Pergamon

Solid State Communications, Vol. 102, No. 8, pp. 599–604, 1997
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0038–1098/97 $17.00+.00

PII: S0038–1098(97)00027-6

TEMPERATURE DEPENDENCE OF RAMAN ACTIVE MODES IN $CuGeO_3$

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(*Received* 27 *November* 1996; *accepted* 9 *January* 1997 *by D.J. Lockwood*)

The Raman scattering spectra of $CuGeO_3$ were studied in a wide temperature range (20–300 K). Significant phonon frequency shifts were observed in the case of the A_g modes at 187 and 859 cm^{-1}, the B_{1g} mode at 224 cm^{-1} and the B_{3g} mode at 388 cm^{-1}. Only the mode at 859 cm^{-1} softens, while the remaining three modes harden with decreasing temperature. The asymmetry observed in the A_g symmetry phonon lines is interpreted as the interference of the phonon modes with the continuum excitations of magnetic origin. © 1997 Elsevier Science Ltd

Keywords: D. optical properties, D. phonons, E. inelastic light scattering.

1. INTRODUCTION

Copper-metagermanate ($CuGeO_3$) is the first known inorganic linear Cu^{2+} ($S = 1/2$) chain compound which exhibits a spin-Peierls (SP) transition [1]. Magnetic fluctuations in such a quantum system are of special interest due to the lack of long-range order and differ substantially from what one expects from a classical system. All the experimental results reported till now [2] strongly suggest that $CuGeO_3$ undergoes a true SP transition at $T_{SP} = 14$ K. However, no theoretical description of coupled lattice and spin fluctuations in the spin-Peierls case has been reported so far.

With respect to the magnetic susceptibility temperature dependence [1], one may define three temperature regions. Below T_{SP}, the system is in the dimerized (D) spin-Peierls phase. The temperature range above T_{SP} corresponds to the uniform antiferromagnetic phase (U) and the magnetic susceptibility has a broad maximum centered at $T_\chi^{max} \approx 60$ K. According to van Loosdrecht *et al.* [3], the U phase may be divided into two regions: $T_{SP} < T < T_\chi^{max}$ and $T > T_\chi^{max}$. In the first one, the short-range order (SRO) regime, the spin-wave continuum fluctuations dominate against the diffusive behavior of the magnetic excitations, which govern the magnetic susceptibility behavior at temperatures higher than T_χ^{max} [3].

In the high-temperature phase, i.e. above the transition temperature, copper metagermanate $CuGeO_3$ has an orthorhombic crystal structure with lattice parameters $a = 0.481$ nm, $b = 0.847$ nm and $c = 0.294$ nm, $Z = 2$ and space group $Pbmm$ [4]. The basic building blocks of the $CuGeO_3$ structure are corner-sharing GeO_4 tetrahedra that form chains along the c-axis. These chains are linked by Cu^{2+} ions. Each Cu atom is surrounded by six oxygen atoms, forming a strongly deformed CuO_6 octahedron. The alignment of these octahedra provides another sort of chain. These two types of chains run parallel to the c-axis of the crystal.

Complete assignment of Raman and infrared active modes for this compound in the U phase, including lattice dynamical calculations, has been published by us recently [5, 6].

Raman scattering spectroscopy of $CuGeO_3$ in the SP phase has been studied extensively [3, 7, 8]. Five additional A_g symmetry peaks, with respect to the U phase, were observed at 30, 107, 228, 370 and 818 cm^{-1}.

Recently, Loa *et al.* [9] have reported additional novel spectral features, in the A_g symmetry polarization configuration, inherent to the SP phase. They found a continuous background below 500 cm^{-1} with a sharp cut-off at 30 cm^{-1}. Based on symmetry properties, line-shape, peak positions and temperature dependence of the measured Raman spectra they assigned a newly observed mode at 17 cm^{-1} to the one-magnon excitation, while the modes at 30 and 230 cm^{-1} were described as two-magnon excitations. On the other hand, it is well known [10] that the two-magnon excitation is followed by a cut-off on the high-energy side. Considering all Raman scattering results reported till now one may infer that no high-energy cut-off exists in the vicinity of the 230 cm^{-1} mode. It is more likely that the two-magnon structure is superimposed on a broad continuous spectrum which peaks around 300 cm^{-1}. Besides, magnetic excitations in $S = 1/2$ Heisenberg chains are not governed by long-range ordering but by spin fluctuations [11]. In the SRO regime of the U phase the existence of the spin-wave continuum, characteristic of a uniform Heisenberg system, is evidenced by a broad structure observed in the spectra, while the quasi-diverging central peak observed in the $T > T_\chi^{\max}$ regime of the U phase clearly demonstrates a low-dimensional diffusive behavior of the spin fluctuations [3, 12].

