Electronic and Vibrational Spectra of $Ba_4NaCuO_4(CO_3)_2$ and $Ba_4LiCuO_4(CO_3)_2$

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The title compounds contain diamagnetic Cu(III) in nearly square planar CuO_4 units linked to each other by alkali ions. The optical and vibrational spectra were measured. A d–d transition at 12,000 cm^{-1} and a charge transfer transition at 22,000 cm^{-1} were observed, each having a large spectral band width. The Raman and infrared spectra were assigned according to a full factor group analysis and with the help of a two-dimensional vibrational analysis of the CuO_4A, where A = Na or Li, network. The electronic spectra are consistent with those of other $Cu(III)O_4$ compounds. © 1995 Academic Press, Inc.

INTRODUCTION

The compounds $Ba_4ACuO_4(CO_3)_2$, where A = Na or Li, containing copper in the formal oxidation state Cu(III) were recently synthesized by VerNooy and Stacy (1). They also determined the structure which was found to belong to the tetragonal space group $I\bar{4}2m = D_{2d}^{11}$ and the Na and Li compounds are isomorphous. The structure determination revealed the presence of isolated square planar CuO_4 units with four equal bond lengths. These squares are linked to Na (Li) ions through linear Cu—O—Na bonds to give a nearly planar network perpendicular to the crystallographic c-axis. The planes are linked by ionic bonds between oxygen and Ba ions which are arrayed in an irregular fashion. The carbonate ion exists as a nearly regular triangle centered about the carbon atom. One of the oxygen atoms of the carbonate group is bonded to sodium at a distance of 2.31 Å in a direction perpendicular to the NaO_4 plane, which has four bonds of 2.28 Å. Thus, the six oxygens form a nearly perfect octahedron surrounding Na. The compounds were also found to be diamagnetic, as required by the d^8 electron configuration of Cu(III) in this geometry. The synthesis produced single crystals in the form of flat plates having the c-axis perpendicular to the plate face. Because of the recent interest in high-temperature superconductors containing square planar copper ox-

ides, we have measured the electronic and vibrational spectra of both compounds and the results are discussed below.

ELECTRONIC SPECTRA RESULTS

Single crystals were mounted in a small cryostat which could be placed at the focus of microscope objectives used to condense the beam of a Cary 14 spectrophotometer. The near infrared spectrum at both 300 K and 77 K of both the Na and Li compounds are shown in Fig. 1. For the Na compound, there is a gradual rise in absorbance to a shoulder near 11,000 cm^{-1}, followed by a sharp rise at 12,000 cm^{-1}. The integrated intensity of this band from 5000 to 12,000 cm^{-1} gives an oscillator strength $f \simeq 10^{-4}$, a value compatible for a localized $d \rightarrow d$ transition of Cu(III). The absorbance of the Li compound is greater than that of the Na compound, and we were unable to prepare a sample sufficiently thin to record spectra at frequencies above about 8000 cm^{-1}. However, the threshold for the absorption is approximately the same for both compounds. In order to obtain spectra at frequencies greater than ca. 14,000 cm^{-1}, we prepared finely powdered samples of the Na compound dispersed in a KBr disk. The contrast was enhanced by using opalized glass scattering plates in both the sample and reference beams, and the measured absorbance is shown in Fig. 2. The estimated refractive index of the compound under study is $n = 6$, whereas that of KBr is approximately 1.5; thus, there is a considerable mismatch and the effect of pure scattering is appreciable. We observe a peak at 450 nm (22,000 cm^{-1}), and although we cannot quantify the absorption strength, the band is many times stronger than that of the IR band at 12,000 cm^{-1}. We interpret the 450-nm band as an allowed charge transfer band.

