Superexchange via Cluster States:
Calculations of Spin-Phonon Coupling Constants for CuGeO₃

S. Feldkemper, W. Weber
Institut für Physik, Universität Dortmund, 44221 Dortmund, Germany
(November 22, 2013)

Calculations for spin-phonon coupling constants in CuGeO₃ are presented, applying fourth order superexchange perturbation theory to an extended Hubbard model. In our treatment, the intermediate oxygen ligand states are described by band-like cluster states, due to the presence of significant O(p)-O(p) hopping. We also include the effect of the Ge ions on the O ligand states.

We find a considerable q-dependence of the spin-phonon coupling. For the π-modes involved in the spin-Peierls transition, our results of the coupling constants are in fair agreement with the work of Werner, Gros, and Braden. Yet some discrepancies remain, especially concerning the coupling to the vibrations, which modulate the O(2)-O(2)-Ge angle δ. Our studies of the pressure dependence of the magnetic coupling constants J₁ and J₂ suggest, that relatively large non-linear effects are present, even at small pressure values, probably due to the existence of a ‘soft’, van-der-Waals-type bond direction in CuGeO₃.

I. INTRODUCTION

In recent years, the magnitudes and origin of the magnetic coupling constants of the quasi-one-dimensional quantum spin system CuGeO₃ have been subject of a variety of papers. In particular, the anti-ferromagnetic first nearest neighbor coupling J₁ is unusually small - believed to arise from superexchange hopping paths forming Cu-O(2)-Cu angles η close to 90°, which is the Goodenough-Kanamori-Anderson (GKA) criterion for vanishing anti-ferromagnetic superexchange.

Some authors have suggested that the hopping paths are strongly modified by the influence of the Ge atoms on the O(2) ions, because of the strong covalent ionic Ge-O(2) bonds. Other authors have obtained very strong variations of J₁ with the angle η; i.e., have predicted very large spin-phonon coupling constants in this system, in contradiction to estimates based on the data of the spin-Peierls transition.

Very recently, Werner, Gros, and Braden (WGB) have presented a detailed evaluation of experimental data, based on a variety of theoretical estimates, to derive the spin coupling to the four phonon modes involved in the spin Peierls transition. In particular, they find a strong coupling to variations of the angle η, and a relatively large coupling to the Ge displacements.

In the present paper we use superexchange perturbation theory to evaluate the spin coupling constants between the magnetic ions and their modulations with atomic displacements. Our method is an extension of earlier perturbative treatments. In particular, we include band-like oxygen ligand states, because there is significant direct O(2)-O(2) hopping in the chain. For our calculations, we start from a Hubbard-type Hamiltonian with five d-orbitals α, β per Cu site and p-orbitals at the O ligand sites. The full number of d orbitals at the Cu sites is considered in order to allow both for symmetry induced orbital mixing and for the possibility of ferromagnetic exchange coupling involving excited Cu d levels. On the oxygen sites, we include the splitting and mixing of the oxygen p-levels caused by the Coulomb fields of the adjacent ions, in particular by Ge.

The rest of the paper is organized as follows. In section II we discuss details of our model, in section III we first discuss our choices of model parameters and then present the results for the spin-phonon coupling constants and for the pressure dependence of J. Concluding remarks are given at the end.

II. DETAILS OF THE MODEL

The Cu atoms form a linear chain along the CuO₂ ribbons (see Fig. 1), where the oxygen atoms in the CuO₂ plane are labeled O(2), the apex oxygen atoms O(1).

We use a multi-band Hubbard-like Hamiltonian, where all electron-electron interaction takes place at the Cu site, for details see Ref. 9. We take five d-orbitals per Cu atom (sites i, orbitals α) and 3 p-orbitals (sites l, orbitals τ) per oxygen and use the hole picture. We allow p-d hopping $t_{i\tau}^{\alpha\beta}$ between Cu ions and next nearest oxygen atoms. Also, oxygen-oxygen hopping $t_{lj}^{\tau\tau'}$ up to third nearest neighbors is included. The Hamiltonian reads

