

## LiVGe<sub>2</sub>O<sub>6</sub>, an Anomalous Quasi-1D, $S = 1$ System, as Revealed by NMR

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(Received 5 November 1999)

We report the results of <sup>7</sup>Li nuclear magnetic resonance (NMR) studies of LiVGe<sub>2</sub>O<sub>6</sub>, a quasi-one-dimensional spin  $S = 1$  model system, at low temperatures. Our data, including NMR spectra and the temperature dependence of the spin-lattice relaxation rate  $T_1^{-1}$ , indicate that a first-order phase transition occurs at  $T_c \approx 23$  K. The NMR response of LiVGe<sub>2</sub>O<sub>6</sub> below  $T_c$  suggests that the ordered phase is antiferromagnetic and has unusual features. Possible reasons for this unexpected behavior are discussed.

PACS numbers: 75.30.Et, 75.30.Kz, 76.60.-k

In recent years there has been considerable progress in the understanding of the physics of low-dimensional spin systems with an antiferromagnetic interaction between nearest-neighbor spins. For a quasi-one-dimensional (1D) Heisenberg chain with integer spins, it is expected that the ground state is isolated from the excited states by an energy gap, the Haldane gap  $\Delta_H$  [1]. This has indeed been observed in many systems [2]. For the case of monoclinic AgVP<sub>2</sub>S<sub>6</sub>, where the V<sup>3+</sup> ions with  $S = 1$  form 1D chains along the  $a$  axis,  $\Delta_H$  is equal to 26 meV [3,4]. A continuous spectrum of excitations is expected, however, if the spins are half integers. In this case the system may lower its energy via a spin-Peierls second-order phase transition, again resulting in the opening of a gap, as observed for CuGeO<sub>3</sub> [5]. Here, the localized spins of the Cu<sup>2+</sup> ions form 1D Heisenberg chains. A spin-Peierls transition is found at  $T_{SP} = 14$  K; the resulting gap is of the order of 2 meV.

Last year a new member, LiVGe<sub>2</sub>O<sub>6</sub>, was added to the growing list of 1D magnets by Millet and co-workers [6]. From the temperature dependence of the magnetic susceptibility  $\chi(T)$  it was inferred that this  $S = 1$  system does not behave as expected. A discontinuous change in  $d\chi/dT$  at approximately 22 K was interpreted as a phase transition of the spin-Peierls type, and quantum chemistry calculations indicated [6,7] that this unexpected behavior might be due to the presence of a substantial biquadratic exchange interaction between the V<sup>3+</sup> spins forming the infinite 1D chains. From these existing experimental data, a more detailed analysis of the phase transition and of the nature of the low-temperature phase was not possible.

In this Letter, we present a detailed <sup>7</sup>Li nuclear magnetic resonance (NMR) study invoking NMR spectra and spin-lattice relaxation rates. We also present new data on the magnetic susceptibility of LiVGe<sub>2</sub>O<sub>6</sub>. We confirm that this system ought to be regarded as an  $S = 1$  quasi-one-dimensional Heisenberg spin system, but the character of our NMR data is substantially different from that of previously investigated 1D,  $S = 1$  model systems [8,9]. Our results reveal very unusual low-temperature properties, including a phase transition at 23 K which is not, as previ-

ously suggested, a second-order spin-Peierls transition to a dimerized phase, but rather a first-order phase transition to a magnetically ordered phase, rather unusual for a 1D,  $S = 1$  system.

LiVGe<sub>2</sub>O<sub>6</sub> crystallizes with a monoclinic structure, space group  $P2_1/c$  [6]. The structure consists of isolated chains of VO<sub>6</sub> octahedra, joined at the edges. These chains are linked together and kept apart by double chains of distorted GeO<sub>4</sub> tetrahedra, keeping the interchain coupling small. The Li atoms are sixfold coordinated and are located inside distorted oxygen octahedra as in the case of LiVSi<sub>2</sub>O<sub>6</sub> [10]. Our powder sample of 0.13 g was prepared as described by Millet *et al.* [6].

