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Magnetic and resonant properties of quasi-one-dimensional antiferromagnet $LiCuVO_4$

A. N. Vasil'ev and L. A. Ponomarenko
Low Temperature Physics and Superconductivity Department, Moscow State University, Moscow, 119899, Russia

H. Manaka and I. Yamada
Department of Physics, Faculty of Science, Chiba University, Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

M. Isobe and Y. Ueda
Institute for Solid State Physics, University of Tokyo, Roppongi 7-22-1, Tokyo 106, Japan

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The electron-spin-resonance (ESR) and dc magnetization measurements of the spinel-type compound $LiCuVO_4$ in a temperature range 2–300 K are presented. At cooling, the magnetization shows a broad maximum at $T_M = 28$ K, characteristic of a quasi-one-dimensional magnetic system. Then, the magnetization somewhat increases at temperatures below ~ 9 K, shows a second maximum at $T_{N'} \sim 4$ K, and a subsequent sharp drop. Both magnetization and ESR data indicate that the three-dimensional antiferromagnetic ordering occurs at $T_N = 2.3$ K. Above T_N the asymmetric ESR spectra of the $LiCuVO_4$ powder sample are in correspondence with the symmetry of the crystal field on Cu^{2+} ions. The $g_\parallel$ and $g_\perp$ values diverge at cooling as is anticipated for a quasi-one-dimensional Heisenberg antiferromagnet. According to the Bonner-Fisher model the interchain exchange interaction is $J_1 = 22$ K, while the intrachain exchange interaction is estimated to be $J_2 \sim 1$ K.

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I. INTRODUCTION

The discovery of diverse cooperative quantum phenomena in complex metal oxides has stimulated the search for inorganic materials with a low-dimensional magnetic subsystem. This search has uncovered a variety of quasi-one- and quasi-two-dimensional compounds, as well as systems of intermediate dimension, i.e., coupled magnetic chains or spin ladders. Such compounds are distinguished by specific temperature dependencies of magnetic properties and are characterized usually by quite low magnetic ordering temperatures. In certain cases magnetic ordering does not occur at all, and one or another interaction mechanism opens up a spin gap in the magnetic excitation spectrum of a low-dimensional magnet.[1,2] In the last three decades a large number of quasi-one-dimensional antiferromagnets with different values of spin S has been discovered. The examples of the most studied ones[3,4] are TMMC and $CsMnCl_3 \cdot 2H_2O$, both with $S = \frac{5}{2}$. After first observation of the spin-Peierls transition in inorganic compounds performed by Hase, Terasaki, and Uchinokura[1] on $CuGeO_3$ the attention of researchers has been focused on magnetic materials that contain chains of ions with $S = \frac{1}{2}$. The experimental realization of such magnetic ions are Cu^{2+} and V^{4+}. That is why in the last years many experimental papers have been devoted to the investigation of magnetic properties of metal-oxide compounds with chainlike arrangements of copper and vanadium atoms in a crystal structure.[1,2,5–7] Rather diverse variations of low-dimensional magnetic structures are encountered in compounds where these ions coexist with lithium ions Li^{1+}. Thus, in the lithium cuprate $LiCuO_2$ the copper ions Cu^{2+} ($S = \frac{1}{2}$) in linear CuO_4 chains are bound with one another by a ferromagnetic interaction, while the interaction between chains is antiferromagnetic.[5] Magnetic V^{4+} ($S = \frac{1}{2}$) and nonmagnetic V^{5+} ($S = 0$) ions are present in the layered structure of lithium vanadate LiV_2O_5, and each of the ions form zig-zag chains of vanadium pyramids VO_5. A magnetic phase transition occurs in this system only at ultralow temperatures.[8] Recently, fascinating heavy-fermion behavior has been observed in the LiV_2O_4 system.[6]

II. EXPERIMENT AND RESULTS

The orthorhombic metal-oxide compound $LiCuVO_4$, where all of the ions listed above are present, is genetically related with the spinel structure, where the lithium ions Li^{1+} and magnetic copper ions Cu^{2+} ($S = \frac{1}{2}$) are located in an octahedral environment, while the nonmagnetic vanadium ions V^{5+} ($S = 0$) are located in a tetrahedral environment consisting of oxygen ions O^{2-}.[9] As shown in Fig. 1, the chains of copper-oxygen octahedra CuO_6, which are coupled along an edge in the basal plane, extend along the b axis, and they form almost regular triangles in the a-c plane. Chains of lithium-oxygen octahedra LiO_6 extend along the a axis, and the vanadium-oxygen tetrahedra VO_4 are isolated from one another. The room-temperature lattice constants are $a = 0.5652$ nm, $b = 0.5810$ nm, and $c = 0.8750$ nm,[9] so that copper-oxygen octahedra are characterized by a strong tetragonal distortion, the long axis of the CuO_6 octahedra being oriented along the c axis. In nonstoichiometric samples of $Li_{1-x}CuVO_4$ ($0 < x < 0.2$) a structural phase transition of the cooperative Jahn-Teller effect type has been observed above room temperature.[10]