$$H = \sum_{\alpha,\tau,\sigma} \epsilon_{\alpha\tau} \hat{n}_{\alpha\sigma}(i) + \sum_{l,\tau,\sigma} \epsilon_{l\tau} \hat{n}_{l\sigma}(l) + \frac{1}{2} \sum_{\tau,\tau',\sigma} V_{\tau\tau'}^{\tau\tau'} c_{\tau\sigma}(l)^{\dagger} c_{\tau'\sigma}(l) + \sum_{\alpha,\tau,\sigma} \left[ t_{il}^{\alpha\tau} c_{\alpha\sigma}(i)^{\dagger} c_{\tau\sigma}(l) + h.c. \right]$$
\[ + \sum_{l, l', \tau, \tau', \sigma} [t_{l l'}^{\tau \tau'} c_{\sigma \tau}^\dagger(l) c_{\tau', \sigma}(l') + h.c.]
\]
\[ + \frac{1}{2} \sum_{\alpha \beta} U_{\alpha \beta} c_{\alpha \sigma}^\dagger(i) c_{\beta \sigma}^\dagger(i) c_{\beta \sigma}(i) c_{\alpha \sigma}(i) \]
\[ - \frac{1}{2} \sum_{\alpha \beta} I_{\alpha \beta} c_{\alpha \sigma}^\dagger(i) c_{\beta \sigma}^\dagger(i) c_{\alpha \sigma}(i) c_{\beta \sigma}(i). \]  

\(\epsilon_i^\alpha \) and \(\alpha\) are the respective on-site energies of \(d\) and \(p\) orbitals. \(U_{\alpha \beta}\) and \(I_{\alpha \beta}\) are Coulomb and exchange interactions at the magnetic sites, respectively. In the atomic limit, the choice \(I_{\alpha \beta} < 0\) leads to the first Hund’s rule (maximum spin), the choice \(U_{\alpha \alpha} > U_{\alpha \beta}\) would lead to the equivalent of the second Hund’s rule (maximum orbital momentum). Electron-electron interactions at the ligand ions and between different sites are neglected. We will also use the approximation \(U_{\alpha \alpha} = U_{\alpha \beta} = U\) and \(I_{\alpha \beta} = J_H\). We note that although this Hamiltonian does not yield the correct atomic multiplet spectrum, it is sufficiently general for our perturbative approach. In particular, it incorporates the possibility for a competing ferromagnetic coupling of spins.

The main impact of the Ge atoms on the electronic structure is to cause a significant crystal field splitting of the oxygen \(p\) atomic levels. This effect is approximated by a crystal field \(V_{l^\tau \tau'}\) (including non-diagonal terms). Admixture of Ge \(4s, 4p\) hole states to the \(O\) \(p\) hole states appears to be rather small and thus is neglected here.

Changes of hopping integrals \((abr)\) due to variations of inter-atomic distances away from the equilibrium separation are considered using relations like \((abr) \sim (abr)_0 e^{2i(r_0 - r)}\), where \(r_0\) is the respective equilibrium distance.

The main difference to earlier perturbation theory calculations of spin coupling constants lies in the handling of the ligand ions. Usually, the ligands are treated in the atomic limit; i.e., only those hopping processes are considered, which occur along the spin exchange paths. Here we extend the method and include band-like ligand states. This extension is justified by the observation that O-O hopping integrals of considerable magnitude exist in the CuO2 ribbons leading to O(2) \(p\)-band widths of several eV. As we investigate the spin coupling for finite size CuO2 clusters, we actually deal with a finite number of O(2) cluster states instead of the complete set of band states.

Our calculations are carried out in a sequence of three steps. First, the oxygen cluster states are determined. As mentioned above, only O(2) \(p\)-orbitals are considered in the one-particle model. Input are O(2)-O(2) hopping integrals, bare O(2) \(p\)-orbital energies and the crystal field caused by the adjacent ions. The cluster states are then obtained by diagonalizing the cluster Hamiltonian, using up to 16 O(2) atoms and periodic boundary conditions. In a second step, environmentally adapted Cu one-particle levels are determined. This calculation is carried out by coupling the atomic Cu levels (which are fivefold degenerate) of a single Cu atom to the O(2) cluster and also to the apical O(1) atoms. Here, the additional input are the \(p\)-\(d\) level separation and the values of \(pd\tau\) and \(pd\pi\) hopping integrals. The coupling is calculated in second order perturbation theory and leads to an effective on-site \(d\)-\(d\) hopping matrix, which is then diagonalized. We note that a rather similar \(d\)-level ordering (with respect to both \(d\) character and separation) can be obtained using Coulomb-type ligand fields. In the third step, the adapted Cu \(d\)-levels are then used to calculate the spin coupling constants by usual fourth order superexchange perturbation theory, yet the Cu spins are transferred via the O cluster states instead of atomic ligand states. As the cluster (or band) states are delocalized, one might expect that the interaction between the magnetic sites decays rather slowly with distance.

