Antiferromagnetism in CaCu$_3$Ti$_4$O$_{12}$ studied by magnetic Raman spectroscopy

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For CaCu$_3$Ti$_4$O$_{12}$ – an insulator that exhibits a giant dielectric response above 100 K – Cu$^{2+}$ antiferromagnetic spin ordering has been investigated by magnetic Raman scattering and magnetization measurements. Below the Néel temperature, $T_N = 25$ K, magnetic excitations have been identified. Above $T_N$ Raman spectra reveal short-range antiferromagnetic fluctuations that increase with cooling like $T^{-1}$. No deviations from Curie-Weiss law have been observed above $T_N$.

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Recently the insulating cubic compound CaCu$_3$Ti$_4$O$_{12}$ has attracted much interest because of its giant change in the dielectric response with temperature. This compound possesses a low-frequency dielectric constant, $\epsilon \sim 10^4$, which is only weakly varying in the temperature range 100–600 K. Below 100 K, however, there is an abrupt 100-fold reduction in the value of $\epsilon$ but no structural phase transition which is usually associated with a large dielectric response has been observed. X-ray diffraction and thermodynamic data argue against an explanation in terms of collective ordering of local dipole moments [1]. It has been suggested that at low temperatures a redistribution of electric charge in the unit cell occurs accompanied by strong changes in the relaxational characteristic of dipolar fluctuations [2]. The CaCu$_3$Ti$_4$O$_{12}$ magnetic structure has been investigated by neutron diffraction and susceptibility measurements [3]. The system is antiferromagnetic below the Néel temperature $T_N = 25$ K.

In this paper we investigate the magnetic properties of CaCu$_3$Ti$_4$O$_{12}$ single crystals by Raman spectroscopy, magnetization and heat capacity measurements. The data reveal local antiferromagnetic fluctuations between room temperature and $T_N$ that rapidly strengthen with cooling like $T^{-1}$. This surprising result cannot be explained by frustration effects since the magnetization exhibits no deviations from the Curie-Weiss law and the Weiss constant is very close to the $T_N$ value.

Figure 1 shows the crystal structure of CaCu$_3$Ti$_4$O$_{12}$ [4], a cubic perovskite-like compound with space group Im3 (point group $Ih$) [5]. Important features of this structure are the TiO$_6$ octahedrons, which are considered to be responsible for the giant electrical polarizability. If the position of the Ti$^{4+}$ ion slightly shifts with respect to the oxygen cage [4] local dipole moments arise. Because of the tilted arrangement of the octahedrons the ordering of the dipole moments is frustrated and no ferroelectric phase transition has been observed [4]. However, the Ti-O bonds are set under tension.

Figure 2 shows the heat capacity and magnetization measurements that indicate an antiferromagnetic phase transition at 25 K with a Weiss-constant of $\theta_W = -30$ K. $1/\chi$ is linear with temperature showing Curie-Weiss behavior almost to $T_N$. The Cu$^{2+}$ ions carry a hole with spin $S=1/2$ in the 3d-shell, giving rise to magnetic moments which order antiferromagnetically due to the superexchange interaction. According to the Goodenough rules [6] it has been suggested [7] that the superexchange interaction between the copper spins is promoted via the titanium ions rather than via the usual oxygen path. However, the interactions are expected to be weak.

The arrangement of the Cu$^{2+}$ spins and thus the magnetic structure is shown in Fig. 3. We consider the effective exchange integrals $J_1$, $J_2$ and $J_3$ between nearest, next nearest and third nearest neighbors. The spins are ordered antiferromagnetically along the (111) direction with a ferromagnetic alignment in the [111] planes [8].

FIG. 1. Crystal structure of CaCu$_3$Ti$_4$O$_{12}$. The unit cell is built up by the atoms inside the dotted lines. It contains eight distorted TiO$_6$ octahedrons, copper atoms bonded to four oxygen atoms, and large Ca atoms at the edges and in the middle without drawn bonds.

FIG. 2. Shows the heat capacity and magnetization
energy loss is the result of the perturbed spin position with respect to the ground state \( \{4\} \). Possible two-magnon excitations would correspond to the exchange of the spin in position 1 with the spins in position 1’ or 2’. As will be shown below these processes can be resolved spectroscopically. Furthermore the magnetic behavior above \( T_N \) can be investigated and compared to the magnetization measurements.