The $LiCuVO_4$ samples were prepared by solid-phase synthesis from a stoichiometric mixture of lithium carbonate Li_2CO_3, copper oxide CuO, and vanadium pentoxide V_2O_5. Synthesis had been conducted at 530 °C for one week and then synthesis continued after additional repeated mixings for one month. The final product—a light-yellow powder—consisted of a monophase sample, as was verified by x-ray

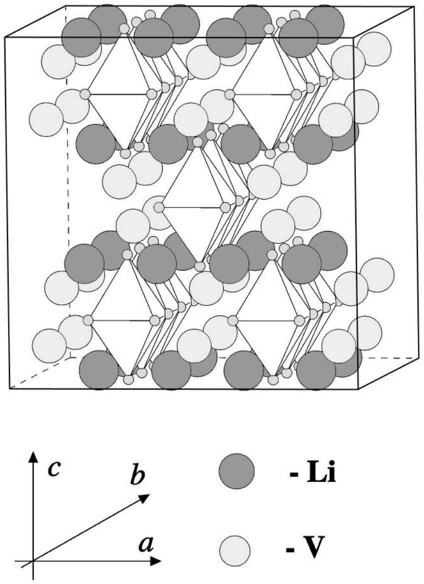

FIG. 1. The crystal structure of $LiCuVO_4$. The copper ions are situated within edge-sharing oxygen octahedra.

diffraction. Magnetic measurements were performed on a Quantum Design superconducting quantum interference device magnetometer in fields up to 5 T in the temperature range 2–300 K. The electron-spin resonance (ESR) spectra were taken over 1.3–300 K using a 100-kHz field-modulated spectrometer operated at 24.5 GHz, so that the derivatives of the absorption signals were recordered.

The temperature dependence of the magnetic susceptibility of $LiCuVO_4$ taken at $H = 0.1$ T is presented in Fig. 2. The solid line represents the best fit according to a Bonner-Fisher model for a quasi-one-dimentional magnetic system.[11] As temperature decreases, the magnetic susceptibility χ passes through a wide peak at $T_M = 28$ K, then increases somewhat at ~ 9 K, and once again sharply decreases at $T_{N'} \sim 4$ K. The magnetization M as a function of the field H is linear above $T_{N'}$; below these temperatures the dependence $M(H)$ shows weak nonlinearity. In contrast to the wide peak in $\chi(T)$ at T_M, the position of the low-temperature peak in χ at $T_{N'} \sim 4$ K depends nonmonotonously on the magnetic field. In weak fields the peak first shifts somewhat to higher temperatures and then rapidly shifts to lower temperatures as the field increases further. This dependence is shown in Fig. 3, where the solid line connecting the experimental points is drawn only for visual clarity.

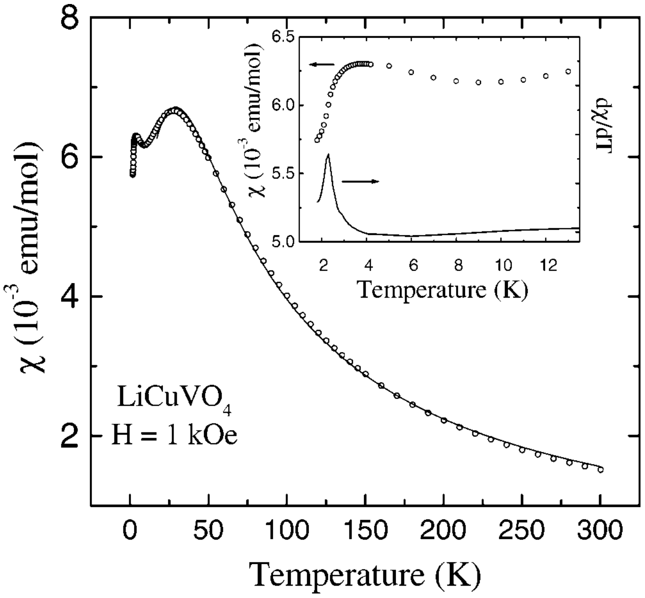

FIG. 2. The temperature dependence of the magnetic susceptibility of $LiCuVO_4$. The solid line is a fit corresponding to a Bonner-Fisher model. The inset represents the temperature dependence of susceptibility and the first derivative of susceptibility in the low-temperature region.