The spectra measured here are quite similar to those observed for Cu(III) in the bisperiodato-compounds (2). The crystal spectrum of $Na_5Cu(HIO_6)_2$ has a weak shoulder near 1.5 eV (12,000 cm^{-1}) and a strong maximum near 2.9 eV (24,000 cm^{-1}). The spectra may be interpreted using the molecular orbital analysis for square planar transition metal complexes (3). The shoulder near 1.5 eV is a d–d

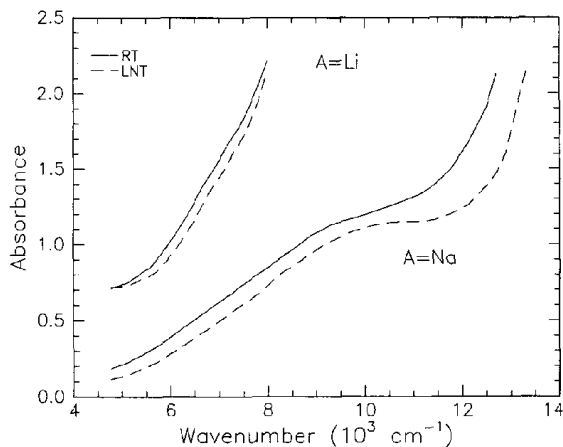[1] To whom correspondence should be addressed.

FIG. 1. Absorbance of $Ba_4ACuO_4(CO_3)_2$, where A = Na or Li in the near IR.

transition, and the 2.9 eV peak is a ligand-to-metal charge transfer band. There are three spin-allowed $d \rightarrow d$ transitions from the ground $^1A_{1g}$ state of the d-orbital configuration $(3z^2 - 1)^2(xz, yz)^4(xy)^2$ to the excited states $^1A_{2g}, ^1B_{1g}$, and ^1E_g, corresponding to transitions into the $(x^2 - y^2)$ orbital. The local coordinate system is that in which the plane of the square is in the xy plane with the Cu-O bonds along the x- and y-axes and the z-axis is perpendicular to the plane. In the present study, the crystals were mounted with the c-axis (and thus the local z-axis) parallel to the direction of light propagation; thus only perpendicular polarizations should be observed. However, we believe that the lowest energy symmetry-forbidden transition is made allowed by the e_u vibrations—to be discussed in the next section. The temperature dependence shown in Fig. 1 suggests a vibronic mechanism. Therefore, the low energy shoulder is assigned as the transition from the one electron
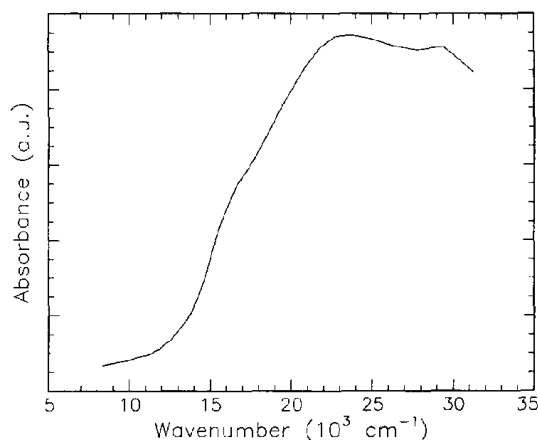

FIG. 2. Diffuse transmittance of powdered $Ba_4NaCuO_4(CO_3)_2$ dispersed in a KBr disk.

$3d$ nonbonding (xy) orbital to the $3d$ antibonding $(x^2 - y^2)$ orbital, corresponding to the state transition $^1A_{1g} \rightarrow ^1A_{2g}$. The width of this band is estimated to be 7000 cm^{-1}, surprisingly large even for a vibrationally allowed $d \rightarrow d$ transition.

According to the MO diagram (3), there are two allowed transitions, from the one-electron ligand b_{2u} and e_u π orbitals to the empty b_{1g} metal atom orbital. Both transitions should be observed in diffuse transmittance, however we observe only the lowest energy one.

VIBRATION SPECTRA

A vibrational analysis of the $Ba_4ACuO_4(CO_3)_2$ compounds, where A = Li or Na, is of particular interest because of the occurrence of square planar Cu—O networks in many high T_c oxide superconductors and the continuing discussion on the role of the phonons in the superconducting mechanism. We have done a full factor group and site group analysis of the $\Gamma = 0$ normal modes of the primitive cell of $Ba_4ACuO_4(CO_3)_2$, space group $D_{2d}^{11} = \bar{I}42m$. Excluding the acoustic modes, there are 51 modes, of which three are inactive A_2 modes. The IR allowed modes are B_2 and E and the Raman allowed modes are A_1, B_1, B_2, E. Treating the square planar CuO_4 group and the two CO_3 groups as molecules, there are 16 internal modes $(5A_1 + B_1 + 5B_2 + 5E)$. The rotational modes of these molecules are $2A_1 + B_1 + 3E$. The remainder are lattice modes $(2A_1 + A_2 + B_1 + 4B_2 + 8E)$, from which we should exclude the $B_2 + E$ acoustic modes.

