Electron-spin-resonance study of Na1-xLixV2O5

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Electron-spin-resonance study of $Na_{1-x}Li_xV_2O_5$

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We measured *X*-band electron-spin resonance of single-crystalline sodium vanadate doped with lithium $Na_{1-x}Li_xV_2O_5$ for $0 \leqslant x \leqslant 1.3\%$. The phase transition into a dimerized phase that is observed at 34 K in the undoped compound, was found to be strongly suppressed upon doping with lithium. The spin susceptibility was analyzed to determine the transition temperature and the energy gap with respect to the lithium content. The transition temperature T_{SP} is suppressed following a square dependence of the lithium concentration while the energy gap is found to decrease linearly. At high temperatures ($T > T_{SP}$) the susceptibility remains nearly independent of doping.

I. INTRODUCTION

Since 1996, when Isobe and Ueda[1] reported the observation of an exponential decrease of the susceptibility in NaV_2O_5 below 34 K, this material has been the subject of intense investigation. The transition was at first considered to be a spin-Peierls transition similar to that observed in $CuGeO_3$.[2] This assumption was based on an early determination of the structure by Carpy and Galy,[3] who proposed alternating chains of V^{4+} (spin-1/2) and nonmagnetic V^{5+}. This picture was able to explain the physical properties above the transition, such as the susceptibility that closely follows that of a one-dimensional spin-1/2 Heisenberg antiferromagnet as calculated by Bonner and Fisher[4] or more recently by Eggert, Affleck, and Takahashi.[5] It could not explain most of the experimental findings connected with the transition itself nor the low-temperature state: the ratio of the energy gap $\Delta(0)$ to the transition temperature was found to be much larger than the expected mean-field value of $2\Delta/k_BT_{SP}=3.53$;[6] the entropy of the jump in the specific heat is also much higher than expected;[7] and in thermal-expansion measurements two transitions close to each other were observed[8]. In the low-temperature phase satellite reflections were reported in x-ray measurements corresponding to a doubling of the unit cell in the *a* and *b* directions and a quadrupling in the *c* direction.[6,9]

However, recent structural investigations[10–12] have shown that instead of the originally proposed noncentrosymmetric space group $P2_1mn$, the structure of NaV_2O_5 at room temperature has to be described by the centrosymmetric space group $Pmmn$. In this structure only one kind of vanadium site exists with an average vanadium valence of $V^{+4.5}$. NaV_2O_5 can therefore be regarded as a quarter-filled ladder system with one electron per rung. This excludes the possibility of a simple spin-Peierls transition in this material. The occurrence of a charge-ordering transition followed by a dimerization is discussed.[13–15] Different types of low-temperature structures were proposed. Whereas theoretical models mainly discuss an inline or a zigzag ordering, a recent determination of the low-temperature structure suggests a separation into modulated and unmodulated vanadium ladders.[16]

Electron spin resonance (ESR) measurements of NaV_2O_5 were carried out in 1986 by Ogawa, Onoda, and Nagasawa.[17] Due to a large Curie contribution in the susceptibility they did not observe the characteristic decrease below 34 K. The discovery of the transition by Isobe and Ueda stimulated many other ESR studies in this compound.[18–21] In this article we present ESR results of single-crystalline $Na_{1-x}Li_xV_2O_5$ for $x=0$, 0.15, 0.3, 0.5, 0.7, 0.9, and 1.3 % in the temperature range 4.2–700 K. We discuss the ESR linewidth and the signal intensity that is directly proportional to the spin susceptibility. Assuming a mean-field-like dependence of the energy gap $\Delta(T)$ that opens below the transition, we determine the value of the energy gap at zero temperature and the transition temperature as a function of the lithium concentration.

II. SAMPLE PREPARATION AND EXPERIMENT

The samples were small single crystals, prepared from a $NaVO_3$ flux.[22] In the first step a mixture of Na_2CO_3 and V_2O_5 is heated up to 550 °C in air to form $NaVO_3$. In a second step the $NaVO_3$ is mixed with VO_2 in the ratio of 8:1 and then heated up to 800 °C in an evacuated quartz tube and cooled down at a rate of 1 K/h. The excess $NaVO_3$ was dissolved in water. The doped samples were produced by substituting in the first step Na_2CO_3 with Li_2CO_3. However, due to a low distribution coefficient during the flux growth process, the real amount of Li in the sample is much lower. The real cation composition was determined in two doped samples using inductive coupled plasma for the V content and atomic absorption spectroscopy for the Li and Na content (see Table I). The result shows that the real Li content is a factor of 7.5 lower than the nominal one. For the other samples the Li concentration was scaled accordingly, as given in Table I. All the samples were investigated using x-ray powder diffraction. Only at high Li content, a small decrease of the *c* lattice parameter was observed.