Single crystals of CaCu$_3$Ti$_4$O$_{12}$ were grown by the traveling-solvent floating-zone method using a four-ellipsoidal mirror type image furnace. Dried starting materials of CaCO$_3$, CuO and TiO$_3$ were mixed and baked at 800°C and 850°C for 24 hours each with intermediate grindings to make the single-phase powder of CaCu$_2$Ti$_3$O$_{12}$. The feed rod was formed by a rubber tube in a hydro-static press, and baked in air at 900 °C for 12 hours. The pelletized solvent with the composition of CaCu$_2$Ti$_3$O$_4$ : TiO$_2$ = 80 : 20 in molar ratio was placed between the feed rod attached to the upper shaft and a seed attached to the lower shaft and was melted at the focal point. Each growth was performed for \( \sim 8 \) hours with the growth speed of 6 mm/hour in an oxygen atmosphere. During the growth, the upper and lower shafts rotated at 30 rpm in opposite directions of each other to mix the molten zone. The typical crystal size was 5 mm in diameter and 20 mm in length.

Raman measurements were performed from the [100] surface of the crystal mounted in a continuous helium flow optical cryostat. All spectra were taken in a backscattering geometry with excitations from a Kr$^+$ laser. The laser power was less than 10 mW and was focused to a 50 μm diameter spot on the sample surface. The spectra were analyzed by a custom triple grating spectrometer. All spectra were corrected for the spectral response of the spectrometer and detector. The temperatures were corrected for laser heating.

In Figure 4 we present the temperature dependence of the Raman response of CaCu$_3$Ti$_4$O$_{12}$ in parallel \( \{z(xz)z\} \) and cross \( \{z(xy)z\} \) polarizations for blue excitation with \( \omega_i = 2.6 \) eV. The intense peaks at high-frequency are identified as phonons. From the polarization dependence shown in Fig. 4 and spectra taken for \( \{z(x+y, x+y)z\} \) and \( \{z(x+y, x+y)z\} \) polarizations after sample rotation by 45° we conclude that the 500 cm$^{-1}$ phonon in cross polarization has \( T_g \) symmetry, the phonons at 450 and 520 cm$^{-1}$ in parallel polarization obey \( A_g \) symmetry and the phonon at 580 and 300 cm$^{-1}$ have \( E_g \) symmetry.

With cooling a new feature develops at low frequencies for the \( \{z(xy)z\} \) polarization with a broad peak forming above \( T_N \) and a sharp structured band below \( T_N \), suggesting a magnetic origin for these excitations. To exclude a possible one magnon origin we applied an 8 T magnetic field. No shift or splitting of the peak was
FIG. 4. Raman spectra in parallel (a) and cross (b) polarization for different temperatures using an excitation laser wavelength of $\lambda = 482.5$ nm. The peaks at 450, 520 and 580 cm$^{-1}$ in the parallel polarization and 500 cm$^{-1}$ in cross polarization correspond to phonons. The low-frequency band in cross polarization corresponds to two-magnon excitations. The inset shows spectra for excitation with $\lambda = 752$ nm in cross polarization. The magnon intensity is suppressed indicating resonant behavior.

observed in the field confirming its singlet two-magnon nature. In parallel polarization the peak is strongly suppressed. Its polarization dependence reveals $T_g$ symmetry, typical for two-magnon excitations. The inset in Fig. 4b shows the low frequency part of the spectra with red excitation $\omega_i = 1.65$ eV for which the two-magnon intensity is suppressed. This demonstrates the resonance behavior of the two-magnon excitation. The magnon intensity is expected to be sensitive to the excitation energy because the photon-induced spin exchange process involves a virtual electron-hole excitation to a higher energy level [10]. If the excitation energy is close to interband transitions a resonance enhancement occurs.

FIG. 5. Low frequency excitations of CaCu$_3$Ti$_4$O$_{12}$ in cross polarization. Below $T_N$ the excitation consists of a clear peak (A) at 66 cm$^{-1}$ and two shoulders (B and C) at 87 and 112 cm$^{-1}$. The spectra above $T_N$ are fitted with a damped harmonic oscillator function and are enlarged by a factor of two for comparison with the magnon peak. The 13 K spectra is fitted with three lorentzians. The left inset shows the integrated intensity of the magnetic excitations above $T_N$ (filled circles) and below $T_N$ (empty circles) fitted with $I(T) \sim T^{-1}$. The right inset shows the peak positions of the excitations above $T_N$ and peak A below $T_N$.