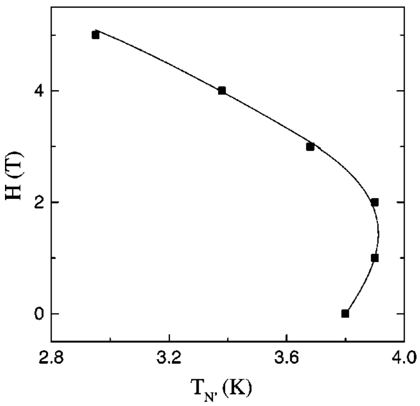

FIG. 3. The position of the low-temperature maximum $T_{N'}$ at various magnetic fields.

All experimental data presented are characteristic of a quasi-one-dimensional magnet, which, as the temperature decreases, first exhibits short-range magnetic correlations within the chains and then undergoes three-dimensional antiferromagnetic ordering at low temperatures. The antiferromagnetic ordering temperature T_N is somewhat different from $T_{N'}$, and it can be determined according to the position of the peak in the temperature dependence of the derivative $\partial\chi/\partial T$ (see the inset to Fig. 2). In weak fields $T_N = 2.3$ K, and it decreases to 2 K at $H = 5$ T.

At high temperatures ($T \geqslant 150$ K) the magnetic susceptibility of $LiCuVO_4$ can be approximated by the Curie-Weiss law

$$\chi = \frac{C}{T - \Theta}, \tag{1}$$

with $\Theta = -15$ K and the effective g factor is 2.26. However, in a wide temperature range the best fit for the temperature dependence of magnetic susceptibility is given by a polynomial corresponding to the Bonner-Fisher curve.[11] The latter is a numerical calculation of $\chi(T)$ for an ideal one-dimensional Heisenberg chain of spins $S = \frac{1}{2}$.[12]

The ESR measurements were performed over 1.3–300 K using a 100-kHz field-modulated K-band spectrometer operated at 24 GHz. Examples of the spectra observed at several temperatures are shown in Fig. 4. When we see the spectra

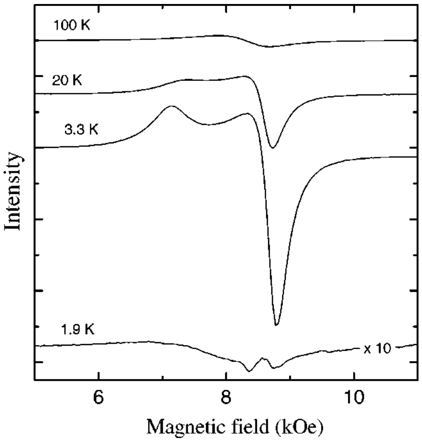

FIG. 4. The ESR spectra of $\mathrm{LiCuVO_4}$ taken in a wide temperature range. At $T<T_N$ the spectrum observed exhibits a qualitative transformation.

obtained at 100 K, 20 K, and 3.3 K, it seems as if they consist of two derivative lines, but that is not correct. Since the sample was a powder, the observed ESR spectra should be a superposition of those of many single crystals, and therefore the spectra should be a asymmetric, as can be seen in Fig. 4. The spectrum obtained at 1.9 K is different from those obtained at higher temperatures, which indicates that the magnetic state at 1.9 K is not paramagnetic.

The electron-paramagnetic-resonance (EPR) line of one-dimensional Heisenberg magnets is not necessarily Lorentzian.[13] At present, however, we assume a Lorentzian line shape to elucidate approximate characteristics of the EPR in the present compound.

Assuming a derivative Lorentzian line for a single crystal, we analyze the observed spectra. The observed line profile $I'(H)$ corresponds to the expression given by

$$I'(H)\propto-\int_{\pi}^{0}\frac{2[\Gamma(\theta)]^2\cdot[H-H_r(\theta)]\sin\theta}{\{[\Gamma(\theta)]^2+[H-H_r(\theta)]^2\}^2}d\theta, \tag{2}$$

where H is the external field, $\Gamma(\theta)$ and $H_r(\theta)$ are the half-width at the maximum and the resonance field, respectively, while θ is an angle between H and the crystal axis along which $g_\parallel$ is determined. The derivative peak-to-peak linewidth ΔH_{pp} is $2\Gamma/\sqrt{3}$. In $\mathrm{LiCuVO_4}$, $g_\parallel$ and $g_\perp$ are the g components parallel and perpendicular to the c axis.