It has been pointed out recently [13] that the continuum in the Raman scattering spectra in the uniform phase is caused by the creation of four spinon excitations, according to calculations using soliton mean field theory.

The present paper reports on polarized Raman scattering spectra in a wide temperature range, from above T_{SP} to room temperature. A significant frequency shift was observed in the case of A_g modes at 187 cm^{-1} and 859 cm^{-1}, B_{1g} mode at 224 cm^{-1} and B_{3g} mode at 388 cm^{-1}. Only the mode at 859 cm^{-1} softens upon temperature decrease. The observed asymmetry of the A_g modes is interpreted as an interference of the phonon modes with the continuum excitations of magnetic origin.

2. EXPERIMENT

The $CuGeO_3$ single crystals used in this study were cleaved from cylindrical crystals (6 mm in diameter and 8 cm long) grown from the melt by a floating zone method [14]. Single crystal samples used here were $1.5 \times 4 \times 3$ mm^3 in size, the orientation of the principal axes being obtained from conventional Laue photographs.

The Raman spectra were excited by the 514.5 nm line of an argon ion laser (average power was about 100 mW), focused on a line using a cylindrical lens. The geometry used was that of a quasi-back-scattering. Samples were held in a closed-cycle cryostat (Leybold), equipped with a low-temperature controller (Leybold LTC-60). The monochromator used was a Jobin–Yvon model U 1000 with 1800 groves per mm holographic gratings. As a detector we used a Pelletier-effect-cooled RCA 31034 A photomultiplier with a conventional photon-counting system. Experiments were carried out in the temperature range 20–300 K with a spectral resolution of 1 cm^{-1}.

3. RESULTS AND DISCUSSION

Figure 1 presents the polarized Raman spectra of two A_g modes, centered at 187 and 861 cm^{-1} (for the (cc) polarization configuration), a B_{1g} mode at 224 cm^{-1} and a B_{3g} mode at 388 cm^{-1} at three temperatures, 20, 50 and 300 K. Temperature dependencies of the phonon peak positions and the corresponding linewidths are given in the insets of Fig. 1. One can see that the A_g mode at 859 cm^{-1} softens, while the remaining three harden with decreasing temperature. The overall phonon energy change in the 20–300 K temperature range is $\Delta\omega \approx 2$ cm^{-1} for the A_g and $\Delta\omega \approx 4$ cm^{-1} for the B_{1g} and B_{3g} phonon modes. The first mode at 187 cm^{-1} originates from the in-phase vibration (along the c-axis) of the Ge and O atoms of the GeO_4-chains, while the second A_g mode at 859 cm^{-1} is the full-symmetric mode of oxygen vibrations in the CuO_4 square. The B_{1g} symmetry mode originates from the scissor-like oxygen atom vibrations, while the B_{3g} mode at 388 cm^{-1} comes from out-of-phase oxygen (O_2) atom vibrations in CuO_4 squares [5, 6].

Frequency shifts of other Raman active modes in the temperature range 20–300 K are of the order of $\Delta\omega \approx 1$ cm^{-1} for the A_g and B_{1g} modes and between 1 and 3 cm^{-1} for the B_{2g} modes [15]. It was observed that the A_g modes at 332 cm^{-1} and 594 cm^{-1} as well as the B_{1g} mode at 879 cm^{-1} soften while other B_{1g} and B_{2g} modes harden by lowering the temperature down to 20 K. Such temperature dependencies are in agreement with recent Raman scattering frequency vs temperature results [16].