The IR spectra were measured using a Nicolet FTIR instrument. In the region 50–675 cm^{-1} we used a fine powder of the sample dispersed in mineral oil pressed between two LDPE sheets. In the region 600–4000 cm^{-1} we used samples both dispersed in KBr disks and as single crystals in normal incidence reflectance, using a microscope attachment, from a platelike face, whose normal is parallel to the crystal c-axis. The Raman spectra were measured using an incident beam at a glancing angle from a single crystal plate face, and the scattered beam along the c-axis was collected, for both 458 and 488 nm radiation from an Ar ion laser. Because of experimental limitations on the mounting geometry, the small size of the crystals, and the irregular sized plate faces, polarized spectra with respect to the crystallographic axes were not done. In addition, the very strong absorption of the excitation radiation by the crystal limited the detection of Raman lines to shifts greater than about 200 cm^{-1}. There may also be interfering resonance Raman effects because of the strong absorbance at the laser excitation frequencies.

The IR spectrum from 50 to 750 cm^{-1} is shown in Fig. 3. We expected that the bands observed here would be due mainly to the square CuO_4 unit, and to assist in assigning the bands we carried out a vibrational analysis of
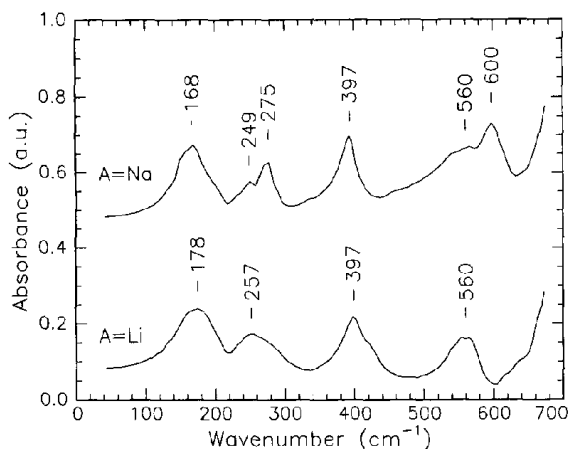
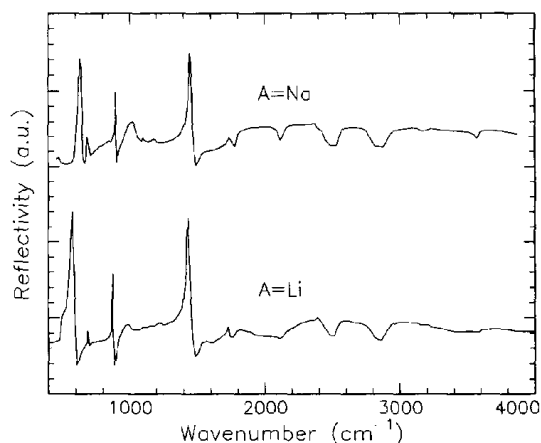FIG. 3. Far IR absorption spectra of the Na and Li compounds.

FIG. 5. Mid-IR reflectance spectra of the Na and Li crystals from (001) faces.

the $k = 0$ modes of a square planar $ACuO_4$ lattice, to be described below. The IR spectra at higher frequencies are shown in Fig. 4 for a mull sample and Fig. 5 shows the reflectance spectra of single crystals. In this region, 700–1500 cm^{-1}, we expected to see mainly CO_3^{-2} modes. Figure 6 shows the Raman spectra from 200 to 1500 cm^{-1} for both compounds. The assignment of the bands observed was aided by the symmetry analysis, by the normal mode analysis of the $ACuO_4$ square lattice, and by comparison with the spectra of other cuprates and carbonates.