The ESR measurements were performed using a Bruker

TABLE I. Composition and lattice parameter of the investigated samples.

Nominal Li content (%)	Resulting Li content (%)	a (Å)	b (Å)	c (Å)	V (Å ^{3})
0	0	11.312(3)	3.6106(9)	4.8031(10)	196.17(12)
1	0.15 (scaled)	11.307(3)	3.6095(8)	4.8014(7)	195.96(9)
2.4	0.3 (scaled)	11.312(1)	3.6112(11)	4.8012(3)	196.13(7)
3.7	0.5 (scaled)	11.316(2)	3.6123(7)	4.8033(4)	196.35(7)
5	0.7 (measured)	11.314(3)	3.6103(9)	4.8018(7)	196.13(11)
7	0.9 (scaled)	11.312(2)	3.6096(11)	4.7974(7)	195.88(10)
10	1.3 (measured)	11.313(5)	3.6104(19)	4.7927(15)	195.75(22)

Elexsys 500 CW spectrometer at X-band frequency (9.48 GHz). In the temperature range 4.2–300 K a continuous flow He cryostat (Oxford Instruments) and between 300 and 700 K a nitrogen cryostat (Bruker) was used. The samples were orientated in a way that the applied external field was always perpendicular to the crystallographic b axis and could be rotated about this axis. All measurements were made at the orientation with the narrowest resonance line, i.e., the external field H being parallel to the a axis.

III. ELECTRON-SPIN RESONANCE

NaV_2O_5 shows one single Lorentzian-shaped resonance line with an anisotropic g value between 1.976 (H parallel to the a axis) and 1.936 (H parallel to the c axis).[18] At high temperatures the linewidth of this resonance decreases monotonically with decreasing temperature and is independent from lithium doping as shown in the inset of Fig. 1 for the undoped and the 0.7% lithium doped sample. Below 34 K the linewidth increases again. This increase was found to be rather strongly suppressed by doping (Fig. 1). While the linewidth in the undoped sample increases by a factor of 4 from 34 K down to 15 K, for 1.3% lithium content the increase is only about 40%. This clearly indicates that the increase of the linewidth below 34 K is directly connected to the transition, which is suppressed upon lithium doping as will be shown below. In the whole temperature range the ESR signal is strongly exchange narrowed and no hyperfine structure due to the ^{51}V spin ($I=7/2$) is observed.[23] We therefore propose that the broadening of the linewidth below the transition appears because the exchange narrowing becomes less effective, probably due to charge localization.

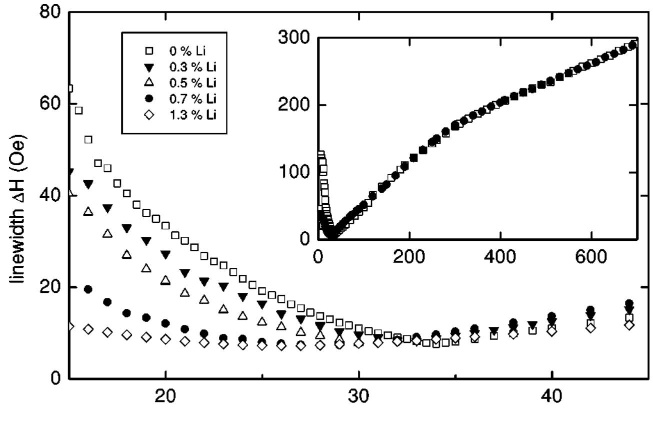

FIG. 1. ESR linewidth of $Na_{1-x}Li_xV_2O_5$ below 50 K for different lithium concentrations; the inset shows the linewidth for $x=0$ (open squares) and 0.7% lithium (filled circles).

A similar overall temperature dependence of the linewidth is observed in $CuGeO_3$.[24] Yamada and co-workers qualitatively explained the high-temperature behavior in both $CuGeO_3$ and NaV_2O_5 by identifying the anisotropic Dzyaloshinsky-Moriya exchange interaction H_{DM} as the dominating interaction responsible for the line broadening.[21,24] The Dzyaloshinsky-Moriya interaction is given by $\Sigma_i d_{ii+1}(\mathbf{S}_i \times \mathbf{S}_{i+1})$ for neighboring spins $\mathbf{S}$, where d_{ii+1} can be estimated as $d_{ii+1} \simeq (\Delta g/g)|J|$.[25] We found that both the g value and exchange coupling constant J [that can be determined from the spin susceptibility, see Fig. 2(a)] remain nearly unaffected by doping. This is consistent with the fact that no concentration dependence of the linewidth was detected at high temperatures.