This procedure yields all magnetic coupling constants from the same order of perturbation theory, irrespective of the range of the coupling. As we deal with delocalized ligand states, instead of atomic ligand states, hopping processes are included up to infinite order, in principle. Yet, this approach remains limited to the interaction of pairs of magnetic sites. It should finally be noted that each hopping path yields a certain amplitude, and a bilinear expression of such amplitudes leads to the value of the respective coupling constant. The hopping paths may be divided into two classes, one where the interacting spins meet at a magnetic site (the conventional picture of superexchange), and the other where they meet in a cluster state. The latter processes dominate, because of the presence of the many cluster states. Interference effects play a very important role, leading to some important consequences:

- They limit the range of coupling to essentially first and second nearest neighbors.
- The \(\pi/2\) destructive interference of the GKA rule is removed (actually shifted in angle). Thereby the crystal fields at the ligand sites, produced by the neighbor atoms (and modulated by their motion) play an important role.
- Electron-electron interaction at the ligand sites will also modify the interference; however, there does not appear a tractable way to include it into our perturbative approach.

Changes of atomic positions can be included easily in our calculations, this allows to determine the variations of the nearest and second nearest neighbor magnetic coupling constants \((J_1 \text{ and } J_2)\) with atomic displacements.

III. CALCULATION OF SPIN-PHONON COUPLING CONSTANTS
A. Model Parameters

We have performed the calculations using cluster sizes of twelve and sixteen oxygen ions and have used three different sets of parameters (A, B, C). The values of the parameters lie in the range of values discussed in the literature, e.g., for the hopping integrals we used values similar to those given by Matthiess. As our main goal is to investigate the reasonable range of spin-phonon coupling constants, we have chosen the model parameters to yield the standard values of $J_1 \sim 160$ K and $J_2/J_1 = \alpha \sim 0.3$. The model parameters are given in Tab. A. Set A describes a model without coupling of the Cu $d$ levels to O(1). Sets B and C include the Cu $d$ level coupling to the apex oxygens. For set C smaller O-O hopping parameters than in A and B have been used. The slight difference between O(2)-O(2) hoppings along $x$ and $z$ is incorporated by the $\beta$ parameters; i.e. by the distance dependence of $pp\sigma$ and $pp\pi$. We consider sets A and B as typical for CuGeO$_3$, while set C with its much smaller $pp\sigma$ value may indicate the range of variations possible with still physically rather meaningful hopping parameters.

The crystal field acting on the O(2) $p$ levels has been calculated using a point charge model with a shell of seven neighbor ions. These are O, Ge, Cu ions, where we assumed nominal ionic charges of $-2, +4, +2$, respectively and a dielectric constant $\varepsilon = 6$. For the calculation of the crystal field integrals, hydrogen-like $2p$ wave functions of the O(2) sites were used. At equilibrium separation, the monopole contribution ($l=0$) to the crystal field matrix was removed (as this term is incorporated in the value of the atomic energy $\epsilon_p$). The resulting crystal field splitting of the O(2) $p$ levels is given in Tab. A. We note that for atomic displacements, e.g., for the motion of the Ge ions, the monopole terms are included in the calculation of the spin-phonon coupling.

Tab. A shows the Cu $d^9$ hole energies for the three sets of parameters A, B, and C for 16 oxygen ions in the cluster. In all cases, including the spin-phonon calculations, the Cu $d^9$ ground state is predominantly of $xz$ symmetry, with very little admixture of the other $d$ orbitals. The $dz^2$ orbital is always lowered considerably, caused by the strong $pdl\sigma$ hopping between the $dz^2$ hole orbital and the oxygen-$p$ cluster states. All other $d^9$ levels are much less affected. Since for set C the $p$-$p$ hopping is considerably smaller than for sets A and B, the band width of the oxygen-$p$ cluster states is reduced and, as a consequence, also the $d$ level splitting. Experimental information on the positions of the excited Cu $d^9$ levels in CuGeO$_3$ is not known to us, a range between 1.5 eV and 3 eV appears to be reasonable. Our calculations of the magnetic coupling constants also include the spin hopping paths involving excited Cu $d^9$ levels. However, these contributions turn out to be negligible, both for ferromagnetic and anti-ferromagnetic exchange paths. As a consequence, the energy positions of the excited $d^9$ levels actually turn out to be irrelevant for the values of the magnetic coupling constants.

B. Spin-Phonon Coupling

The coupling constants in the equilibrium structure obtained with the three parameter sets A, B, and C are displayed in Tab. B. For all sets, the results for $J_1$ and $J_2$ are very similar. Typically, the difference between 12 and 16 site clusters is negligible. We have also determined values for $J_3$ and $J_4$, here we find $J_3/J_2 \sim 0.02$ and $J_4/J_3 \sim 0.1$. Therefore, we find only $J_2/J_1$ to be unusually large. If we further enhance the O(2) $p$ band width by using larger $p$-$p$ hopping integrals, for example, we find larger ratios $J_3/J_1$ and $J_4/J_1$, i.e. longer range coupling constants.

