PHYSICAL REVIEW B VOLUME 42, NUMBER 7 1 SEPTEMBER 1990

Temperature-dependent lifetime of spin excitations in $R\mathrm{Ba_2Cu_3O_6}$ (R = Eu, Y)

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(Received 9 April 1990; revised manuscript received 20 June 1990)

We have measured the light scattering by spin-pair excitations in single crystals of $R\mathrm{Ba_2Cu_3O_6}$ (R=Y, Eu) for several polarization directions in the temperature range of 10–700 K. A strong broadening of the B_{1g} and an enhancement of the A_{1g} component is observed with increasing temperature. For all temperatures agreement between calculations and experimental light-scattering data has been obtained with J=810 cm^{-1} and a zone-edge spin-excitation damping Γ which changes from 184 ± 50 cm^{-1} (T=10 K) to 913 ± 100 cm^{-1} (T=600 K). We conjecture that spin-lattice interaction significantly decreases the spin-excitation lifetime.

The antiferromagnetism in the CuO_2 planes of the semiconducting modification of the high-T_c materials is of special interest for several reasons. First, a possible coexistence of magnetic moments at the Cu atoms and superconductivity may be of importance in order to explain the unusually high superconducting transition temperatures in those materials. Second, the antiferromagnetism of the cuprates itself offers many new, still unresolved problems because of the two-dimensionality, the spin $\frac{1}{2}$, and the high superexchange constant of around 100 meV. In that context, all kinds of interactions of and with the spin system are important for a better understanding of the behavior of the CuO_2 planes. Such interactions can be studied by observing the lifetime of the spin excitations (magnons) in scattering experiments involving either neutrons or photons.[1,2] One main question is whether the lifetime observed in those experiments is caused by intrinsic spin-spin interactions (i.e., magnon-magnon interactions) or takes place with other quasiparticles (phonons, excitons, etc.). So far, the interest has been focused mainly on the two-dimensionality and the spin-$\frac{1}{2}$ nature of the phenomena. In such systems quantum fluctuations become important and influence the ground state of the antiferromagnetic CuO_2 planes. It was shown[3] that such a ground state exhibits a spectral intensity of light scattering by spin-pair excitations distributed over a large frequency range.

In this paper we show that additional mechanisms exist which decrease the spin-excitation lifetime and broaden the B_{1g} two-magnon spectral feature. We present results of temperature-dependent light-scattering experiments on $R\mathrm{Ba_2Cu_3O_6}$ and quantitatively determine the short-wavelength spin-excitation damping. We compare these results with those for La_2CuO_4 at low temperature. Our measurements reveal significant contributions to the spin-excitation damping which is not intrinsic to the $s=\frac{1}{2}$ Heisenberg antiferromagnet. We have calculated the two-magnon component of the light-scattering spectra for various temperatures and found good agreement with the experiments if an additional, temperature-dependent damping of signal-magnon excitations is assumed. From model calculations of a simplified CuO_2 plane we have estimated the contribution of spin-lattice interaction to that additional damping. We conclude that this effect is strong enough to significantly decrease the spin-excitation lifetime and can explain differences between La_2CuO_4 and $R\mathrm{Ba_2Cu_3O_6}$ as well as the observed strong temperature dependence. This mechanism becomes strong in the high-T_c materials due to the unusually large exchange energy.

As intrinsic features of the nearest-neighbor Heisenberg system, the following properties are expected: (i) each energy (line position, linewidth, etc.) has to scale with the exchange energy J. This statement is rigorous. (ii) For $T<J$ only weak temperature effects are expected. (In the high-T_c compounds this is true even for $T>300$ K.) (iii) For a given exchange energy the Néel temperature of a quasi-two-dimensional system is strongly affected by quantum fluctuations. We have checked these points experimentally.

The experiments were performed on a flux-grown $2\times3\times0.05$ mm^3 $\mathrm{EuBa_2Cu_3O_6}$ single crystal and on a highly oriented $4\times1\times4$ mm^3 multicrystal stack of $\mathrm{YBa_2Cu_3O_6}$ prepared by the K_2CO_3 method.[4] The oxygen content in our samples was approximately 6.0 per formula unit and magnetic-susceptibility measurements indicated the antiferromagnetic phase transition to be at 430 K. The samples were mounted in good thermal contact to a heated metal block within an optical vacuum chamber or a closed-cycle cryostat. The Raman spectra were taken in nearly backscattering geometry, using a 488-nm Ar-ion line. The spectra were corrected for the response function of the system for all polarization directions. The composition, oxygen content, defects, etc., of the sample within the laser spot were monitored for all temperatures through the phonon spectrum which showed, up to 600 K, only the usual softening of about 2 cm^{-1} per 300 K. At temperatures higher than 700 K reversible processes occurred, due to oxygen rearrangement, and after long-time heating irreversible sample decomposition was observed. We found

the spin-excitation scattering to be very sensitive to the surface conditions; best results were obtained after annealing the samples in vacuum at 680 K for several hours. In order to avoid any systematic effect of a possible change of oxygen concentration the temperature-dependent spectra were taken from high to low temperatures.