We also determined the spin susceptibility of $Na_{1-x}Li_xV_2O_5$ from the intensity of the ESR signal. Since it is difficult to determine the absolute values of the susceptibility by ESR, only relative values are given, the curves being scaled to one at 300 K. An estimation of the absolute intensity is consistent with one vanadium per formular unit contributing to the signal. As mentioned before, the spin susceptibility above the transition is nearly insensitive to lithium doping. In Fig. 2(a) the undoped sample is compared with the 0.7% lithium doped sample. For $T>200$ K both curves

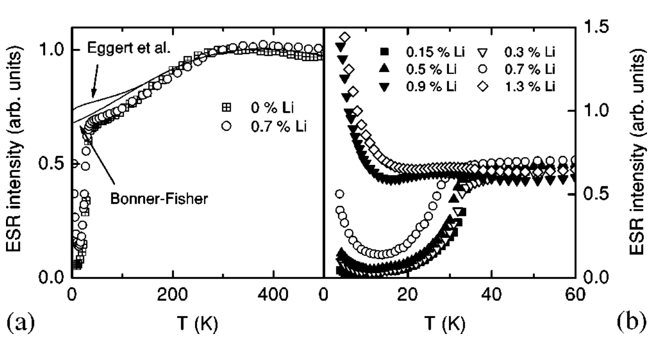

FIG. 2. Spin susceptibility of $Na_{1-x}Li_xV_2O_5$: (a) $x=0$ (squares) and 0.7% lithium (circles); the solid lines represent the fits using the theory of Bonner and Fisher (Ref. 4) and Eggert, Affleck, and Takahashi (Ref. 5) with $J=578$ K. (b) susceptibility below 60 K for different lithium concentrations.

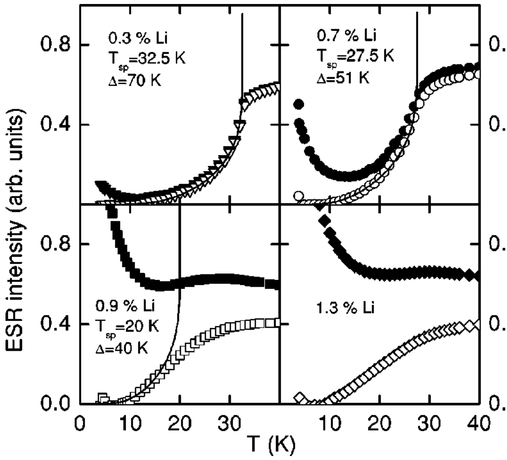

FIG. 3. Spin susceptibility of $Na_{1-x}Li_xV_2O_5$ for different lithium concentrations. The filled symbols are original data, the open symbols represent the data after substraction of the Curie contribution, and the solid lines show the fits assuming a mean-field-like energy gap $\Delta(T)$.

nicely agree with the theoretical fit using the dependence calculated by Bonner and Fisher[4] or Eggert, Affleck, and Takahashi[5] with $J = 578$ K. Both calculations give the same results above $T = 0.3J \simeq 175$ K. Below this temperature the more exact calculation of Eggert, Affleck, and Takahashi shows an even more pronounced disagreement with the data. The reason for this deviation is not totally resolved. It could be due to a dimensional crossover as was suggested from x-ray investigations (Ravy, Jegoudez, and Revcolevschi[9] predict a deviation from the Bonner-Fisher theory up to temperatures much higher than 90 K) or due to the existence of structural fluctuations.

Figure 2(b) displays the spin susceptibility below 60 K for different lithium concentrations. The transition shifts to lower temperatures and the decrease of the susceptibility becomes less pronounced with increasing lithium content. We also observe a Curie-like increase at lowest temperatures that increases with doping. In the sample $Na_{1-x}Li_xV_2O_5$ with $x = 1.3\%$ the transition is no longer visible [see Fig. 2(b)].

To analyze the data, a Curie law was fitted to the data points below 10 K and subtracted. The curves were then analyzed using a mean-field-like temperature dependence of the energy gap and $\chi(T) \propto \exp(-2\Delta/k_B T)$. For the temperature dependence of the energy gap $\Delta(T)$ the exact mean-field values were taken, $\Delta(0)$ and T_{SP} being the only fitting parameters. In this case it is preferable to use this method rather than fitting with the theory of Bulaevskii[26] because the uncertainty at low temperatures caused by the Curie contribution strongly influences the determination of the energy gap $\Delta(0)$. Examples of the fitting procedure for different x are given in Fig. 3. In the samples with $x \leqslant 0.7\%$ perfect agreement of the data and the fitting curves is found. The transition is broadened with increasing lithium content thus causing an increasing uncertainty for the high doped samples $x = 0.9\%$ and $x = 1.3\%$. While a determination of $\Delta(0)$ and T_{SP} is still possible in the $x = 0.9\%$ lithium doped sample, in the 1.3% doped sample no clear choice of $\Delta(0)$ and T_{SP} could be made, because the phase transition is strongly broadened in temperature and it is not clear how to determine the Curie contribution exactly (if the data are treated like those of the other samples assuming that at low temperature only the Curie contribution exists this contribution is probably overestimated leading to a seemingly linear decrease of the susceptibility as shown in Fig. 3).