In order to explain the temperature dependencies of the Raman active mode frequencies given in Fig. 1, calculations of the lattice dynamics were carried out using a shell model [6, 17] and crystallographic data on $CuGeO_3$ at 300 and 20 K [18]. The ionic charges, Z, of Cu and Ge atoms at 300 K (20 K) are 2.125 (2.132) and 3.956 (3.928), respectively. The other shell model parameters are given in Table 1.

Note that O_2 polarizabilities are assumed to be anisotropic according to the thermal ellipsoids discussed in detail in reference [18]. For the O–O short-range potential we use, as before [6, 17], $V = 22764\,e^{-6.741r} - 20.37/r^6$ and only the four nearest neighbors of each Ge ion in the Ge–O short-range interactions are taken into account. The measured and calculated Raman mode frequencies at 300 K and 20 K are given in Table 2.

As can be seen from Table 2, the change in the calculated phonon frequencies with decreasing temperature is the same as that found in the experimentally obtained ones, except for the B_{3g} mode. As stated before, the B_{3g} mode represents the out-of-phase vibration of O_2 atoms only. According to structural investigations [18],

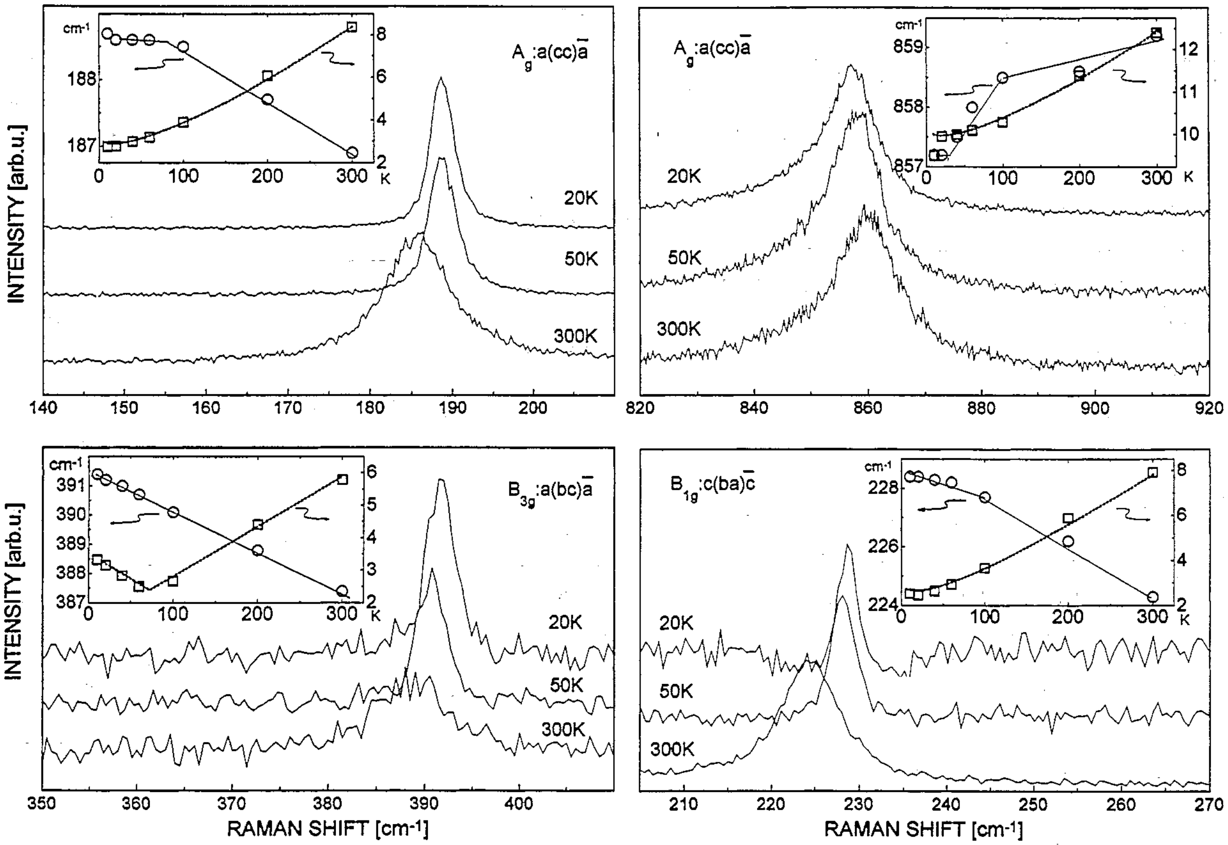

Fig. 1. Raman spectra of CuGeO$_3$ for 187 and 861 cm^{-1} (A_g), 224 cm^{-1} (B_{1g}) and 388 cm^{-1} (B_{3g}) phonon modes at three temperatures: 20, 50 and 300 K. Insets: Temperature dependencies of the phonon peak positions (circles) and the corresponding linewidths (squares); lines are a guide for the eye.

the O$_2$ atoms exhibit the largest displacements upon lowering of the temperature. Namely, on cooling the samples a rotation or twisting of the O$_2$–O$_2$ octahedron edges occurs accompanied by a translation of the tetrahedra. Such a behavior is probably due to the large vacant space in the unit cell resulting in its strong sensitivity to temperature changes, while the magnetic interaction itself may be responsible for this anharmonic structural behavior too. From the frequency dependence of the B_{3g} mode (inset of Fig. 1), no connection with the magnetic interaction is observed. On the other hand, the linewidth temperature dependence of this mode maps very well the magnetic susceptibility temperature dependence [1], indicating that the anharmonic structural behavior of the O$_2$ ions, at least in part, has a magnetic interaction origin.