An important issue concerning the basic physics of LiVGe<sub>2</sub>O<sub>6</sub> is to verify that the V ions are in a trivalent oxidation state and, hence,  $S = 1$ . This claim is supported by our results for the electrical resistivity  $\rho$  which, measured on a sample prepared from pressed powder of LiVGe<sub>2</sub>O<sub>6</sub>, was found to be larger than  $2 \times 10^7 \Omega \text{ cm}$  at room temperature, indicating that LiVGe<sub>2</sub>O<sub>6</sub> is indeed an insulator. Taking into account the known oxidation states of O<sup>2-</sup>, Li<sup>1+</sup>, and Ge<sup>4+</sup>, the valence of V must be +3. Further support for this simple, yet important, clarification is provided by the results of the magnetic susceptibility  $\chi(T)$  (Fig. 1). Our results are similar to those of Ref. [6], albeit with a smaller paramagnetic contribution at low temperatures. The high-temperature part of  $\chi(T)$  can reasonably be fitted only by assuming a trivalent configuration of V. The phase transition, suggested by a kink in  $\chi(T)$  at  $T_c = 23$  K (see inset of Fig. 1), is much more evident by plotting  $d\chi/dT$  versus  $T$ , as demonstrated in Fig. 2. The well-defined maximum is only weakly, if at all, shifted by an external magnetic field. The upturn of  $\chi(T)$  at the lowest temperatures is associated with a small amount of paramagnetic impurities (a few parts per million of  $S = 3/2$ ) and will not be considered further.

In Fig. 3 we show three examples of the <sup>7</sup>Li NMR (nuclear spin  $I = 3/2$ ) spectra measured at a fixed frequency of 70.64 MHz and at temperatures of 15.8, 22.0, and 24 K. For these measurements, a two-pulse spin-echo sequence was employed and the data represent the integrated

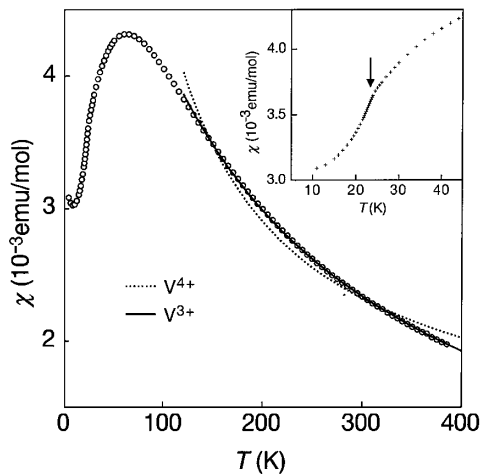


FIG. 1. Magnetic susceptibility  $\chi$  as a function of temperature for  $\text{LiVGe}_2\text{O}_6$ . The solid line represents the best fit to the data assuming a Curie-Weiss law for  $\text{V}^{3+}$  and the dotted line the corresponding fit for  $\text{V}^{4+}$ . The inset displays  $\chi(T)$  in the region near the phase transition. The arrow indicates  $T_c$ .

spin-echo intensity. An example of the NMR spectrum for randomly oriented powder of  $\text{LiVGe}_1\text{O}_6$  at 39 K is shown in the inset of Fig. 3. These data were acquired at a fixed applied field of 4.28 T. This spectrum reveals the absence of quadrupolar wings, and its shape indicates an anisotropic shift. The maximum intensity and the prominent shoulder correspond to grains where the Li sites have their quadrupolar axis orthogonal and parallel to the applied field, respectively. Below 30 K, the shape of the signal develops into a well-defined and symmetrical line with a width (HWHM) of approximately 35 G (see the NMR spectrum at 24 K), which we take as evidence for the alignment of the grains of our powdered sample in the presence of applied magnetic fields of the order of a few tesla at low temperatures. Another scenario where the observed changes in the NMR spectrum simply reflect changes in the