The spectra in the far IR region for both the Na and Li compounds shown in Fig. 3 are similar. There are four bands which lie at approximately the same energy for each compound, although there is not a perfect match in the relative intensities of the bands. The two lowest energy bands for the Na compound are split and asymmetric and have average energies near 170 and 265 cm^{-1}. The lowest energy bands of the Li compound are centered at 170 and

257 cm^{-1}. The third band is similar for both compounds and lies at 397 cm^{-1}. The bands near 550–600 cm^{-1} are different for the two compounds; there are two distinct bands for the Na compound, a weak peak near 560 cm^{-1} and a strong peak at 600 cm^{-1}. For the Li compound, there is a single band at 560 cm^{-1} with an absorption minimum at 605 cm^{-1}.

Square planar CuX_4 with D_{4h} symmetry has three in-plane IR active bands, somewhere in the range 150 to 600 cm^{-1} (4). As the symmetry is lowered, additional bands may appear and the exact frequencies of the bands depend on both the symmetry and the force constants. There have also been numerous studies of the Raman and IR spectra of oxide superconductors which contain both square planar CuO_4 and linear $O-Cu-O$ chains in some cases. Depending on the compound and the crystal symmetry, seven
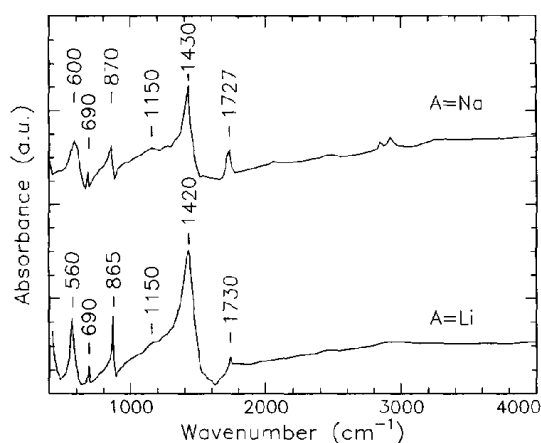

FIG. 4. Mid-IR absorption spectra of the Na and Li compounds diluted in KBr disks.
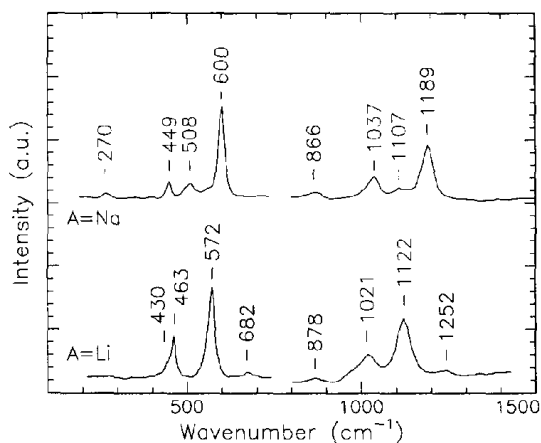

FIG. 6. Raman spectra of the Na and Li compounds. The spectra were recorded in two different spectral ranges, as indicated by the break, and the intensities of the two regions are not directly comparable.

TABLE 1

Observed Raman and Infrared Bands below 650 cm^{-1} and Calculated Vibrational Frequencies of a Square Lattice ACuO$_4$, Where A = Na or Li and f(Cu–O) = 1.65, f(Na–O) = 0.5, f(Li–O) = 0.15, f(O–O) = 0.05, and $r\alpha$(O–Cu–O) = 0.065, All in mdyne/Å

	A = Na		A = Li	
	Calc	Obs	Calc	Obs
Raman modes				
B_{1g}	195 cm^{-1}	270 cm^{-1}	195 cm^{-1}	—
B_{2g}	477	449	437	430 cm^{-1}
A_{1g}	488	508	449	463
	—	600	—	572
IR modes				
E_u	154	168	157	178
E_u	281	249, 275	273	257
	—	397	—	397
E_u	564	560, 600	532	560

or more bands lying in the 50 to 650 cm^{-1} frequency range have been found and attributed to Cu—O modes (5, 6).

In the present case we have isolated CuO$_4$ squares which are linked to AO$_4$ squares, where A = Na or Li, by a linear A-O-Cu link. This nearly planar oxide network is joined to another network by Ba—O bonds. In order to determine how the presence of the A-O-Cu link and how the mass change when A = Na or A = Li influences the modes of square planar CuO$_4$, we calculated the k = 0 modes expected for an idealized planar two dimensional lattice of ACuO$_4$. There are twelve modes for this planar lattice, three of which have zero frequency (two translation and one pure rotation). The nine internal modes are grouped as three IR active E_u and three nondegenerate Raman active modes. A modified Urey–Bradley force field was used with Cu—O stretch force constants ranging from 1.50 to 1.95 mdyne/Å (4, 6), the bending constant $r\alpha$(O—Cu—O) = 0.065, and f(O—O) repulsion of 0.05 was used. Several different force constants for Na—O and Li—O in the range 0.1 to 0.5 were used, and the calculated frequencies lie in the range 85 to 600 cm^{-1}.