Besides the line shifts given above, we noticed an anomaly in the phonon line shape of the A_g symmetry modes. The observed asymmetry suggests a Fano type coupling [19] to the magnon-like continuum of states. The line shape for such a coupled spin-phonon process can be expressed as $I(\omega) = I_c(q+\epsilon)^2/(1+\epsilon^2)$, where I_c represents the scattered intensity of the uncoupled continuum, q is the Fano parameter denoting spin–phonon

Table 1. Shell model parameters for CuGeO$_3$ ($\alpha_\perp$, $\alpha_\parallel$ are the O$_2$ polarizabilities perpendicular to and along the Cu–O$_2$ bonds, Y represents the shell charges and a and b are the parameters of the short-range Born–Mayer–Buckingham potential)

Ion	α (cm^3)	$Y \mid e \mid$	Ionic pair	a (eV)	b (Å^{-1})
Cu	1.2	3.00	Cu–O$_1$	565	2.82
Ge	0.1	2.00	Cu–O$_2$	1990	3.62
O$_1$	3.5	−3.2	Ge–O$_1$	4060	3.78
O$_2$	$(3.5)_\parallel$ $(1.3)_\perp$	−3.2	Ge–O$_2$	3680	3.85

Table 2. Measured and calculated (in parentheses) Raman mode frequencies (in cm^{-1}) at 300 and 20 K

Mode	$T = 300$ K	$T = 20$ K
A_g	187 (200.85)	189 (201.48)
B_{1g}	224 (226.95)	228 (228.65)
B_{3g}	388 (390.04)	392 (389.73)
A_g	859 (855.15)	857 (853.41)

coupling and $\epsilon = (\omega - \omega_0)/\Gamma$, with ω_0 being the unperturbed phonon frequency and Γ the linewidth parameter. The resulting line shapes were fitted with the least-squares computer fit using Γ and q as adjustable parameters. Results of the fitting procedure for the 187 and 859 cm^{-1} modes at several temperatures are shown in Fig. 2. The sign of q indicates that the interaction potential for the first mode is positive and is negative for the other. In Fig. 2, besides the fitting parameters, we also gave the sums of square differences for the cases of fitting by Fano as well as by Lorenz-type curves. It can be inferred that in all cases, the Fano profile fits the experimental points at least 10% better than the Lorenzian one.