For comparison with the work of WGB we have calculated the spin-phonon coupling constants of the phonons involved in the spin-Peierls distortion. For this purpose we have determined the change of $J_1$ with respect to

(i) the motion of Cu along the crystallographic $c$ direction ($c = z$, see Fig. A),

(ii) the motion of Ge along $b$,

(iii) the motion of O(2) along $a$,

(iv) the O(2) motion along $b$.

Note that for (iii) and (iv) the two O(2) atoms bridging the Cu chains move opposite to each other. Also note that along the chain direction equivalent ions are displaced in alternating fashion ($a$-mode). Our values given in Tab. B include a factor 1/2, for comparison with WGB, who used a different normalization.

A linear transformation leads to the angular coupling constants $g_\eta$ (to the change of the Cu-O(2)-Cu angle $\eta$) and $g_\delta$ (to the change of the O(2)-O(2)-Ge angle $\delta$) and to the coupling to bond length variations $g_{Cu-O(2)}$ and $g_{Ge-O(2)}$ (see Tab. V). The coupling to the four Peierls-active phonons of $T_2^*$ symmetry can be obtained by another linear transformation, using eigenvectors of these modes as given by WGB (see Tab. V).

As we have used finite atomic displacements to determine the coupling constants of Tab. V, we have checked the accuracy of the linear transformation by directly inserting the angular and bond length variations to our program code. These results, also given in Tab. V, agree very well with the others.

Tab. V indicates that three of the four coupling constants are of similar magnitude. These are $g_{Cu-O(2)}^\delta$, $g_{O(2)}^\delta$, and $g_{O(2)}^\eta$. All three quantities depend on the change of both the Cu-O(2) bond length and on the O(2)-Cu-O(2) angle $\eta$, while $g_{Cu-O(2)}^\delta$ is mainly determined by the Ge-O(2) bond length variation. As evident from Tab. V, $g_\eta$ is much larger in magnitude than $g_\delta$ and is one of the dominant coupling constants in this system. This observation
also transforms to the result of the spin-phonon coupling constants of Tab. VII. Here, $q_1$ represents the coupling to the lowest-lying phonon mode, which mainly involves variations of the angle $\delta$. The coupling $q_2$ is particularly strong, to a large extend this mode incorporates $\eta$ angle distortions.

In Tab. VII, some spin-phonon coupling constants for $q_2 = 0$ displacements are given (now also including values for $J_2$, which are not accessible for $\pi$-modes). We observe a significant $\eta$ dependence of the $J_1$ coupling constant of order 15-30 %.

We note that the WGB results differ considerably from our calculations. The differences may be best discussed looking at Tab. VII. While the $g_\eta$ values agree satisfactorily, the $g_\delta$ values are larger by an order of magnitude in the WGB paper. The two other coupling constants $g_{Cu-O(2)}$ and $g_{Ge-O(2)}$ are comparable in magnitude, yet exhibit a different sign.

We have also determined values for the spin-Peierls temperature $T_{SP}$ using the same approach as employed by WGB. All our sets of coupling constants $g_i$ yield much smaller values of $T_{SP}$.

We presume that the difference in the results for $g_\delta$ is the key to the discrepancies. As the $\delta$-mode is the lowest-lying mode of the four Peierls active phonons, yet strongly involves bond-length and bond-angle $\eta$ conserving displacements of the light oxygen ions, we suspect strong anharmonic contributions especially to $g_\delta$. These contributions may show up as pseudo-harmonic in the WGB evaluation - thereby, via eigenvector sum rules of the harmonic problem, also effecting the other coupling constants. We note that our pressure results below also indicate the presence of non-linear effects, even at small pressures.

An earlier calculation of $g_\eta$ using exact diagonalization techniques performed by Braden et al. [14] has produced results for the spin-phonon coupling which are considerably larger than our results. The calculation was performed using a cluster of two Cu ions, two oxygen ions, and two Ge ions.

The biggest difference between our model and that of Ref. 13 is probably their use of an on-site interaction $U_p$ at the ligand sites. This interaction affects all spin hopping amplitudes (in our perturbative picture), it therefore reduces the interference effects leading to the GKA minimum. Additionally, there may exist a problem concerning the signs of the p-p hopping integrals. Using the model parameters of Ref. 13, we find reasonable agreement to our results only, if we change the signs of the p-p hopping integrals. (Note that our choice of sign is consistent - in the hole picture - with the assumption that the cluster states of predominantly $\sigma$ bonding type are lowest in energy.)