Treating $\Gamma(\theta)$ and $H_r(\theta)$ as adjustable parameters, we tried to get the best fit of Eq. (2) on each experimentally observed spectrum. In the simulation over the high-temperature region where no magnetic short-range order exists, we used a relation[14]

$$\Gamma(\theta)=\Gamma_0(1+\cos^2\theta), \tag{3}$$

where Γ_0 is the minimum.

The $g(\theta)$ in $S=\frac{1}{2}$ compounds with a uniaxial symmetric ligand is given by

$$g(\theta)=\sqrt{g_\perp^2\sin^2\theta+g_\parallel^2\cos^2\theta}. \tag{4}$$

Then the θ dependence of H_r is given by

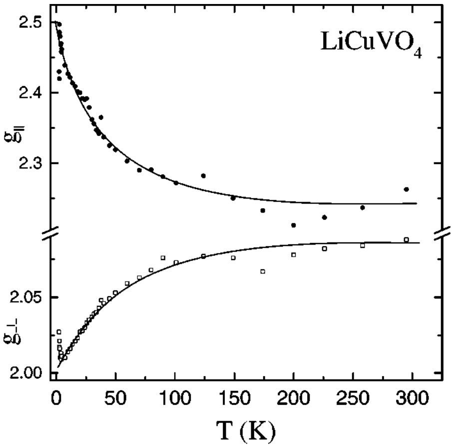

FIG. 5. The temperature dependencies of the g factors observed in asymmetric ESR spectra of $\mathrm{LiCuVO_4}$.

$$H_r(\theta)=\frac{\hbar\omega}{g(\theta)\mu_B}=\frac{\hbar\omega}{\mu_B\sqrt{g_\perp^2\sin^2\theta+g_\parallel^2\cos^2\theta}}, \tag{5}$$

where ω is a fixed microwave frequency. Equation (3) is established in one-dimensional Heisenberg magnets, which have no effect on spin diffusion and therefore have a Lorentzian line shape in their ESR spectra.

Over the temperature region where the magnetic short-range order develops, spin correlations act as an effective internal field and therefore cause a shift of the resonance field H_r from that at high temperatures where no magnetic short-range order exists.[15] The shift $\delta H_r(\theta)$ has the angular dependence as

$$\delta H_r(\theta)\propto(3\cos^2\theta-1). \tag{6}$$

Taking these assumption and conditions, we tried to obtain the best fit of Eq. (2) on each observed spectrum.

As a result, we obtain the temperature dependence of H_r and ΔH_{pp} for $\theta=0$ and $\pi/2$, which are shown in Figs. 5 and 6. Instead of $H_r(T)$, we plot $g(T)$, which we obtain using equation

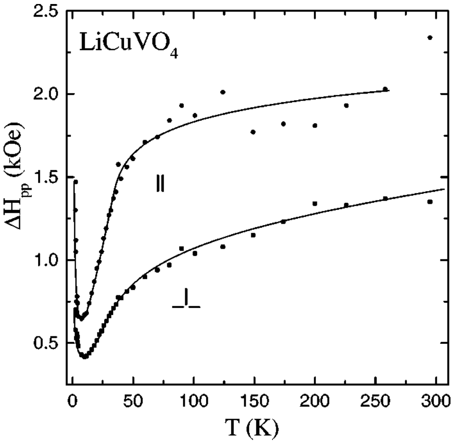

FIG. 6. The temperature dependencies of the peak-to-peak widths of ESR signals ΔH_{pp}.

$$g(T)=\frac{\hbar\omega}{\mu_B H_r(T)}. \tag{7}$$

III. DISCUSSION

The temperature dependence of the magnetic susceptibility observed in $LiCuVO_4$ is somewhat different from that expected of a quasi-one-dimensional antiferromagnet that experiences a three-dimensional magnetic ordering at low temperatures. As is well known, an ideal Heisenberg chain does not undergo long-range ordering at any temperature. However, the short-range ordering, which does not imply phase transition, results in the smooth increase of the correlation length. Three-dimensional ordering is possible at low temperatures when the interchain interaction becomes comparable with the thermal energy kT. For example, this behavior has recently been observed in another quasi-one-dimensional inorganic compound CuV_2O_6.[7] In this compound the broad maximum at the $\chi(T)$ dependence has been accompanied by the decrease of magnetic susceptibility at the Néel point. No upturn of χ when approaching the Neel point has been detected in CuV_2O_6.

