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Isotope effects in CuGeO_3 studied by Raman spectroscopy

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Abstract

Effects of isotopic substitution of Cu and Ge in CuGeO_3 are studied by Raman spectroscopy. We present detailed information on the isotope-induced shifts of nearly all Raman modes in the dimerized phase of CuGeO_3 . Our study unambiguously reveals phononic contributions to the asymmetric Raman peaks observed at 108 and 228 cm^{-1} which have been related to magnetic excitations previously. Furthermore, we observed an upshift by $0.9 \pm 0.1 \text{ cm}^{-1}$ for the two-magnon bound state at 30 cm^{-1} in $^{65}\text{CuGeO}_3$ compared to $^{nat}\text{CuGeO}_3$. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Being the first inorganic spin-Peierls (SP) compound, CuGeO_3 has attracted much theoretical and experimental attention for the last few years [1,2]. The SP effect denotes a magneto-elastic transition where a dimerization of quasi one-dimensional antiferromagnetic Heisenberg chains is driven by a gain in magnetic energy which overcompensates the energetic cost for the lattice distortion [3,4]. A vast amount of experimental data is available but the conclusions are partly contradictory. Many theoretical studies recently addressed the central issues of magnetic exchange interaction and spin–phonon coupling in CuGeO_3 from a microscopic point of view [5–8].

We present here a Raman study of isotope effects in CuGeO_3 . Samples containing the enriched ^{65}Cu and ^{70}Ge are investigated in comparison with CuGeO_3 containing the natural abundance of isotopes. We quantitatively report the peak shifts for most Raman modes of the dimerized phase of CuGeO_3 . The observed peak shifts reveal phononic contributions to Raman modes which have been controversially assigned to be of magnetic or phononic origin

previously. Our investigation also reveals an unexpected isotope effect of the Raman peak at 30 cm^{-1} which is currently interpreted as a purely magnetic excitation. Altogether we provide new experimental data on the lattice dynamics and the spin–phonon coupling in CuGeO_3 .

2. Experimental

Single crystals of CuGeO_3 with natural isotopic composition were grown from a 1:2 mixture of GeO_2 (99.99%, Heraeus) and CuO (Alfa, ultrapure) as described earlier [9,10]. Isotope-substituted samples with ^{65}Cu (enrichment >99%) and ^{70}Ge were grown on the basis of the respective isotopically purified metal oxides [11]. The $^{65}\text{CuGeO}_3$ crystals were of high optical quality. They were used before in a study of the isotope-dependence of the SP transition temperature T_{SP} determined from magnetization and specific-heat measurements [11]. The $\text{Cu}^{70}\text{GeO}_3$ samples had some inclusions (probably CuO flux), but they were well suited for Raman measurements. They showed, however, a small unintended doping with Si of about 1.5% [12] presumably from a contamination of the $^{70}\text{GeO}_2$. Doping with Si affects the phonon frequencies due to its smaller ionic radius compared to Ge. This leads to a contraction of the crystal lattice and consequently to a general increase of phonon frequencies. However, based on additional experiments on intentionally Si-doped samples

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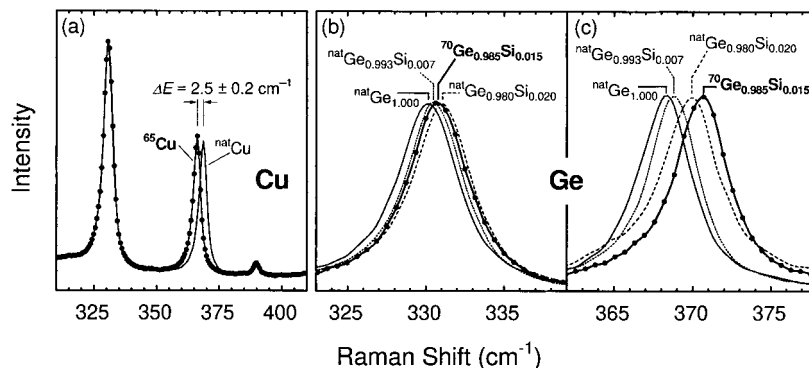


Fig. 1. (a) Raman spectra of $^{nat}\text{CuGeO}_3$ and $^{65}\text{CuGeO}_3$ ($T = 2$ K) illustrating the Cu isotope effect of the 368-cm^{-1} phonon. In the region of the 330-cm^{-1} phonon the spectra of both samples are identical. (b) and (c) Raman spectra showing the 330-cm^{-1} and 368-cm^{-1} phonons for samples with natural isotopic composition and Si contents of 0, 0.7 and 2.0% and a sample with ^{70}Ge and 1.5% of Si.