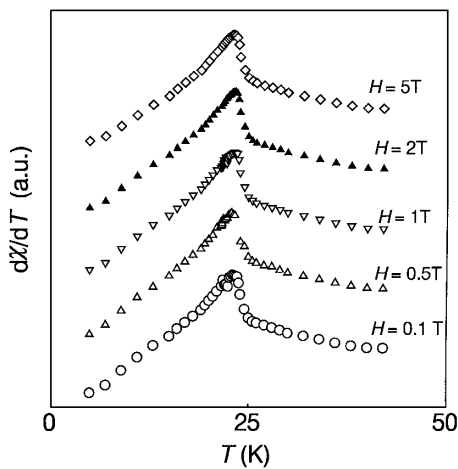


FIG. 2.  $d\chi/dT$  as a function of the temperature for different applied fields. The clear maximum in  $d\chi/dT(T)$  signals the transition temperature  $T_c$ .

susceptibility and/or hyperfine field coupling, yielding an isotropic line shift below 30 K, cannot really be ruled out.

From the NMR line shift  $K$  data (not shown here), we estimate the hyperfine field at the Li nuclei to be of the order of 0.65 kG per  $\mu_B$  of V magnetic moment. This value seems consistent with a direct dipolar coupling between the V magnetic moments and the Li nuclei, and we conclude that the  $^7\text{Li}$  NMR response is dominated by the magnetism of the V ions. The temperature evolution of the NMR spectrum above 23 K shows no indication of a gap in the spectrum of excitations of the spin system.

At temperatures below  $T_c$ , the NMR spectrum changes dramatically and its width increases very rapidly with decreasing  $T$ . At temperatures not far below  $T_c$  (see the spectrum for 22 K in Fig. 3), we note the coexistence of two phases. The narrow line, related with the high-temperature paramagnetic phase, appears on top of a broad background representing the low-temperature phase. At even lower temperatures, only the signal due to the low-temperature phase is measured. This behavior is compatible with a first-order phase transition at  $T_c$  but not with a second-order phase transition such as a standard spin-Peierls transition or a simple magnetic ordering phenomenon. In particular, one also may argue that the coexistence of the two phases is due to a spread of transition temperatures within the sample material [11]. In the latter case, it would seem quite unlikely to observe the distinct peak in the temperature variation of  $T_1^{-1}$ , displayed in Fig. 4.

On the basis of the presently available experimental data, nothing definitive can be said concerning the nature of the low-temperature phase. The broad NMR spectrum may either represent the powder spectrum of a distorted antiferromagnetically ordered phase or, in the case that the powder grains are indeed aligned at low temperature, a modulated magnetic structure is also conceivable. Further

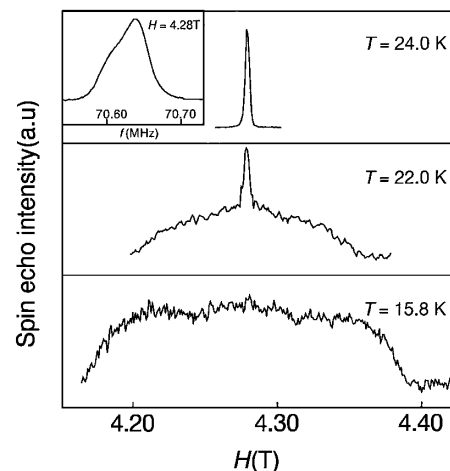


FIG. 3.  $^7\text{Li}$  NMR spectra of  $\text{LiVGe}_2\text{O}_6$  measured at a fixed frequency of 70.64 MHz for three different temperatures. Below 23 K the  $^7\text{Li}$  NMR spectrum becomes very broad. The inset of the top figure shows the  $^7\text{Li}$  NMR spectrum measured at a fixed applied field of 4.28 T and 39 K.

