Quasi-One-Dimensional Spin Chains in $CuSiO_3$: an EPR Study*

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Abstract. Temperature-dependent electron paramagnetic resonance (EPR) studies were performed on $CuSiO_3$. This recently discovered compound is isostructural with the spin-Peierls compound $CuGeO_3$. The EPR signals show characteristics different from those of $CuGeO_3$ and are due to Cu^{2+} spins located along quasi one-dimensional chains. For $T > 8.2$ K the spin susceptibility closely follows the predictions of an $S = 1/2$ one-dimensional Heisenberg antiferromagnet with $J/k_B = 21$ K. Below $T = 8.2$ K the spin susceptibility immediately drops to zero indicating long-range magnetic order.

1 Introduction

The linear spin-chain system $CuGeO_3$ is the first and up to now the only inorganic compound that exhibits a spin-Peierls transition [1]. Regarding the magnetic properties the partial substitution of Ge by Si was an important subject in terms of studying frustration effects [2] and the coexistence of the spin-Peierls state with long-range antiferromagnetic order [3, 4].

To characterize the nature of antiferromagnetic interactions in Si-doped and pure $CuGeO_3$ electron paramagnetic resonance (EPR) of Cu^{2+} spins provided important results [5–9]. In pure $CuGeO_3$ the EPR parameters differ from those of conventional one-dimensional (1-D) Heisenberg antiferromagnets. The antisymmetric Dzyaloshinsky-Moriya (DM) exchange interaction was claimed to explain this difference [6]. In Si-doped $CuGeO_3$ the coexistence of spin-Peierls and antiferromagnetic order is reported for Si concentrations below about 1%. For higher

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Si concentrations (up to 50%) a long-range antiferromagnetic ground state is observed [4].

However, for $T > 15$ K the temperature dependence of the EPR parameters does not change significantly for Si-doping concentrations up to 7% [7, 8]. This paper reports the first EPR results on pure $CuSiO_3$ which are very different from pure and slightly Si-doped $CuGeO_3$.

2 Material and Methods

The EPR measurements were performed at X-band frequency on a Bruker ELEXSYS spectrometer and at temperatures between 4 and 300 K. For cooling a continuous-flow helium cryostat was used. The polycrystalline sample of $CuSiO_3$ was synthesized by dehydration of the mineral dioptase [10]. DC magnetization measurements at low fields $H \leq 10$ kOe were carried out on a commercial superconducting quantum interference device magnetometer [11]. Reported EPR spectra of CuO [12] did not show up in our EPR spectra which indicated the high quality of our sample.

3 Results and Discussion

Figure 1 shows the temperature dependence of the EPR linewidth ΔH (HWHM) and EPR g factor (determined from the EPR resonance field) of the investigated $CuSiO_3$ sample. The inset of Fig. 1 shows a representative EPR spectrum of $CuSiO_3$ at $T = 40$ K (solid line, derivative of the EPR absorbed power). At all temperatures the spectra could be nicely fitted with a Lorentzian derivative (dashed line in the inset of Fig. 1).

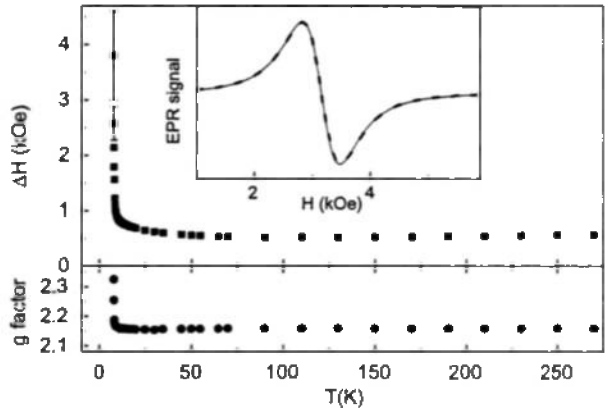

Fig. 1. Temperature dependence of the EPR linewidth ΔH (HWHM) and EPR g factor, determined by the resonance field. Inset: typical EPR spectrum (derivative of absorbed power, $T = 40$ K) (solid line) and Lorentzian line fit (dashed line).

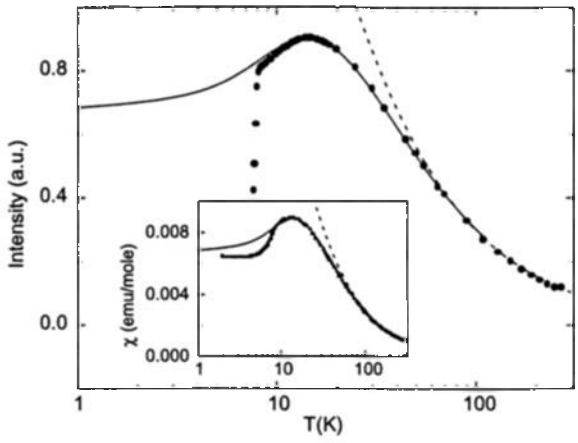

Fig. 2. Temperature dependence of the EPR intensity (integrated EPR signal, solid circles). Inset: magnetic susceptibility vs. temperature [11]. The solid lines represent the behavior of a 1-D Heisenberg antiferromagnet with $S = 1/2$ [14]. The dashed lines are Curie-Weiss laws with $\Theta = -7.2$ K.