We have also determined the value of the exchange constant splitting $\delta_{SP} = |J_1^2 - J_2^2|/(J_1^2 + J_2^2)$, i.e. the difference between the nearest neighbor couplings in two adjacent cells in the dimerized phase. We find $\delta_{SP} = 0.012$. This is in good agreement with the results of Riera and Doby, who report $\delta_{SP} = 0.014$. Note that $\delta_{SP} \sim 0.012$ (together with $J_2/J_1 = \alpha = 0.32$, which is necessary to reproduce the spin gap $\Delta = 2.1$ meV).

C. Pressure dependence of $J_1$ and $J_2$

The distortions of the seven crystallographic parameters under pressure have been studied by various groups. [14] While the pressure data on $a$, $b$, and $c$ are quite well established, there are somewhat larger discrepancies in the results for the four internal lattice parameters such as the value $x$ for O(2). These data also show large scattering, especially at low pressures. Additionally, we note a relatively large sample dependence of the $p = 0$ crystallographic data.

We have used two approaches to incorporate the experimental data, especially those of Braden et al. [14] into our calculation:

(i) we use a linear interpolation

(ii) we allow non-linear dependence of the experimental data on pressure, using Murnaghan-type relations as previously proposed by Bräuninger et al. for CuGeO$_2$. [15] This is motivated by the existence of the ‘soft’ $b$ direction, where a van-der-Waals coupling dominates, see Fig. 4.

Our results depend strongly on the kind of interpolation of the experimental pressure data. The $p = 0$ gradients differ considerably (see Tab. XIII), especially affected are lattice constants involving the ‘soft’ $b$ direction. The resulting logarithmic derivatives of $J_1$ and $J_2$ with respect to pressure deviate by almost an order of magnitude, see Fig. 4. Yet, even using the linear approach, the variation of $J_1$ with pressure is rather non-linear.

For $\frac{\partial \ln J_1}{\partial p}$ we find -1.6 %/GPa for the linear interpolation and -10.7 %/GPa for the non-linear one. In Ref. 14 an experimental value of -8 %/GPa has been reported. For $\frac{\partial \ln J_2}{\partial p}$ we obtain 1.1 %/GPa (linear) and 9.6 %/GPa (non-linear). In a theoretical study using density matrix renormalization group techniques, Raupach et al. obtain $\frac{\partial \ln J_2}{\partial p} \sim 15 \%$/GPa (under the assumption $\frac{\partial \ln J_2}{\partial p} = -8 \%$/GPa and $\alpha \sim 0.3$). [15] WGB report a value of $\frac{\partial \ln J_2}{\partial p} \sim -6 \%$/GPa, however they extrapolate all coupling constants to the homogeneous deformation of the lattice from the four $\pi$-mode spin-phonon coupling constants, neglecting the $q$-dependence of the coupling.

In summary, our pressure results are based on an incomplete experimental data base. Nevertheless, there are indications that there exists a considerable non-linearity in the pressure dependence, even at small pressures, probably due to the ‘soft’ $b$-direction of the crystal.
In this paper we present results of calculations for spin coupling constants in CuGeO$_3$. In an extension of earlier work we have applied fourth order superexchange perturbation theory to a Hubbard-type model with five d orbitals at the Cu sites and three p orbitals at the O ligand sites. Because of the significant direct p-p hopping, delocalized O(2) cluster states have been used. In this way, hopping processes up to infinite order have been included, equivalent, in principle, to the RKKY treatment of the interaction of spin pairs in metals. In our treatment we also incorporate the effects of the Ge sites, which mainly cause splittings of the O(2) p levels and modulate them with atomic displacements.

Our main results are:

1. The largest contributions to the spin-exchange coupling constants arises from those hopping paths, where doubly occupied cluster states are involved. Doubly occupied Cu states are less important. Further, only processes involving the Cu d ground-state level contribute significantly, all processes involving excited Cu d levels can be ignored.

2. The range of spin coupling constants is limited to $J_1$ and $J_2$. Any longer distance coupling can be ignored for the range of parameters we used for our calculations. Increasing the oxygen band width (by increasing the p-p hopping integrals) leads to a longer range of the magnetic coupling.

3. The spin-phonon coupling constants show considerable q-dependence. The results for the $\pi$-modes are in satisfactory agreement with the values presented by WGB. There are, however, also significant differences, in particular, concerning the magnitude of the coupling to the angle $\delta$ (O(2)-O(2)-Ge). We have investigated a certain range of O(2)-O(2) hopping integrals (in limits which we believe are physically meaningful), yet we could not find significantly better agreement with WGB results.

4. Calculations of the pressure dependence of $J_1$ and $J_2$ yield very different results depending on the interpolation (either linear or non-linear) of the crystallographic data. The results using a non-linear interpolation agree much better with experimental data and other theoretical estimates of the pressure dependence of $J_1$ and $J_2$.