Figure 5 shows the low frequency region of the Raman response. The spectral shape depends strongly on the temperature. Four temperature regions are distinguishable. Above 70 K the spectra are basically flat and show weak features. Only small deviations from the background are visible. Below 70 K a clear peak develops around 35 cm$^{-1}$. The peak has a rather broad shape and its intensity grows with decreasing temperature. At 25 K, the value of the antiferromagnetic phase transition, the peak shifts to higher energies and the shape becomes more structured. Below 25 K a sharp structured two-magnon band with three components A, B and C at 66, 87 and 112 cm$^{-1}$ is observed. The two-magnon excitation has been fitted with 3 lorentzians between 50 and 130 cm$^{-1}$ (solid line). The left inset shows the intensity development of the magnetic excitation above and below $T_N$ with a linear background intensity subtracted. The fit shows that the intensity of the fluctuations (above $T_N$) is proportional to $T^{-1}$. Note that the intensity enhancement occurs in the temperature region of the anomalous T-dependence of the dielectric constant. The peak positions in the right inset are constant above the Néel temperature and increase suddenly around 30 K. A slight anomaly is observed around 100 K.
We explain the three components of the two-magnon band below 25 K with the different spin exchange processes described above. We suggest that the two excitations at 66 and 87 cm\(^{-1}\) arise from the spin exchanges in positions 1 and 2’ (along \(J_1\)) and 1 and 1’ (along \(J_2\)). The exchange along \(J_2\) gives no effect. Thus the highest excitation at 112 cm\(^{-1}\) could be a four-magnon process with instantaneous exchanges of two neighboring spin pairs. To estimate \(J_i\) \((i = 1, 2, 3)\) we calculated the spin exchange energies by counting the interaction energies given by

\[
H = \sum_{<k,l>} J_{kl}^I (S_k \cdot S_l)
\]

where \(S_k\) and \(S_l\) are the vectors of neighboring spins and the sum is over nearest neighbor, next nearest neighbor and third nearest neighbor sites \((i = 1, 2, 3\) correspondingly). The energy of the two-magnon components correspond to the difference between the total magnetic energy calculated by (1) before and after the spin exchange. Thus we yield a set of three linear equations to combine with three excitation energies. The highest energy must correspond to the assumed four-magnon process, reducing the number of solutions to two. One solution gives ferromagnetic exchange (and is therefore unphysical) the second gives antiferromagnetic exchange with \(J_1 = 23, J_2 = 3\) and \(J_3 = 2\) cm\(^{-1}\). According to this solution we assign feature A in Fig. 5 to the \(1 \leftrightarrow 2’\) spin exchange, feature B to \(1 \leftrightarrow 1’\) and feature C to \(1 \leftrightarrow 2’\) and \(2 \leftrightarrow 1’\) (a double spin exchange). Note that the double spin exchange \(1 \leftrightarrow 2’\) and \(2 \leftrightarrow 3’\) yields similar results. The Weiss constant is approximately given by \(k_B \theta_W = -J_1 + 2J_2 - 2J_3\), thus \(\theta_W = -31\) K is in good agreement with the experiment. Our value of \(J_1 = 23\) cm\(^{-1}\) is somewhat smaller than \(J_1 = 34\) cm\(^{-1}\) estimated in \([6]\) and we obtain \(J_1 \gg J_2, J_3\) instead of \(J_3 \gg J_1, J_2\) as predicted in \([6]\). However our minimal model has no adjustable parameters and the result is consistent with the magnetization measurements.

Above the Néel temperature no magnon excitation is expected. We ascribe the peak around 35 cm\(^{-1}\) to local antiferromagnetic spin fluctuations, e.g. to excitations of locally ordered spins, which we identify as overdamped magnons. Above \(T_N\) the long-range magnetic order is thermally destroyed. Nevertheless, on a short-range scale spin fluctuations persist and can be excited by light. The fluctuations reduce the number of spins that respond to an external field and contribute to the susceptibility. Since the intensity of the overdamped magnons measured by Raman increases with cooling a deviation from linearity of the inverse susceptibility is expected. In spite of that the susceptibility is in agreement with the Curie-Weiss law almost down to \(T_N\) as can be seen in Fig. 2. Therefore we conclude that the fluctuations are emphasized by the resonant Raman response.

The microscopic origin of the \(T^{-1}\) dependence of the intensity of the fluctuations is not obvious. We suggest that the proposed charge redistribution in the unit cell at low temperatures which increases the ionicity of the bonds may enhance the superexchange interaction and hence the intensity of the fluctuations. On the other hand when the temperature is increased the giant dielectric response is observed and the intensity of the fluctuations drops. Assuming that the increase in \(\epsilon\) is due to a displacement of the \(\text{Ti}^{4+}\) inside the \(\text{TiO}_6\) octahedra one expects the fluctuations be disturbed if \(\text{Ti}^{4+}\) is essential for the superexchange interaction as is proposed in \([3]\). In this sense the increase of \(\epsilon\) with temperature is accompanied by a decrease of the fluctuations.

In conclusion, we have investigated the low frequency magnetic excitations of \(\text{CaCu}_3\text{Ti}_4\text{O}_{12}\) using Raman spectroscopy. Below the Néel temperature \(T_N = 25\) K magnetic excitations are identified as a three component two-magnon band. The exchange integrals are estimated within the framework of the Heisenberg interaction model. Short-range magnetic fluctuations well above \(T_N\) were observed to develop with cooling as \(T^{-1}\). A possible connection between dielectric and magnetic behavior is discussed.

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