The simplest approximation using nearly equal force constants for Na—O and Li—O gave a shift to higher frequency of the two lowest energy bands, whereas the highest energy band had only a small shift when Li was substituted for Na. In order to mimic the observed shifts between the Na and Li compound, we used f(Cu—O) = 1.65, f(Na—O) = 0.5, and f(Li—O) = 0.15. The Cu—O force constant is close to that deduced for a copper oxide superconductor (6), and the values of the Na- and Li-stretch were chosen to give a reasonable fit to the three in-plane E_u modes. The calculated frequencies for these force constants are given in Table 1.

There is not a perfect match between the calculated and observed frequencies, but the shifts between the Na and Li compounds are similar to those observed. The IR band observed near 397 cm^{-1} for both compounds is not given by the planar model, which only gives in-plane motion. There is an out-of-plane IR mode expected near 350 cm^{-1} for square planar CuO$_4$ (4), however, so we assign the 397 cm^{-1} band to this out-of-plane mode. We have not sought a better fit since the model ignores out-of-plane atoms and the Ba ions may be expected to contribute significantly to the low frequency modes, as was found for yttrium barium cuprates (5, 6).

The IR absorption spectra in the range 600–4000 cm^{-1} for both compounds are shown in Fig. 4, and the reflectance spectra are shown in Fig. 5. The reflectance is from a plate face which has the crystallographic c-axis normal to it, thus for normal incidence, the spectra should contain only E modes. The spectra are nearly identical for the two compounds. For the Na compound there are strong reflection maxima at 870 and 1430 cm^{-1}, with minima at 877 and 1475 cm^{-1} for the Li compound maxima at 865 and 1423 cm^{-1}, with minima at 877 and 1470 cm^{-1}. The spectra are characteristic of TO–LO lattice modes. There are also strong absorption maxima for the KBr disk samples at frequencies corresponding to the reflectance maxima in both cases. Typical frequencies and the assignments for the planar CO$_3^{-2}$ ion are shown in Table 2 (7). The peaks observed at 870 and 1430 cm^{-1} are thus assigned to ν_2 and ν_3; ν_4 appears as a weak, sharp band in absorption at 690 cm^{-1}.

The complex structure between the 870 and 1430 cm^{-1} bands seen in infrared may be related to the Raman bands which occur most strongly between 1000 and 1250 cm^{-1} (see Fig. 6). The Raman spectra in this region are quite different for the Na and Li compounds, although we had expected them to be similar, since the carbonate groups are nearly planar in both cases according to the structure determination (1). However, the two carbonate groups are coupled through a linear O$_2$C-O-A-O-CO$_2$ linkage, which could couple the CO$_3^{-2}A_1$ stretching modes to produce a pair of bands having odd and even phases of the two carbonate groups. Other carbonate modes would be

TABLE 2

Group Vibrational Frequencies for CO$_3^{-2}$ in D_{3h} and Observed Values for the Na Compound

	D_{3h} predicted		Observed	
	Selection rule	Nominal value	IR	Raman
$\nu_1 - A_1'$	R	1090 cm^{-1}	1085 vw	1037, 1107, 1189
$\nu_2 - A_2''$	IR	850	870 s	866 w
$\nu_3 - E'$	R + IR	1450–1500	1430 s	
$\nu_4 - E'$	R + IR	710	690 w	

less strongly coupled. The large mass and/or O–A–O force constant difference between A = Na or Li may account for the difference between the Raman spectra of the Na and Li compounds in the 1000 to 1200 cm^{-1} region shown in Fig. 6.