Although the crystallographic pressure data exhibit significant scattering, in particular for the internal lattice parameters, and further appear to be sample dependent to some extend, we think that the non-linear pressure dependence may, indeed, be a real effect. The CuGeO$_3$ lattice structure exhibits a ‘soft’ direction along the b axis with van-der-Waals-type bonding between the sheets containing the CuO$_2$ chains. Crystals with similarly anisotropic bonding, such as the spiral structures of Se or Te also show significant non-linearity in the pressure data. It would be highly desirable to have available improved crystallographic pressure data.

Non-linear, i.e. anharmonic behavior of certain phonon modes may also cause some of the discrepancies between our results on spin phonon coupling and those of WGB. A candidate for large anharmonicities is the lowest lying mode of the four phonon modes involved in the spin-Peierls transition. This mode mainly consists of O(2) displacements, which modulate the O(2)-O(2)-Ge angle $\delta$.

Finally, we should remark that some of the assumptions underlying our studies may be questionable. This does not so much concern the values of the model parameters - we think, we have studied a physically meaningful range. It concerns more the assumption that on-site interactions at the ligand sites can be neglected, since we find that doubly occupied cluster states are very important in the spin exchange paths. But note that there is also a dilution effect, as the extended nature of the cluster states reduces the impact of the on-site interactions. Unfortunately, this could not be quantified, since we do not see any simple way to include electronic interactions at ligand sites into our perturbative (cluster) treatment. Moreover, the magnitude of the interaction parameters are much less established than those for Cu$^{2+}$. Exact diagonalization studies are limited to a few Cu and O(2) atoms and also have to rely on estimates of the O(2) interaction parameters. Density functional theory calculations of $J_1$ and $J_2$ are hampered by the problem that the anti-ferromagnetic state is not the DFT ground state of the solid. In our view, the only way to improve the present level of quality in magnetic coupling calculations is to use ab initio quantum chemistry methods for small [CuO$_2$]$_n$ clusters, properly embedded.

In view of the above discussion we think that our method is a reliable tool for the calculation of magnetic coupling constants and related quantities such as spin-phonon couplings in relatively complex materials like CuGeO$_3$. The main advantage is that band-like properties of the system under consideration are taken into account. In addition, it allows to investigate the distance dependence of coupling constants in an easy manner.

ACKNOWLEDGMENTS

We acknowledge that part of the project has been supported by the Deutsche Forschungsgemeinschaft.
FIG. 1. CuO$_2$ spin chains (along z direction) with neighboring Ge atoms. z direction lies in the CuO$_2$ plane, y perpendicular to the plane. Also shown are the crystallographic axes $a$, $b$, and $c = z$. Hopping paths are denoted by the heavy, broken line for O-O hopping and the light, full line for Cu-O hopping. In addition, the broken line between O and Ge indicates the ligand field of the Ge ions.
FIG. 2. Dependence of $J_1$ on the Cu-O(2)-Cu angle $\eta$ for out of phase ($q_z = \pi$, full line) and in phase ($q_z = 0$, broken line) distortions of neighboring cells. At the minima around $84^\circ$ ($88^\circ$) $J_1$ is slightly negative, due to interference effects discussed in Ref. 5. The vertical line at $\sim 99^\circ$ indicates the equilibrium angle. The dot-dashed curve shows the results of Ref. 3.

FIG. 3. Dependence of the O(2)-O(2)-Ge angle $\delta$ on pressure. The symbols show the experimental values, the full (dotted) line shows $\delta(p)$ calculated from a linear (Murnaghan-like) fit to the experimental crystal parameters. 6
FIG. 4. Dependence of $J_1$ (upper part) and $J_2$ (lower part) on pressure. The squares (triangles) show the values of $J_1$ ($J_2$) calculated from the experimental structure parameters at the respective pressures. The full line shows $J_i(p)$ calculated from a linear fit to the experimental crystal data of Ref. 13, the dashed lines represent the $J_i(p)$ of the non-linear fit.

TABLE I. Parameter sets A, B, and C for CuGe$_2$O$_3$ in eV and eV/Å for $\beta$ parameters. Subscript 1 represents O(1), Subscript 2 represents planar O(2).