Figure 3 illustrates temperature dependencies of the $(1/\Gamma q^2)$ quantity which is proportional to the density ρ of continuum states (see e.g. [20]). One can see that, in all A_g polarization configurations, ρ closely mimics the magnetic susceptibility of $CuGeO_3$ [1], i.e. it has the same broad extremum at around 60 K. The highest value of the density of continuum states is found in the (cc) polarization configuration that corresponds to the direction of the Cu^{2+}-chains. The same behavior was observed for the remaining two A_g modes, while in other polarization configurations the phonon modes have pure Lorentzian line-shapes. This is in complete agreement with the fact that magnetic excitations exist in the A_g configuration only [3, 7, 8].

Besides, our results are in agreement with Pytte's treatment of the Peierls instability in the Heisenberg chains [21]. Namely, in order to determine the temperature of the spin-Peierls transition, he treated a Hamiltonian that includes the interaction between a three-dimensional phonon and a one-dimensional magnetic system. He proved that the existence of this interaction in the antiferromagnetic phase is essential for the appearance of the spin-Peierls transition.

On the other hand, Müller *et al.* [11] have reported a

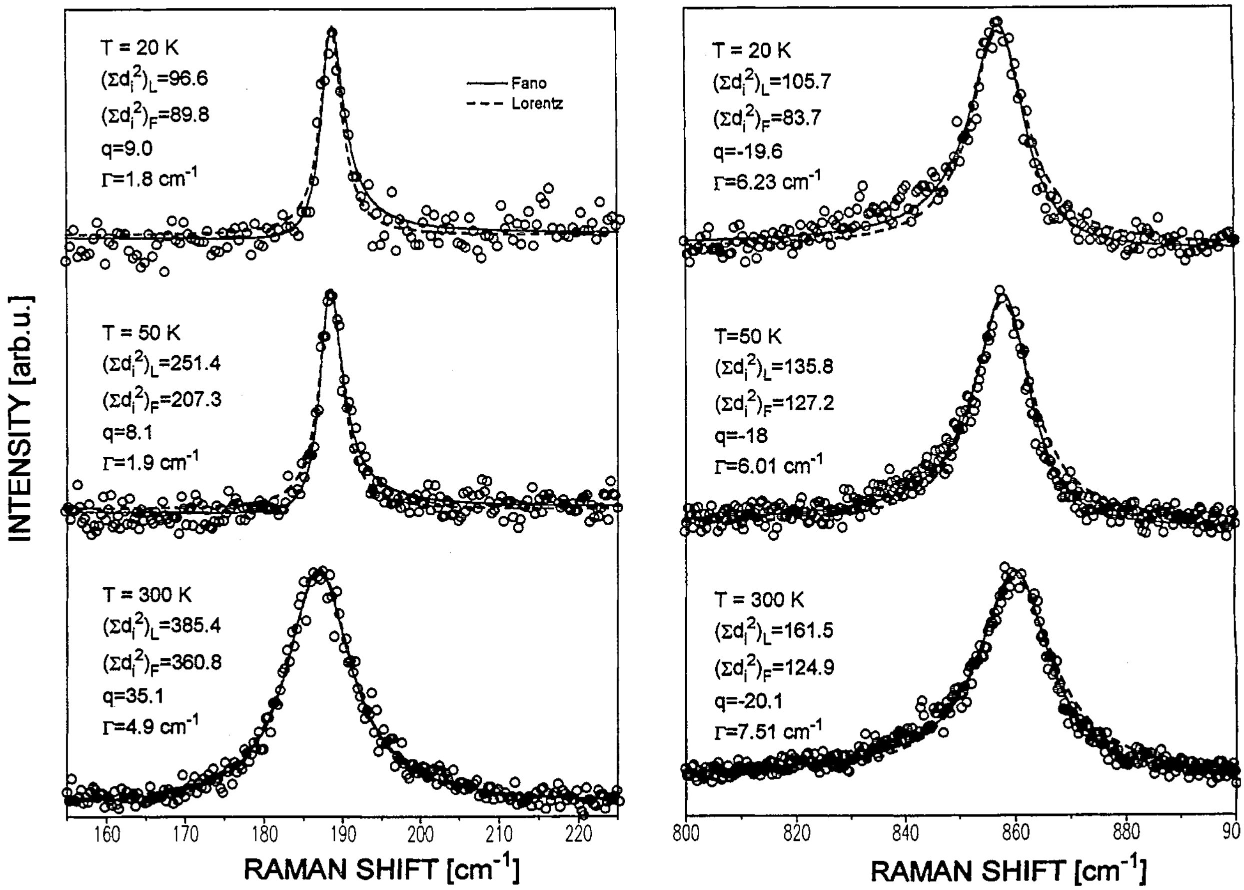

Fig. 2. Lorentzian and Fano shape fits of 187 and 859 cm^{-1} (A_g) Raman active phonon modes at several temperatures.