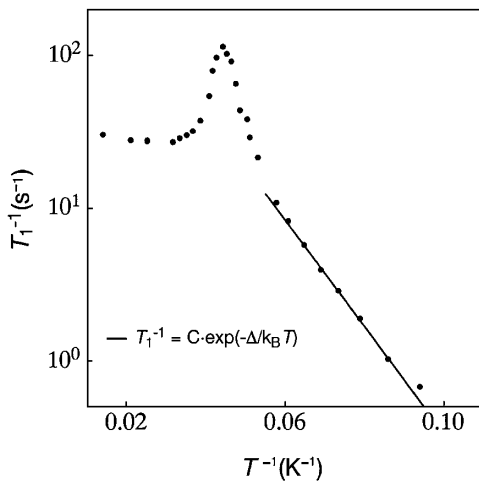


FIG. 4. Temperature dependence of the  ${}^7\text{Li}$  spin-lattice relaxation rate in  $\text{LiVGe}_2\text{O}_6$ . Above 28 K,  $T_1^{-1}$  is only weakly  $T$  dependent, but, at low temperatures,  $T_1^{-1}$  decreases exponentially with decreasing temperatures.

experiments on single crystals will have to answer this question.

In order to probe the low-energy spin excitations in  $\text{LiVGe}_2\text{O}_6$  at low temperatures, we measured the spin-lattice relaxation rate  $T_1^{-1}$  by monitoring the recovery of the  ${}^7\text{Li}$  nuclear magnetization after the application of a long comb of rf pulses above and below  $T_c$ . Both above and below  $T_c$ , a single exponential recovery was observed, the first as expected and the latter in spite of the fact that the NMR spectrum is very broad and, hence, cannot fully be irradiated. Various changes of irradiation conditions yielded, within the usual error limits, identical results for  $T_1^{-1}$ , however.

In Fig. 4 we display the temperature dependence of the spin-lattice relaxation rate. A prominent peak in  $T_1^{-1}(T)$  reflects the phase transition at  $T_c$ . Above  $T_c$ ,  $T_1^{-1}$  varies only weakly with temperature, a further evidence for the absence of a significant energy gap in the spin excitation spectrum. For an insulator, the relaxation rate is very high and is most likely caused by fluctuations of the localized V-ion moments. Below  $T_c$ ,  $T_1^{-1}$  decreases very rapidly, signaling the opening of a gap in the spectrum of spin excitations. From the relaxation data between 17 and 10 K, we calculate a gap  $\Delta/k_B = 83$  K, obviously a feature of the low-temperature phase.

The magnitude of this gap is very surprising because it is substantially larger than the estimated exchange interaction  $J$  above  $T_c$ . For standard  $S = 1$  chain systems, the maximum of the susceptibility at 60 K would imply that, for the high-temperature phase,  $J/k_B \approx 45$  K. This suggests that some kind of modification, presumably involving the crystal structure, takes place at the transition, changing the local quantum chemistry and enhancing the exchange interaction. In case of a standard transition to magnetic order with  $J/k_B \approx 45$  K, and recalling that the anisotropy

$D/k_B$  is smaller than 20 K [6], the spin-orbit gap would be of the order of  $(2DJ/k_B^2)^{1/2}$ , i.e., at most 40 K.

The unexpected properties of  $\text{LiVGe}_2\text{O}_6$ , not typical for quasi-1D,  $S = 1$  systems, are very likely related to the three  $t_{2g}$  orbitals accommodating the two  $3d$  electrons of  $\text{V}^{3+}$ , as for  $\text{V}_2\text{O}_3$  [12]. The orbital  $d_{xz}$ , which is separated from the other two by a second-order crystal-field splitting  $\Delta_{\text{CF}}$  due to the trigonal distortion [6], may modify the usual description in terms of a Heisenberg model in two ways.

