effects, we consider the simplified model of a Hubbard chain with an on-site repulsion U. We treat the phonons adiabatically, as in Ref. [29], but take into account the electron-electron interaction following Ref. [28], i.e. calculate the polarization bubble exactly for the Luttinger liquid. In this case it is known that $T_c(H = 0)$ increases with respect to its value at $U = 0$ [31]. For finite magnetic field we find, at $U \sim 2t$ (where t is the bandwidth), that the coefficient α drops to $\alpha_{CDW} \approx 0.15$, i.e. below the non-interaction value of 0.21. This is not surprising and in fact is quite similar to the difference between the mean-field and the exact treatment in the spin-Peierls case ($\alpha_{SP} = 0.44, 0.36$, respectively). The essence of the effect is in the different type of divergence in the polarization bubble with and without interactions. While in the free case the polarization diverges logarithmically at small frequencies, in a Luttinger liquid the stronger, power law dependence sets in [28], and the Peierls instability is effectively enhanced. Thus the interaction effects, being naturally more important for the CDW formation (compared to the spin-Peierls case), can produce a weaker $T_c(H)$ dependence. A more realistic calculation based on a Hamiltonian appropriate for NaV_2O_5 would be very desirable.

The orbital and interaction effects discussed above are, strictly speaking, valid only for an isolated chain. It was assumed that inter-chain interactions are sufficiently strong to suppress the fluctuation effects, typically important in one-dimensional systems [32]. The fluctuations are known to reduce $T_c(0)$ below the mean-field value and cause a specific heat jump at the transition Δc_P several times the mean-field one. The large observed ratio $\Delta/T_c(0)$ (twice the mean-field), in combination with a Δc_P about ten times the mean-field value [33] suggest that fluctuations indeed could be important in NaV_2O_5. At the same time one should have in mind that, due to the specific structure of NaV_2O_5, transverse interchain interactions are expected to play a crucial role in the stabilization of the ordered phase, in particular the formation of the spin gap and doubling of the period in the (a,b) plane [9,11]. The vanadium displacements are nearly absent along the ladder direction (b-axis), and largest perpendicular to the ladder direction both along the a- and c-axis [10]. Thus it is not clear whether fluctuation effects have to be necessarily invoked to explain the large $\Delta/T_c(0)$ ratio in this material as is traditionally done, or whether the large $\Delta/T_c(0)$ ratio is intimately related to the anomalously weak variation of T_c with field reported in this work.