(Si contents of 0.7 and 2.0%; natural Cu and Ge isotopic composition) we are able to separate the ^{70}Ge -induced effects from those caused by Si-doping.

Raman spectra of CuGeO_3 were recorded in the back-scattering configuration using a triple-grating spectrometer equipped with a liquid-nitrogen-cooled CCD detector [13]. An Ar^+/Kr^+ laser was used for excitation at 514.5 nm at power levels of $5\text{--}10$ mW. Focusing of the beam down to a spot diameter of ~ 5 μm and collection of the scattered light was achieved by a $f/1.7$ photographic objective. The spectra of all samples were recorded at a sample temperature of 2 K, i.e. well below the SP transition temperature of 14 K. It should be noted that the set of

Γ phonons of the low-temperature dimerized phase includes all zone-center phonons of the ambient-temperature paramagnetic phase.

3. Results and discussion

A group theoretical analysis shows that there are no Raman active zone-center phonons with Cu contribution in the ambient temperature phase of CuGeO_3 [14]. This is fully confirmed by our experiment. There are two Raman peaks related to the dimerized phase of CuGeO_3 which show a ^{65}Cu -induced shift. Fig. 1(a) illustrates that the 368-cm^{-1} peak shifts to lower energies by 2.5 ± 0.2 cm^{-1} upon substitution of the natural Cu with the heavier ^{65}Cu . This value compares with an expected value of $\Delta\omega_{\text{max}} = 4.1$ cm^{-1} for a pure Cu-mode ($\Delta\omega_{\text{exp}}/\Delta\omega_{\text{max}} \approx 60\%$) based on a simple spring model. Thus, the eigenvector of this mode also contains a considerable contribution of oxygen and/or germanium displacement. The second peak showing a Cu isotope effect is the broad asymmetric excitation at 228 cm^{-1} , which will be discussed in detail later.

In order to elucidate the effect of Ge isotope substitution despite the unintended doping with Si, we investigated the Raman spectra of four samples: $^{nat}\text{Cu}^{nat}\text{Ge}_{1-x}\text{Si}_x\text{O}_3$ with Si contents of 0, 0.7, and 2.0%, and the isotope-substituted $^{nat}\text{Cu}^{70}\text{Ge}_{0.985}\text{Si}_{0.015}\text{O}_3$. From the first three samples we obtain for each Raman peak a relation between Si content and peak frequency. From these data we deduce, by linear regression, the peak frequencies for a sample with a Si content of 1.5%. Comparison of these results with the measured peak positions of the fourth sample yield the purely ^{70}Ge -induced peak shifts.

Fig. 1(b) shows Raman spectra of the phonon peak at 330-cm^{-1} for the four samples. The peak shifts towards slightly higher energies with increasing Si content, irrespective of the Ge isotopic composition. The ^{70}Ge -induced peak shift amounts to only 0.1 ± 0.3 cm^{-1} , obtained by the procedure

Table 1

Phonon shifts $\Delta\omega_{\text{exp}}$ in ^{70}Ge substituted CuGeO_3 . The values have been corrected for a Si doping of 1.5% (see text). Phonon frequencies ω refer to a sample with the natural abundance of isotopes. $\Delta\omega_{\text{max}}$ denotes the expected shift of a pure Ge mode