If  $\Delta_{\text{CF}}$  significantly exceeds the hopping integrals between neighboring sites, the low-energy physics can still be described by a pure spin Hamiltonian. However, the third orbital gives rise to a ferromagnetic exchange channel. The Heisenberg coupling may thus considerably be reduced and other exchange couplings, such as a biquadratic interaction  $J''$  between nearest neighbors or a bilinear exchange  $J_2$  between next-nearest neighbors may become significant. In that case, the high-temperature magnetic properties of the system would be described by the Hamiltonian:

$$H = \sum_i [J' \mathbf{S}_i \cdot \mathbf{S}_{i+1} + J'' (\mathbf{S}_i \cdot \mathbf{S}_{i+1})^2 + J_2 \mathbf{S}_i \cdot \mathbf{S}_{i+2}]. \quad (1)$$

While the properties of the Hamiltonian of Eq. (1) with a frustrating next-nearest neighbor coupling have not been investigated yet, it is likely that the frustration due to  $J_2$  will lead to incommensurate fluctuations, as in the case  $J'' = 0$  [13], or the biquadratic interaction  $J''$  will tend to close the Haldane gap, as in the case of  $J_2 = 0$  [14,15]. With  $J''/J' \approx 1$  and  $J_2/J' > 0.35$ , we conjecture that this Hamiltonian leads to a very small gap and to incommensurate fluctuations. This might provoke a spin-Peierls-type instability to an incommensurate phase and explain part of our results. Whether the transition can be of first order remains to be seen.

If  $\Delta_{\text{CF}}$  adopts similar values as the hopping integrals, it will no longer be possible to describe the low energy properties of the system with a pure spin Hamiltonian, and the orbital degrees of freedom have to be included explicitly. The canonical example is  $\text{V}_2\text{O}_3$ , and the properties reported here are reminiscent of the phase transition observed in insulating  $\text{V}_{2-x}\text{Cr}_x\text{O}_3$  between the high-temperature paramagnetic and the low-temperature antiferromagnetic phases [12]. In particular, this transition, due to an orbital ordering of the  $t_{2g}$  orbitals, is strongly first order and there is a dramatic change of exchange integrals at the transition. If an orbital ordering takes place in  $\text{LiVGe}_2\text{O}_6$ , it will quite likely also provoke a first-order transition. The nature of the low-temperature phase will depend on the effective spin Hamiltonian, hence, on the orbital ordering. The possibilities range from a dimerized ground state involving a simple antiferro-orbital ordering with alternating exchange couplings, to more exotic phases including incommensurate phases if the orbital ordering is helical. In that case, the large gap would just be the

spin-orbit gap, the exchange integrals being much larger than in the high-temperature phase because of the orbital ordering. Further investigations testing the orbital occupancy on the  $V^{3+}$  ions are clearly needed to check this possibility. Unfortunately, the shape of the low-temperature NMR spectra does not allow for firm conclusions with regard to orbital ordering.

In summary, our results for  $LiVGe_2O_6$  strongly suggest that this material is a very unusual 1D,  $S = 1$  Heisenberg system. In particular, the Haldane phase is either absent or strongly suppressed, and a first-order phase transition into a magnetically ordered phase occurs at 23 K. On the theoretical front, we have argued that this behavior is probably related to the second-order splitting of the  $t_{2g}$  orbitals, which could either induce significant biquadratic and next-nearest neighbor exchange interactions along the chain, or provide an orbital degree of freedom which is involved in the ordering. Further investigations of the low-temperature phase and of the theoretical models are obviously needed to answer the questions that have been raised by our observations.

F.M. acknowledges useful discussions with D. Poilblanc, E. Sorensen, F.-C. Zhang, and Y. Fagot-Revurat. This work was financially supported by the Schweizerische Nationalfonds zur Förderung der Wissenschaftlichen Forschung.

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