Of the eight distinct bands seen in Fig. 6 for the Na compound, three are distinctly asymmetric, indicating other weaker, unresolved Raman bands. The bands having energies less than about 600 cm^{-1} are internal CuO$_4$ modes with some contribution from the coupled Na (or Li) motion. The square planar lattice calculation discussed earlier predicted Raman lines at 195, 437–477, and 449–488 cm^{-1} leading to the two assignments shown in Table 1. We also observe broad peaks at 600 cm^{-1} for A = Na and at 570 cm^{-1} for A = Li (see Fig. 6). Bands having nearly the same frequencies are also seen in the corresponding IR spectra where they are assigned (Table 1) as E (modes). An E_u mode is Raman forbidden in the two dimensional planar model, but it is formally allowed in the crystal point group. The crystal structure showed only a small departure from planarity (1), however, and we cannot explain why this mode appears strongly in both the IR and Raman spectra.

The Raman bands at energies greater than about 650 cm^{-1} are primarily carbonate internal modes. The free ion-site group–space group correlation analysis gives $3A_1$ + $3B_2$ + $3E$ as the crystal modes for the two carbonate ions at the (4e) sites in Ba$_4$$ACuO_4$(CO$_3$)$_2$. All modes are Raman active and B_2 and E are infrared active. The free-ion carbonate modes, listed in Table 2, are all doubled due to the coupling discussed above and are formally Raman allowed.

Raman bands are observed near the frequency expected for ν_2, 866 for Na and 878 for Li. This is an out-of-plane carbonate mode which should be IR active only (see Table 2). Presumably we are seeing the in-phase component of the coupled carbonate pair in the IR at 870 cm^{-1} (Na) and the out-of-phase component in the Raman at 866 cm^{-1}. The nearly identical frequencies are in accord with the low Raman intensity. The Raman bands in the region expected for the A_1 carbonate mode, discussed above, are strong, as expected for such a mode, while the IR is weak. The Raman intensity for ν_3 and ν_4, the degenerate stretching and bending modes, are close to zero.

The temperature dependent electronic absorption between 5000 and 12,000 cm^{-1} is supposedly mediated by vibrational modes having E_u symmetry in a D_{4h} CuO$_4$ unit. The temperature dependence was not accurately measured, but the intensity increase between 77 and 300 K is estimated to be 10%. Using the relationship $f(T)/f(0)$ = coth $\hbar\omega/2kT$, one finds that the ratio of oscillator strengths at 300 K compared to at 77 K is 1.12 for $\hbar\omega$ = 600 cm^{-1} and 1.60 for $\hbar\omega$ = 300 cm^{-1}. This result shows that a E_u mode 600 cm^{-1} fits the data reasonably well, and in fact, such a frequency is observed in the IR spectrum as shown

in Table 1. This is a Cu—O stretching mode according to the vibrational analysis.

SUMMARY

We have measured the spectrum of Ba$_4$NaCuO$_4$(CO$_3$)$_2$ and Ba$_4$LiCuO$_4$(CO$_3$)$_2$ over the frequency range 50 to 25,000 cm^{-1}. The broad, distinct shoulder for the Na compound observed near 11,000 cm^{-1} is assigned as the vibrationally allowed b_{2g} to b_{1g} $d \to d$ transition. This shoulder lies on the low frequency side of a strong absorption band centered near 22,000 cm^{-1}, observed in powdered samples dispersed in KBr, which we assign as a spin and parity allowed ligand to Cu transition.

We can explain the observed 50–2500 cm^{-1} IR and Raman spectra as consisting primarily of frequencies expected for CO$_3$ ions and a square planar CuO$_4$ molecular ion, perturbed by its linkage to planar NaO$_4$ (or LiO$_4$) units. There are additional features which appear in the Li compound as prominent shoulders on the high-frequency sides of some of the CuO$_4$ bands, although there are no distinct bands which we can attribute to lattice modes. In general, we observe fewer bands than are predicted by the factor group analysis. This may be partly the result of using powdered samples, the limited resolution, and perhaps the use of only room temperature spectra. The assignment seems to be consistent with force constants typical for Cu(II), although the compound has Cu in the +3 oxidation state, and thus the force constant would be expected to be greater than for Cu(II). The force constants chosen for the Na—O and Li—O stretch in order to match the IR band positions are more suspect, and our simple model ignored the Ba—O interactions, which may be quite significant. Spectra having better resolution and calculations using a full three-dimensional normal mode analysis would be desirable.

ACKNOWLEDGMENTS

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