Frequency ω (cm^{-1})	$\Delta\omega_{\text{exp}}$ (cm^{-1})	$\Delta\omega_{\text{max}}$ (cm^{-1})	$\Delta\omega_{\text{exp}}/\Delta\omega_{\text{max}}$
108.0	1.1 ± 0.5	2.1	0.54
185.8	2.6 ± 0.3	3.5	0.74
226.3 ^a	1.1 ± 0.4	4.3	0.25
228.1 ^b	1.9 ± 0.3	4.3	0.44
368.3	1.1 ± 0.3	7.0	0.16
430.9	1.6 ± 0.5	8.2	0.20
568.3	1.7 ± 0.8	10.8	0.16
591.9	1.9 ± 0.7	11.2	0.18
712.5	1.4 ± 0.6	13.6	0.10
816.0	1.0 ± 0.6	15.5	0.06
114.3	0.3 ± 0.9	2.2	≈ 0
330.2	0.1 ± 0.3	6.3	≈ 0
389.7	-0.1 ± 0.3	7.4	≈ 0
855.4	-0.4 ± 1.2	16.3	≈ 0

^a Phonon with B_{2g} symmetry.

^b Broad asymmetric peak with A_g symmetry.

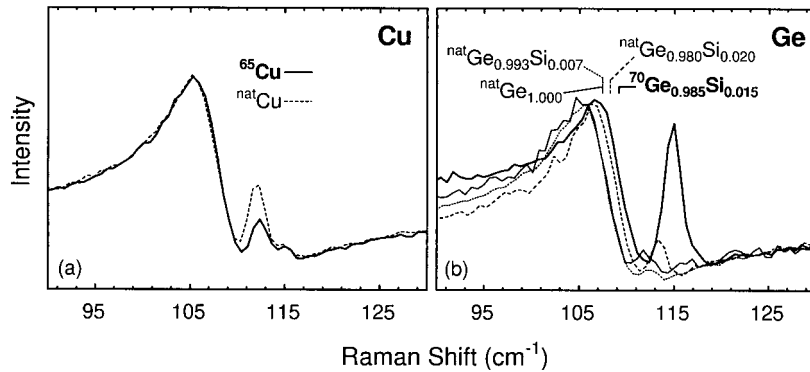


Fig. 2. Isotope effects of the 108-cm^{-1} Raman peak with Fano line shape upon substitution with: (a) Cu; and (b) Ge. Marked peak positions refer to the bare phonon frequencies according to fits with a Fano profile [12,28]. The peaks at 112 and 115 cm^{-1} originate from phonons with B_{3g} and B_{2g} symmetry, respectively.

described above. This value compares to 6.0 cm^{-1} expected for a pure Ge mode. Thus, the 330 cm^{-1} phonon has a negligible contribution of Ge displacement. Similarly, a very small or zero contribution of Ge displacement is deduced for the phonon modes at 114 , 389 and 857 cm^{-1} . Fig. 1(c) illustrates the ^{70}Ge -induced shift of the 368-cm^{-1} phonon. Here, the sample with ^{70}Ge exhibits the highest peak energy. The isotope-induced shift amounts to $1.1 \pm 0.3\text{ cm}^{-1}$ corresponding to 16% of the shift expected for a pure Ge mode.

Table 1 summarizes the ^{70}Ge -related frequency shifts in comparison with the expected shifts ω_{\max} for pure Ge modes. The low-frequency phonons at 108 and 186 cm^{-1} exhibit the largest isotope-induced shifts corresponding to Ge contributions of 54 and 74%, respectively. Many of the higher-energy phonons show a smaller ^{70}Ge -related shift as well, but on average the Ge-contribution to the eigenvector decreases with increasing phonon frequency.

Two spectral features in the Raman spectrum of CuGeO_3 are of special interest, namely the strongly asymmetric peaks at 108 and 228 cm^{-1} . The 108-cm^{-1} excitation

exhibits a pronounced Fano line shape [15,16]. It was originally attributed to a spectral feature in the two-magnon density of states [17]. Because of its Fano line shape it was later assigned to a phonon strongly interacting with the two-magnon continuum [15,16]. The latter assignment is supported by the observation of a phonon with similar frequency at the $(0.5\ 0\ 0.5)$ zone boundary of the high-temperature phase which should become a zone-center Raman active lattice vibration in the dimerized phase [18]. Fig. 2(a) shows that there is no significant shift of the phonon frequency upon isotopic substitution of the Cu. Substitution of the natural Ge with ^{70}Ge , in contrast, leads to an upshift of the phonon energy by $1.1 \pm 0.5\text{ cm}^{-1}$ as illustrated in Fig. 2(b). This amounts to 54% of the shift expected for a pure Ge mode. The absence of Cu displacement thus implies considerable oxygen displacement for the 108-cm^{-1} mode. We can therefore conclude unambiguously that the 108-cm^{-1} peak is of phononic origin and that its eigenvector is composed of Ge and O displacements. These findings agree with the results of shell model calculations by Braden et al. [7,18] which indicate vanishing