The EPR linewidth linearly decreases down to $T \approx 100$ K at a rate of 0.5 Oe/K. This contrasts with a much steeper and nonlinear decrease of the linewidth in $CuGeO_3$ in which the antisymmetric DM interaction was used to explain the linewidth [5, 6]. Therefore in $CuSiO_3$ a DM interaction seems to be less important. Anisotropic exchange interactions also contribute to the EPR linewidth. As the deviation of the in-plane Cu-O-Cu angle from 90° is smaller in $CuSiO_3$ than in $CuGeO_3$ [4, 10], the Cu 3d- and O 2p-orbitals overlap differently and therefore the anisotropic superexchange interactions in both compounds should be different [13]. For temperatures above $T \approx 12$ K the EPR g factor has a nearly temperature-independent value of $g = 2.156 \pm 0.001$. Like in isostructural $CuGeO_3$ [9] this g value is consistent with a polycrystalline-averaged, effective g tensor of the two magnetically inequivalent Cu^{2+} ions of $CuSiO_3$, the Cu^{2+} sites being within strongly elongated oxygen octahedra in the orthorhombic crystal structure [10].

Figure 2 shows the temperature dependence of the EPR intensity $I_{EPR}(T)$ which is determined by integration of the spectra. $I_{EPR}(T)$ is proportional to the spin susceptibility of Cu^{2+} and can be well compared with the magnetic susceptibility $\chi(T)$ [11] as shown in the inset of Fig. 2. However, below $T = 8.2$ K the EPR intensity reduces rapidly to zero, indicating an ordering phenomenon rather than a spin-Peierls state which produces an exponential decrease of the intensity [5]. This is also evidenced by the nonvanishing $\chi(T \to 0)$ which is usually due to an anisotropic antiferromagnetic state [11]. Above $T = 8.2$ K $\chi(T)$ and $I_{EPR}(T)$ are very well described by theoretical calculations for an $S = 1/2$ 1-D Heisenberg antiferromagnet without frustration effects [14]. This leads to an in-plane Cu-O-Cu exchange of $J/k_B = 21$ K, which is much smaller than in $CuGeO_3$ ($J/k_B \approx 160$ K) as can be expected from the smaller Cu-O-Cu angle in $CuSiO_3$ [4, 9, 13]. For high temperatures, $\chi(T)$ and $I_{EPR}(T)$ nicely follow a Curie-Weiss

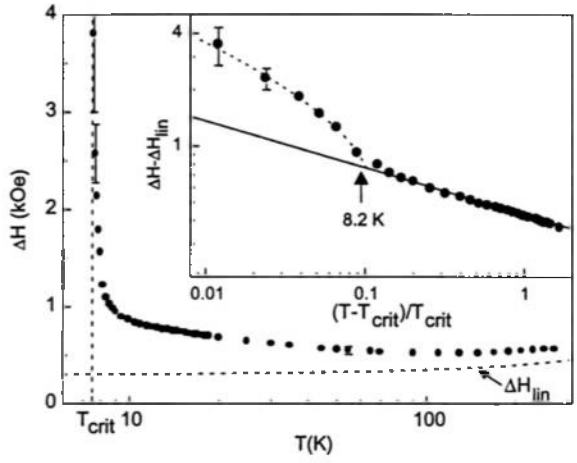

Fig. 3. Temperature behavior of the EPR linewidth ΔH. At high T the dashed line approximates the linewidth with a linear function ΔH_{lin}. The inset displays the reduced linewidth $\Delta H - \Delta H_{lin}$ vs. reduced temperature $(T - T_{crit})/T_{crit}$ ($T_{crit} = 7.5$ K) in order to characterize the critical line broadening ΔH_{crit}. The solid line represents a power law according to $\Delta H_{crit} \sim (T - T_{crit})^{-\alpha}$ ($\alpha = 0.25$). The dashed line guides the eye.

law with a Weiss temperature of $\Theta = -7.2$ K, indicating weak antiferromagnetic coupling.

Figure 3 shows a characterization of the temperature dependence of the EPR linewidth. The high-temperature part is estimated with a linear function $\Delta H_{lin}(T) = 0.5T$ Oe/K + 300 Oe. This linear part was subtracted from ΔH in order to obtain the broadening ΔH_{crit} when the temperature is lowered towards a critical temperature $T_{crit} = 7.5$ K. A power law $\Delta H_{crit} \sim (T - T_{crit})^{-\alpha}$ approximately describes the linewidth with $\alpha = 0.25$ at low temperatures and above $T = 8.2$ K. However, at $T \approx 8.2$ K the type of broadening obviously changes as a noticeable deviation from a power law occurs. This is indicated by the eye-guiding dashed line in the inset of Fig. 3. The linewidth strongly increases nearly below the same temperature ($T \approx 8.2$ K) where a strong decrease of the resonance field H_{res} is observed as well (see Fig. 1, increase of the H_{res}-determined g factor). Such a sudden decrease of H_{res} indicates magnetic ordering which yields strong internal fields. Hence the change of line broadening is indicative for inhomogeneous line broadening effects due to magnetic ordering. Measurements of the specific heat give strong evidence for long-range antiferromagnetic order [11]. From the critical behavior of the linewidth it is not possible to compare $CuSiO_3$ unambiguously with typical antiferromagnets neither for the 1-D case like $CuCl_2 \cdot 2NC_5H_5$ ($\alpha = 0.5$ [15]) nor for the 3-D case like GdB_6 ($\alpha = 1.5$ [16]).

In summary, our EPR results on $CuSiO_3$ do not show evidences for a spin-Peierls state below $T = 8.2$ K. For low temperatures the EPR intensity and EPR linewidth are explained rather by long-range magnetic ordering phenomena. For temperatures above $T = 8.2$ K the EPR intensity is proportional to the magnetic

susceptibility and can be reproduced well with a behavior of a 1-D antiferromagnet. Antisymmetric and anisotropic exchange interactions contribute differently to the EPR parameters in $CuSiO_3$ and $CuGeO_3$.

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