|   | $U$ | $J_{12}$ | $\epsilon_1$ | pd$\sigma_1$ | pd$\pi_1$ | pd$\sigma_2$ | pd$\pi_2$ | pp$\sigma$ | pp$\pi$ | $\beta_{pd}^\sigma$ | $\beta_{pd}^\pi$ | $\beta_{pp}^\sigma$ | $\beta_{pp}^\pi$ |
|---|-----|---------|--------------|--------------|------------|--------------|------------|------------|------------|-----------------|-----------------|-----------------|-----------------|
| A | 8   | -0.8    | -            | -1.2        | 0.4        | -1.0        | 0.4        | 1.5        | 2          | 2               | 2               | 2               | 2               |
| B | 8   | -0.8    | 3            | -0.35       | 0.4        | -1.2        | 0.4        | 1.5        | 2          | 2               | 2               | 2               | 2               |
| C | 8   | -0.8    | 3            | -0.08       | 0.4        | -1.2        | 0.4        | 0.6        | 1.5        | 2               | 2               | 2               | 2               |

TABLE II. Non-zero Crystal field matrix elements for O(2) p orbitals (in eV) from the point charge model described in Sec.III.

|   | $V_{xx}$ | $V_{yy}$ | $V_{zz}$ | $V_{xy}$ |
|---|----------|----------|----------|----------|
|   | -0.3     | +0.2     | +0.1     | -0.2     |

TABLE III. Energies of the symmetry adapted Cu d orbitals (in eV).

|   | $\epsilon_1^d$ | $\epsilon_2^d$ | $\epsilon_3^d$ | $\epsilon_4^d$ | $\epsilon_5^d$ |
|---|----------------|----------------|----------------|----------------|----------------|
| A16 | -3.5         | -0.4          | -0.1          | -0.1          | -0.1          |
| B16 | -3.6         | -0.8          | -0.5          | -0.4          | -0.1          |
| C16 | -2.4         | -0.8          | -0.5          | -0.4          | -0.1          |

TABLE IV. Nearest ($J_1$) and next nearest ($J_2$) neighbor exchange constants for CuGeO$_3$ (in K) for the sets A, B, and C and for O(2) cluster sizes of 12 and 16 oxygen atoms, respectively. In addition, the results using the zero pressure structural parameters of Ref. 13 are given (B16p).

|   | $J_1$ | $J_2$ |
|---|------|------|
| A12  | 163  | 168  |
| A16  | 159  | 158  |
| B16  | 174  |      |
| B16p | 48   | 49   |

TABLE V. Spin phonon coupling constants for different lattice distortions (in K/Å). The superscript labels the crystallographic directions a, b, c, the subscript labels the respective ion. For comparison, the result of WGB are also shown.

|   | $g_i^a$ | $g_i^b$ | $g_i^c$ | $g_i^{O(2)}$ |
|---|---------|---------|---------|--------------|
| $g_{C}^a$ | -271    | -278    | -274    | -319         |
| $g_{Ge}^b$ | 32      | 34      | 32      | 49           |
| $g_{O(2)}^a$ | 397     | 403     | 393     | 610          |
| $g_{O(2)}^b$ | 139     | 146     | 149     | 610          |

TABLE V. Spin phonon coupling constants for different lattice distortions (in K/Å). The superscript labels the crystallographic directions a, b, c, the subscript labels the respective ion. For comparison, the result of WGB are also shown.

| $g_i^a$ | $g_i^b$ | $g_i^c$ | $g_i^{O(2)}$ |
|---------|---------|---------|--------------|
| $g_{C}^a$ | -271    | -278    | -274    | -319         |
| $g_{Ge}^b$ | 32      | 34      | 32      | 49           |
| $g_{O(2)}^a$ | 397     | 403     | 393     | 610          |
| $g_{O(2)}^b$ | 139     | 146     | 149     | 610          |
TABLE VI. Coupling constants to angles and distances obtained from a linear transformation of the $g'$ (except $g_{dCu}^d$ and $g_{dGe}^d$, which have been calculated directly from the respective distortion pattern) in K/Å. For better comparison, the angular coupling constants $g_\eta$ and $g_\delta$ are also given in K/Å, where we related the change of $J_1$ with angle to the distance $d$ between the two outer ions defining the angle via $g_\phi = \frac{\partial J_1}{\partial \phi} \frac{\partial \phi}{\partial d}$.

| $g_i$ | A12 | A16 | B16 | C16 | WGB |
|------|-----|-----|-----|-----|-----|
| $g_\eta$ | 400 | 407 | 395 | 566 | 708 |
| $g_\delta^d$ | 413 | 406 | 582 |
| $g_\delta$ | -15 | -16 | -0.2 | -5 | 224 |
| $g_{dCu}^d$ | -48 | -48 | -114 | 180 |
| $g_{dGe}^d$ | -48 | -47 | -116 |

TABLE VII. Coupling constants $g_n, n = 1, 2, 3, 4$ (in K) of the four Peierls-active modes.