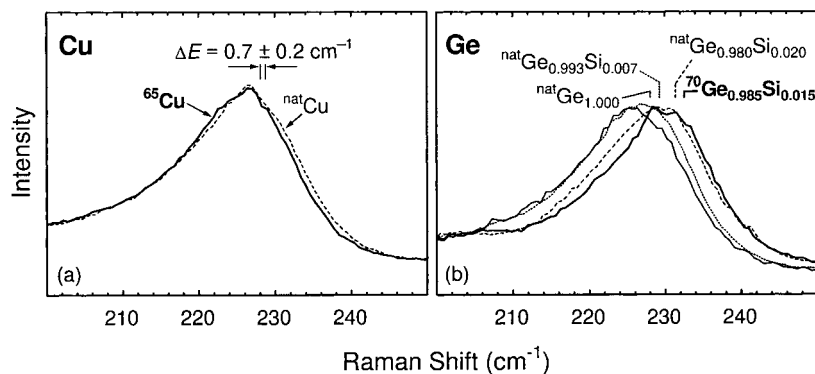


Fig. 3. Isotope effects of the broad asymmetric Raman peak at 228 cm^{-1} upon substitution with: (a) Cu; and (b) Ge. Marked peak positions refer to the bare phonon frequencies according to fits with a Fano profile [12,28].

Cu displacement but significant contributions of both Ge and O.

The 228-cm^{-1} excitation with A_g symmetry is characterized by an asymmetric line shape and a large peak width on the order of 20 cm^{-1} . In contrast to other Raman features related to the dimerized phase it can be observed up to temperatures of $\sim 35\text{ K}$ [16,19], i.e. well above the transition temperature of 14 K . Its energy is close to the upper boundary of the magnetic excitation continuum [20] and it was therefore generally attributed to a two-magnon excitation as was suggested first by Kuroe et al. [17]. However, based on inelastic neutron scattering data and the line shape of the Raman peak, van Loosdrecht and Braden et al. [18,21] recently suggested that the 228-cm^{-1} Raman peak should have at least partially phononic origin. Fig. 3(a) shows that the broad peak at 228 cm^{-1} shows a small shift of $0.7 \pm 0.2\text{ cm}^{-1}$ upon Cu isotope substitution. Ge isotopic substitution, however, leads to a larger shift of $1.9 \pm 0.3\text{ cm}^{-1}$ (Fig. 3(b)). It amounts to 44% of the shift expected for a pure Ge mode. This reveals a phononic contribution to the broad 228 cm^{-1} peak.

Finally, we studied a possible isotope effect of the low-energy excitation at 30 cm^{-1} close to the onset of the magnetic excitation continuum. This mode has been investigated in numerous experimental and theoretical studies and can be attributed to a two-magnon bound state [5,17]. Fig. 4(a) shows that the *two-magnon bound state* exhibits an *upshift* by $0.9 \pm 0.1\text{ cm}^{-1}$ in the CuGeO_3 sample containing ^{65}Cu compared to that with natural Cu. This result is rather unexpected, as we shall see now. The energy Δ_s of the bound state is somewhat lower than twice the singlet–triplet excitation gap $2\Delta_t$, the difference being the binding energy. The ratio $R(\alpha, \delta) = \Delta_s/\Delta_t$ depends on the frustration parameter $\alpha = J_2/J_1$ and the dimerization parameter δ [5]. J_1 and J_2 denote the nearest-neighbor and next-nearest-neighbor magnetic exchange constants. The field-theory prediction $R = \sqrt{3}$ [5], however, is close to the experimental value for CuGeO_3 of $R = 1.76$ ($\Delta_s =$