In principle, the upturn of χ below 9 K could be attributed to paramagnetic impurity. However, the subsequent abrupt drop of χ at $T_{N'}$ contradicts this assumption, besides the ESR data in this temperature range do not reveal any additional paramagnetic signal.

The increase of magnetic susceptibility in $LiCuVO_4$ below 9 K can be attributed to the strengthening of the role of interchain interaction, which is frustrated due to the almost regular triangular arrangement of the Cu^{2+} ions in the *a*-*c* plane. This frustration competes with the tendency to form short-range ordering within the chains. In fact, within the Cu^{2+} triangle the distance between Cu^{2+} ions along the *a* axis is 5.652 Å, while two other distances are 5.209 Å. Accordingly, the exchange integrals within the Cu^{2+} triangle somewhat differ. At a further lowering of temperature this difference becomes significant and the frustration is lifted off. As a result, a three-dimensional magnetic ordering is finally established.

To establish the nature of the decrease of χ at $T_{N'}$ the temperature dependencies of magnetization in various magnetic fields were measured. As can be seen from Fig. 3 the position of the low-temperature maximum is a nonmonotonous function of a magnetic field. This behavior is characteristic of the low-dimensional antiferromagnets.[16] The initial increase in the antiferromagnetic ordering temperature is due to the fact that the external field efficiently decreases the number n of degrees of freedom in the magnetic subsystem, transferring a Heisenberg magnet $(n=3)$ into an XY-type magnet $(n=2)$. The subsequent decrease of the $T_{N'}$ is due to the Zeeman splitting of the levels in a magnetic field.

The ESR data appear to be in accordance with the magnetization measurements. The deviation of g factors from constant values is related to the short-range antiferromagnetic correlations within the chains. Above the Néel point the value of $(g_\parallel g_\perp^2)^{1/3}=2.13\pm0.01$ is constant in accordance with the axial model for the Heisenberg chain[15] in which the dipole-dipole and (or) the anisotropic exchange interactions are the main perturbation terms. The rapid decrease of the ESR signal linewidths in the range of well-developed short-range correlations is not clear. Usually, the linewidths of ESR signals that accompany the deviation of g factors diverge when approaching the Néel point. At lowest temperature the ESR spectrum observed undergoes qualitative change and transforms into an antiferromagnetic resonance spectrum.

Comparing the Bonner-Fisher curve with experiment gives the appreciably large value 2.39 for the g factor averaged over the crystallographic directions, and from the position of the wide peak along the temperature scale,

$$T_M=1.282J_1, \tag{8}$$

it follows[11] that the exchange integral in the chains is $J_1=22$ K. The interchain exchange interaction J_2 can be estimated[17] from the three-dimensional antiferromagnetic ordering temperature T_N as

$$J_2=\frac{T_N}{1.28\sqrt{\ln 5.8J_1/T_N}}. \tag{9}$$

In order of magnitude $J_2\sim1$ K.

IV. CONCLUSION

The electron-spin-resonance (ESR) and dc magnetization measurements have revealed a complicated interplay of different exchange interactions in the spinel-type compound $LiCuVO_4$. At cooling, short-range correlations are established in the chains of edge-sharing CuO_6 octahedra and the magnetization shows a broad maximum at $T_M=28$ K. Then, the magnetization somewhat increases below ~9 K, shows a second maximum at $T_{N'}\sim4$ K, and a subsequent sharp drop. Above T_N the asymmetric ESR spectra of the $LiCuVO_4$ powder sample are in correspondence with the symmetry of the crystal field on Cu^{2+} ions. The $g_\parallel$ and $g_\perp$ values diverge at cooling as is anticipated of a quasi-one-dimensional Heisenberg antiferromagnet. Both magnetization and ESR data indicate that the three-dimensional antiferromagnetic ordering occurs at $T_N=2.3$ K.

Further information about quasi-one-dimensional antiferromagnetic ordering in $LiCuVO_4$ can be apparently obtained through neutron-diffraction investigations. Specifically, the value estimated for the interchain exchange integral may be too low because of frustrations of the exchange interaction in a triangular arrangement of chains, if the interaction between the copper ions in the *a*-*c* plane is antiferromagnetic.

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