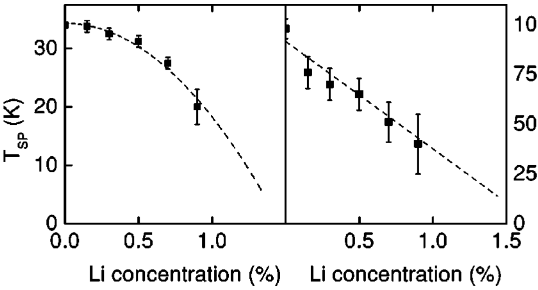

FIG. 4. Variation of the transition temperature T_{SP} and energy gap $\Delta(0)$ with lithium concentration. The dashed line in the left graph represents a fit according to $T_{SP}(x) \propto a - bx^2$; the dashed line in the right graph is a guide to the eye.

The results for the transition temperature T_{SP} and the energy gap $\Delta(0)$ are displayed in Fig. 4. The transition temperature seems to follow a $T_{SP} \propto a - bx^2$ function (dashed line). The energy gap $\Delta(0)$ varies linearly with the lithium content. However, since the errors in the determination of the lithium content have to be taken into account, further investigation is necessary to confirm the exact dependencies. For both cases the value of the assumed functions differs from zero (i.e., no transition occurs) at $x = 1.3\%$ lithium. This suggests that even in the case of 1.3% lithium doping the transition is not completely suppressed. Another interesting result is that the ratio $2\Delta/k_B T_{SP}$ decreases from the strong-coupling value of 5–6 in undoped NaV_2O_5 to values close to the mean field result of 3.53, i.e., 3.7–4 in the samples with $x = 0.5\%$ and $x = 0.7\%$.

IV. CONCLUSIONS

In conclusion we have presented ESR results on $Na_{1-x}Li_xV_2O_5$ for $0 \leqslant x \leqslant 1.3\%$. The linewidth and the spin susceptibility above the transition were found to be nearly independent from the lithium concentration. At low temperatures the increase of the linewidth is suppressed with growing lithium content. The spin susceptibility was analyzed using a mean-field-like model to extract the transition temperatures and the $T = 0$ value of the energy gap with respect to the doping. It was found that the transition temperature and the energy gap decrease monotonically on increasing Li concentration, suggesting a square dependence of the transition temperature and a linear decrease of the energy gap. Considering these dependencies it is highly probable that even in the highest doped sample a transition still persists.

These results can be compared with the effect of Na deficiency in $Na_{1-\delta}V_2O_5$.[27,28] The transition is strongly suppressed in Na-deficient samples and disappears at $\delta \approx 0.03$. The overall behavior of the susceptibility is similar to our results, but the transition seems to be more sensitive to Li doping, where only 1.3% Li is needed to suppress the phase transition.

Although there is no theoretical prediction for the suppression of the transition upon doping in NaV_2O_5, one can speculate about the relevant physical properties. The lattice parameters (Table I) show only a slight doping dependence. It is consequently very improbable that the suppression of the transition can be explained with the change of the lattice. In a normal spin-Peierls system the transition depends on the spin-phonon coupling g and the phonon frequency ω.[29] The transition temperature should be in the order of g/ω^2. Substitution of the lighter lithium ions for sodium is expected to increase the phonon frequency ω thus reducing the transition temperature. This scenario could explain the monotonic decrease of the transition temperature upon doping. Raman investigations of Na-deficient samples have been carried out by Kuroe and co-workers.[30,31] Unfortunately there was no direct observation of the coupling phonon that could be used to estimate this effect.

In $Na_{1-x}Li_xV_2O_5$ the lithium ions are located on the off-chain sodium positions. In contrast to $CuGeO_3$ doped off chain with silicon,[32] where antiferromagnetic order appears for concentrations as low as 0.5%, no signs of magnetic order were found. In $CuGe_{1-x}Si_xO_3$ the spin-Peierls transition decreases linearly as $T_{SP}(x) \propto a - bx$.[32] While in $CuGeO_3$ off-chain substitutions [such as Si (Ref. 32)] and in-chain substitutions [such as Zn (Refs. 33 and 34) or Mg (Ref. 35)] have been extensively studied, in NaV_2O_5 much interesting work in this field remains to be done.

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