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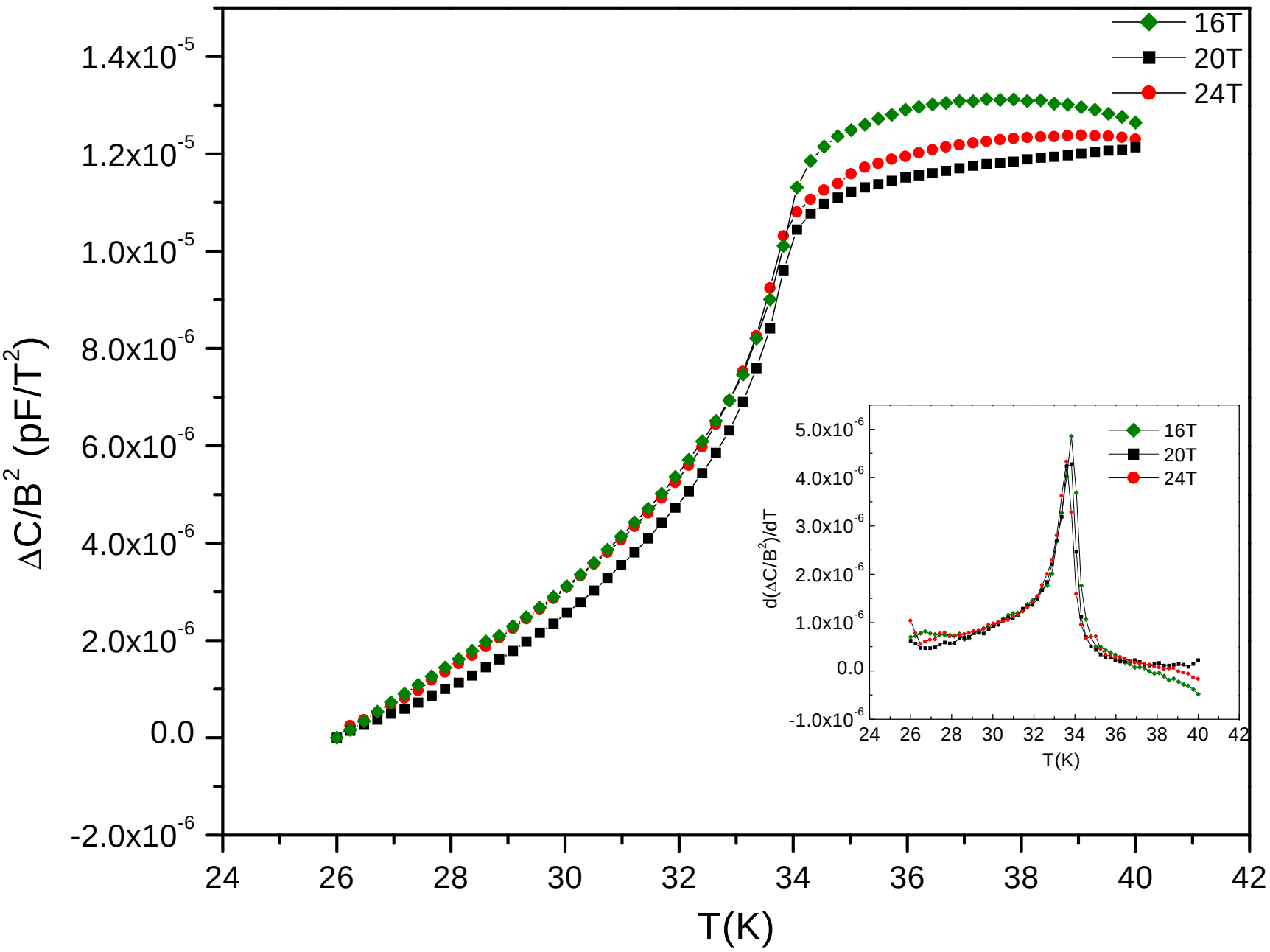
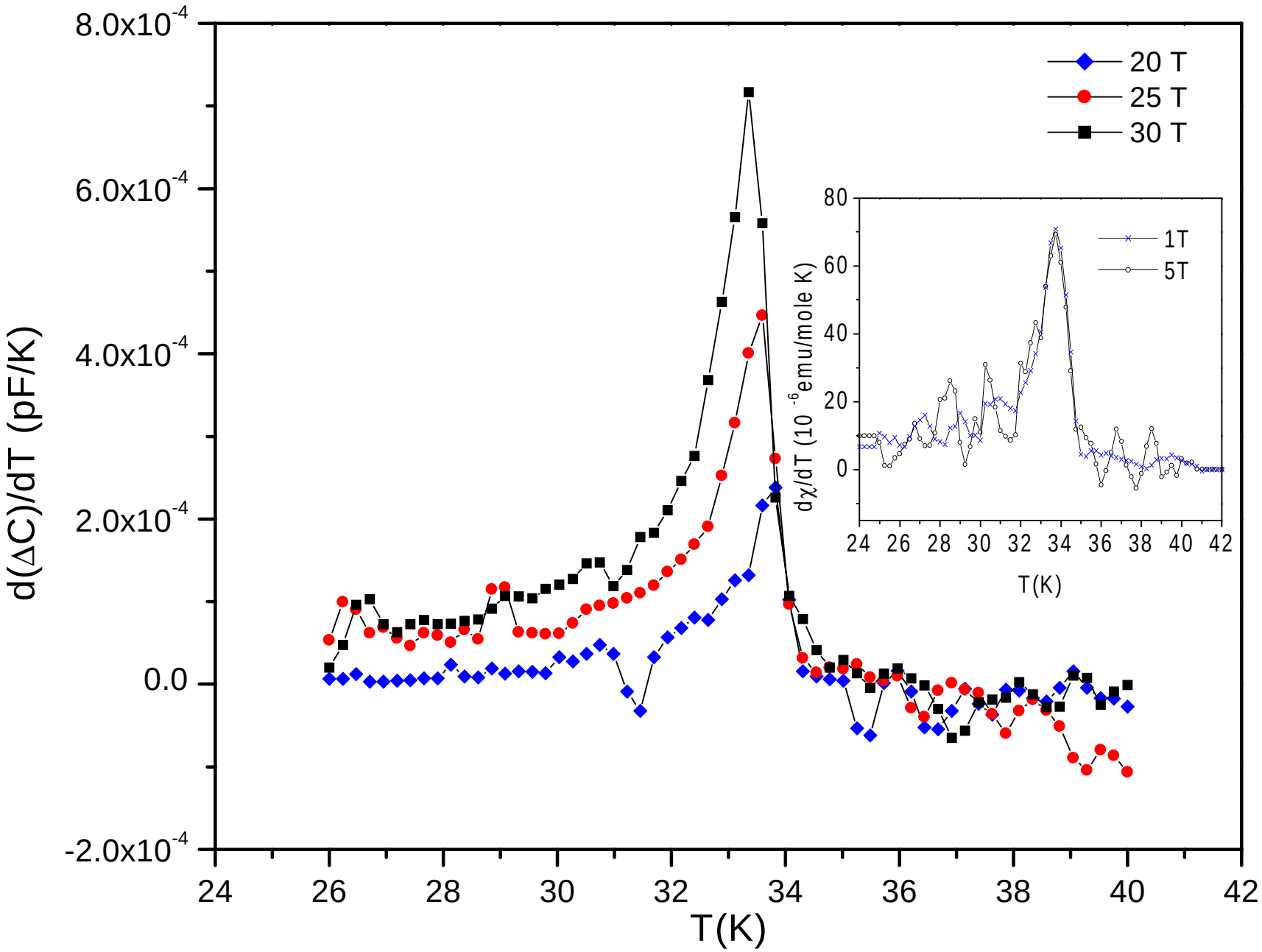
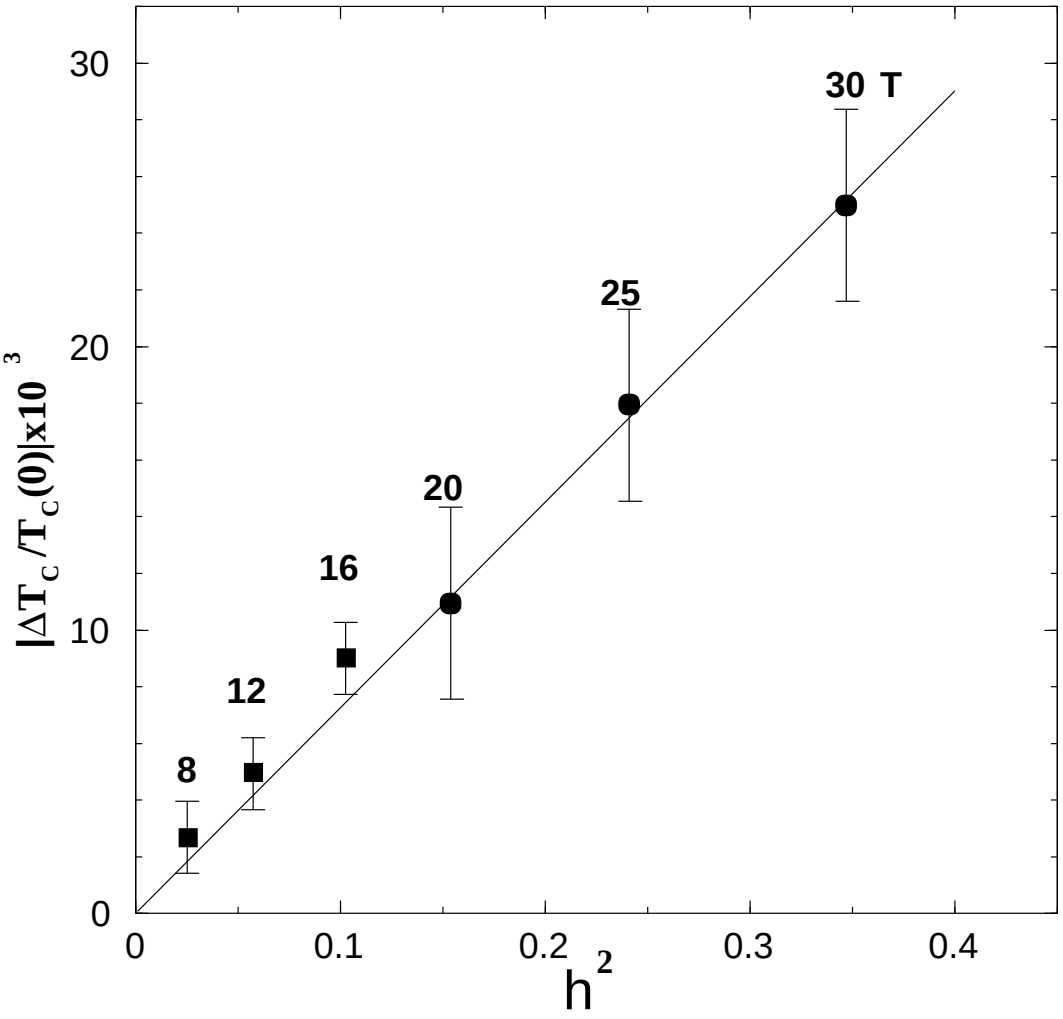
FIG. 1. Change in capacitance measured with a cantilever beam magnetometer off field center for a NaV_2O_5 single crystal in B = 16T, 20T, and 24T. ΔC is proportional to the magnetization of the sample and has been normalized by the square of the magnetic field. The inset shows the derivative of the scaled, background subtracted data with respect to temperature. T_c is determined from the position of the peaks.