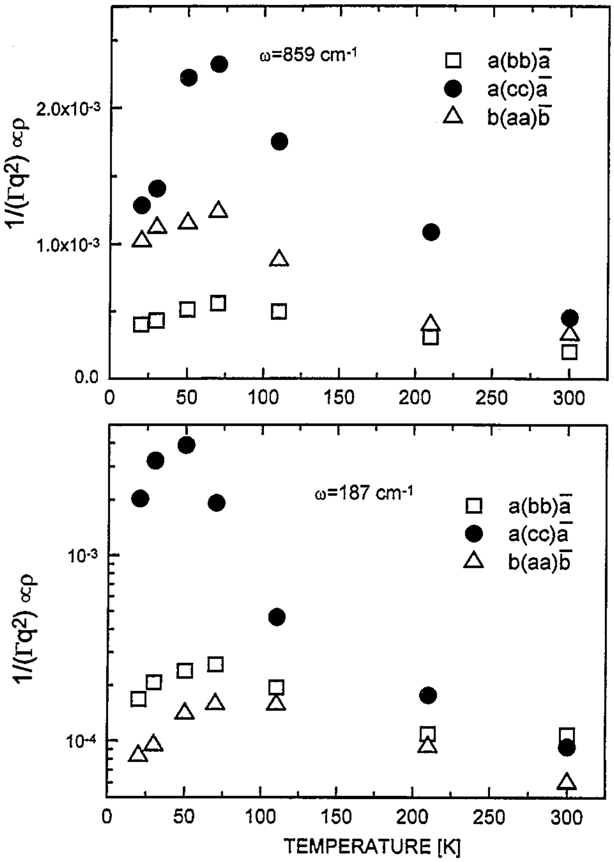

Fig. 3. Temperature dependencies of the ($1/\Gamma q^2$) quantity for different polarizations of A_g symmetry modes.

new approach to the spin dynamics of the same system which does not involve the many-body techniques usually employed. According to these authors, the dynamical two-spin correlation function in zero field is governed by a two-parameter continuum of spin-wave-type excitations.

The obvious asymmetry of all new Raman active modes in the SP phase and the appearance of a clearly Fano-shaped mode at 107 cm^{-1} are strong indications that such a phonon-spin wave interaction in CuGeO$_3$ really exists.

Based on these facts, we conclude that the asymmetry of the A_g modes originates from the phonon interaction with a continuum of magnetic origin.

To summarize, a significant shift in phonon frequency was observed in the case of the A_g modes at 187 and 859 cm^{-1}, the B_{1g} mode at 224 cm^{-1} and the B_{3g} mode at 388 cm^{-1}. Only the mode at 859 cm^{-1} softens, while the remaining three modes harden upon decreasing temperature.

The observed asymmetry of the A_g modes was fitted by Fano profiles. We showed that the temperature dependency, of the corresponding density of continuum states, ρ, closely mimics the susceptibility behavior of antiferromagnetic phase in CuGeO$_3$. The polarization configuration dependency of ρ is in agreement with the orientation of the antiferromagnetic chains. Our results are an experimental evidence for the existence of an interaction between 3D phonon and 1D magnetic systems, at temperatures above the transition temperature, which is essential for the appearance of the spin-Peierls transition.

Acknowledgements—We are grateful to Dr F. Vukajlović, Dr Z. Radović and Dr M. Konstantinović for useful discussions. This work was supported by the Serbian Ministry of Science and Technology under project E09. G.D. and A.R. thank NEDO for financial support.

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