| $g_i$ | A12 | A16 | B16 | C16 | WGB |
|------|-----|-----|-----|-----|-----|
| $g_1$ | -1.5 | -1.5 | -2.2 | -1.6 | -15 |
| $g_2$ | 26 | 26 | 26 | 35.9 | 58 |
| $g_3$ | -8 | -8 | -8 | -8.2 | -30 |
| $g_4$ | -22 | -22 | -21 | -34.1 | -12 |

TABLE VIII. Spin phonon coupling constants of $J_1$ and $J_2$ (in K/Å) for the ($q_z=0$) displacements, using set B16.

| $g_{O(2)}^a$ | $g_{O(2)}^b$ | $g_{Ge}^b$ | $g_\eta$ |
|--------------|--------------|------------|---------|
| $J_1$ | 258 | -180 | 56 | 460 |
| $J_2$ | -167 | 119 | 2 | 92 |

TABLE IX. Pressure gradients of the seven crystal parameters at $p=0$ from linear and non-linear fits to the data (in Å/GPa for a, b, and c and in 1/GPa for the internal lattice parameters).

| $a$ | $b$ | $c$ | $xGe/a$ | $xO1/a$ | $xO2/a$ | $yO2/b$ |
|-----|-----|-----|---------|---------|---------|---------|
| lin | -0.013 | -0.12 | -0.0045 | -0.0054 | -0.0053 | -0.0037 | -0.0015 |
| n-lin | -0.021 | -0.17 | -0.0044 | -0.0093 | -0.0062 | -0.010 | -0.0024 |
1 M. Nishi, O. Fujita, J. Akimitsu, Phys. Rev. B 50, 6508 (1994); G. Castilla, S. Chakravarty, V.J. Emery, Phys. Rev. Letters 75, 1823 (1995); Y. Mizuno, T. Tohyama, S. Mackawa, T. Osafune, N. Motoyama, H. Eisaki, S. Uchida, Phys. Rev. B 57, 5326 (1998)
2 J. Riera, A. Dobry, Phys. Rev. B 51, 16098 (1995)
3 W. Geertsma, D. Khomskii, Phys. Rev. B 54, 3011 (1996)
4 K. Fabricius, A. Klümper, U. Löw, B. Büchner, T. Lorenz, G. Dhalenne, A. Revcolevschi, Phys. Rev. B 57, 1102 (1998)
5 M. Braden, G. Wilkendorf, J. Lorenzana, M. Aín, G.J. McIntyre, M. Behruzi, G. Heger, G. Dhalenne, A. Revcolevschi, Phys. Rev. B 54, 1105 (1996)
6 J.B. Goodenough, Phys. Chem. Solids 6, 287 (1958); J. Kanamori, ibid. 10, 87 (1959); P.W. Anderson, Phys. Rev. 115, 2 (1959); P.W. Anderson, in G.T. Rado, H. Suhl (editors) Magnetism I, Academic Press, New York und London (1963)
7 The result of Riera and Dobry concerning the exchange constant splitting δ in the dimerized phase indicates a relatively small coupling to the angle η.
8 R. Werner, C. Gros, M. Braden, Phys. Rev. B 59, 14356 (1999)
9 S. Feldkemper, W. Weber, Phys. Rev. B 57, 7755 (1998)
10 L.F. Mattheiss, Phys. Rev. B 49, 14050 (1994)
11 The magnitude of the O-O hopping is supposed to be very similar to the O-O hopping in the cuprate planes.
12 B. Büchner, H. Fehske, A.P. Kampf, G. Wellein, preprint, condmat/9806022
13 M. Braden, B. Büchner, S. Klotz, W.G. Marschall, J.S. Loveday, M. Behruzi, G. Heger, to be published
14 S. Bräuninger, U. Schwarz, M. Hanfland, T. Zhou, R.K. Kremer, K. Syassen, Phys. Rev. B 56, R11357 (1997)
15 D.M. Adams, J. Haines, S. Leonard, J. Phys.: Condens. Matter 3, 5183 (1991); J. Haines, D.M. Adams, Phys. Rev. Lett. 77, 204 (1996)
16 F.D. Murnaghan, Proc. Natl. Acad. Sci. USA 30, 244 (1944)
17 B. Büchner, U. Ammerahl, T. Lorenz, W. Brenig, G. Dhalenne, A. Revcolevschi, Phys. Rev. Lett. 77, 1624 (1996); H. Takahashi, N. Möri, O. Fujita, J. Akimitsu, T. Matsumoto, Solid State Com. 95, 817 (1995); M. Nishi, O.Fujita, J. Akimitsu, K. Kakurai, Y. Fujii, Phys. Rev. B 51, 16098 (1995)
18 R. Raupach, A. Klümper, F. Schönfeld, preprint
19 R.M. Martin, T.A. Fjeldly, W. Richter, Solid State Com. 18, 865 (1976)