FIG. 2. Derivative of the unscaled capacitance readings (proportional to magnetization) with respect to temperature for the sample shown in Fig. 1 located at field center. Inset shows low field SQUID magnetization measurements.

FIG. 3. Relative variation of T_c as a function of the scaled magnetic field $h = g\mu_B H/2kT_c(0)$ (see text). The circles are our data (numbers represent the values of the field in Tesla), and the squares are data from Ref. [23], based on measurements of the specific heat jump at the transition.


16T
20T
24T
1.4x10-5
1.2x10-5
1.0x10-5
8.0x10-6
6.0x10-6
4.0x10-6
2.0x10-6
0.0
-2.0x10-6
ΔC/B2 (pF/T2)
24
26
28
30
32
34
36
38
40
42
T(K)
d(ΔC/B2)/dT
5.0x10-6
4.0x10-6
3.0x10-6
2.0x10-6
1.0x10-6
0.0
-1.0x10-6
T(K)


8.0x10-4
6.0x10-4
4.0x10-4
2.0x10-4
0.0
-2.0x10-4
d(ΔC)/dT (pF/K)
24
26
28
30
32
34
36
38
40
42
T(K)
20 T
25 T
30 T
80
60
40
20
0
dχ/dT (10 -6emu/mole K)
1T
5T
24
26
28
30
32
34
36
38
40
42
T(K)


30
20
10
0
0
0.1
0.2
0.3
0.4
h^2
$|\Delta T_c/T_c(0)|x10^3$
30 T
25
20
16
12
8