29.8 cm^{-1} , $\Delta_t = 2.1\text{ eV} = 16.9\text{ cm}^{-1}$ [22,23]). Furthermore, in the weak-coupling limit the SP transition temperature T_{SP} is proportional to the size of the spin gap: $\Delta_t = 1.765 k_B T_{\text{SP}}$ [3] which again is in good agreement with the experimental data. Altogether we find $\Delta_s \approx 3.1 k_B T_{\text{SP}}$ for CuGeO_3 . The effect of isotopic substitution of the Cu on the transition temperature has been studied before: there is a very small downshift of T_{SP} on the order of 0.1 K in $^{65}\text{CuGeO}_3$ compared to $^{\text{nat}}\text{CuGeO}_3$ [11]. Therefore, one should expect a *downshift* of the 30-cm^{-1} mode by $\sim 0.2\text{ cm}^{-1}$ but the experimental data clearly show an *upshift* by 0.9 cm^{-1} . For the weak soliton-bound state at 16.6 cm^{-1} [24–26], whose energy is closely related to Δ_t , the data do not indicate a significant Cu-isotope induced shift [Fig. 4(b)]. This is in agreement with the observation that T_{SP} is nearly the same in the two samples. These findings suggest that the anomalous shift of the 30-cm^{-1} two-magnon bound state may originate from a significant reduction of its binding energy ($\sim 20\%$) but not from a change of the spin gap itself. Fig. 4(b) shows that the intensity of the defect-induced excitation is significantly higher in case of the ^{65}Cu -containing sample implying a larger impurity concentration than for the sample with natural Cu. Experiments on intentionally Si and Zn-doped samples (at much higher concentrations [$>0.4\%$]) than in the present case) have shown that the one-magnon and, to a smaller degree, also the two-magnon state shift to lower energies with increasing doping concentrations [12,27]. The observed upshift of the two-magnon bound state in the sample with ^{65}Cu (and higher defect concentration) is therefore unlikely to originate from differences regarding the impurities in both samples. However, the observed upshift of the two-magnon bound state would represent an exceptionally large effect of isotope substitution and needs therefore be confirmed in further experiments, e.g. on ^{63}Cu -substituted samples. Bouzerar et al. pointed out that inclusion of dynamical phonons in the theory would renormalize the spin excitation spectrum and as a direct consequence also renormalize the ratio R [5]. Whether a

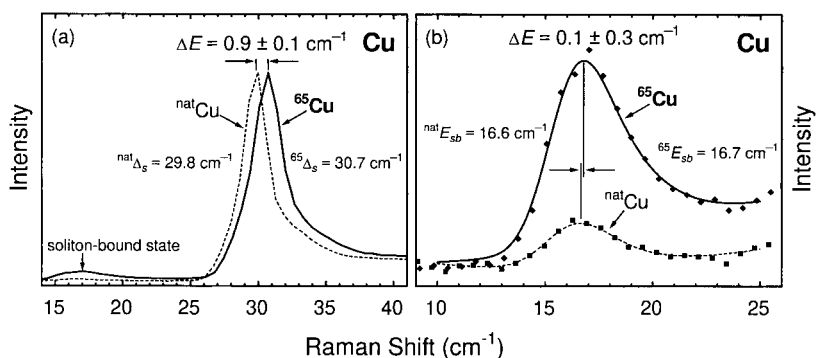


Fig. 4. Raman spectra of $^{\text{nat}}\text{CuGeO}_3$ and $^{65}\text{CuGeO}_3$ in the spectral regions of: (a) the two-magnon bound excitation at 30 cm^{-1} ; and (b) the soliton-bound state at 17 cm^{-1} . In (b) the symbols represent the experimental data and the lines are guides to the eye. The two-magnon bound state shows an unexpected upshift by 0.9 cm^{-1} .

theoretical description including dynamic spin–phonon coupling provides an explanation of the anomalous isotope effect of the two-magnon bound state in CuGeO_3 thus remains to be investigated.

In summary, we have presented a Raman study of Cu and Ge isotope effects in CuGeO_3 . The investigation provides new data for a detailed modeling of the lattice dynamics of CuGeO_3 which is crucial for an understanding of the SP transition. Our results unambiguously reveal phononic contributions to the asymmetric A_g Raman modes observed at 108 and 228 cm^{-1} which have previously been related to magnetic excitations. We have reported an anomalous isotope effect of the two-magnon bound state in CuGeO_3 which remains to be explained.

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