Some of the experimental results are shown in Fig. 1 (dots). For clarity, the low-energy phonon structures have been removed. With increasing temperature the B_{1g} feature at around 2600 cm^{-1} decreases in height and broadens. Additionally, a broad background arises which strongly increases near the laser line. This increasing background is observed in B_{1g} as well as in A_{1g} geometry. Above the Néel temperature this background starts to decrease. We do not find any significant difference in the (xx) and $(x'y')$ high-energy spectra. For all temperatures no intensity was seen in the (xy) polarization and, except for a weak featureless background, no scattering in (zz) polarization. Very recently, a report on Raman spectra up to temperatures of 450 K has been submitted for publication by another group.[5] It is in agreement with our results. Below 300 K the temperature dependence is not pronounced as in the high-temperature region but on the high-energy side an asymmetric tail appears, which is not present in the high-temperature spectra. At 11 K the halfwidth [full width at half maximum (FWHM)] of the spin-excitation band turns out to be as large in the $YBa_2Cu_3O_6$ as in La_2CuO_4, although the exchange energy in the La compound is 20% larger than in $RBa_2Cu_3O_6$. We conclude that the width of the spin-excitation spectrum does not completely scale with the exchange energy. That might be due to sample inhomogeneities but then a temperature-independent broadening of the spectral features is expected. Since in $RBa_2Cu_3O_6$ the Néel temperature is about twice that of La_2CuO_4 quantum-fluctuation effects should be less important.

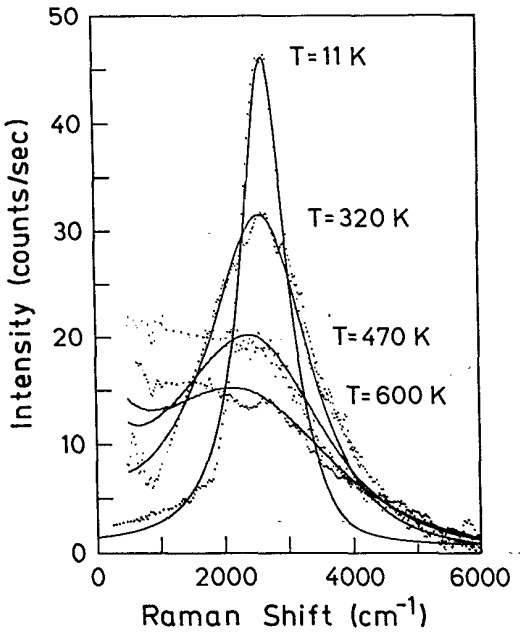

FIG. 1. Measured (dots) and calculated (solid line) two-magnon spectra of $EuBa_2Cu_3O_6$ for various temperatures. The experimental high-energy tails of the 11- and 320-K spectra merge.

A formalism for calculating the two-magnon Raman spectrum was worked out by Parkinson[6] and Elliott and Thorpe[7] for $T=0$. For finite temperatures the formalism has been improved by Balucani and Tognetti[8] and Wenzel and Wagner[9] using an expression originally derived by Davies, Chinn, and Zeiger.[10] This approach has given good agreement with experiments[8] even for the layered antiferromagnets K_2NiF_4 (Ref. 11) and K_2MnF_4 (Refs. 9 and 11) up to temperatures quite above the Néel temperature. The projection to boson operators is carried out by the Dyson-Maleev transformation, thus avoiding the usual $1/s$ expansion of the Holstein-Primakoff transformation. However, this transformation is still critical in the case of low spin, especially at higher temperatures. One can obtain an estimate of the expected validity by checking a critical parameter $c=n(E)/2s$ [$n(E)$ represents the magnon occupation number]. In the layered antiferromagnets[11] good agreement with the experiments has been obtained up to $c=0.05$ and, correcting for kinematical interactions by using magnon statistics,[9] agreement is extended up to $c=0.35$. For the $s=\frac{1}{2}$ high-T_c cuprates at $T=700$ K we expect reliable results for spin excitations above 300 cm^{-1}. Therefore, we mainly follow this approach and extend it for extrinsic interaction effects by introducing an additional phenomenological one-magnon damping, as suggested in Ref. 12. Neglecting the weak interlayer coupling, which will not affect the high-energy spin fluctuations mainly seen in Raman scattering, the part of the Hamiltonian intrinsic to the spin system is given by

$$H=J\left[\sum_{ij}\mathbf{S}_i\cdot\mathbf{S}_j-\Delta zS\left[\sum_i S_i^z-\sum_j S_j^z\right]\right], \tag{1}$$

where z, S, $\mathbf{S}$, and S^z are the number of nearest neighbors, the spin, the spin operator, and the z component of the spin operator, respectively. An anisotropy $\Delta(=4.37\times10^{-4})$ (Ref. 1) is still present and keeps the Néel temperature finite. We obtain a solution of Eq. (1) by Dyson-Maleev transforming to boson operators and taking into account higher magnon terms in second order,[8,9] including the Oguchi correction.[13] Because of intrinsic magnon-magnon interaction, the magnon energy E_k turns out to be complex and temperature dependent. The scattering intensity $I(\omega)$ is calculated[8-11] by extending the imaginary part of E_k with an additional damping Γ_k due to some extrinsic damping mechanisms,

$$I(\omega)=[n(\omega)+1]S^2\eta(T)^2\,\mathrm{Im}\frac{-L(\omega)}{1-JL(\omega)}, \tag{2}$$

$$L(\omega)=\frac{1}{N}\sum_k f_k^2(u_k^2+v_k^2)^2\frac{-2n(E_k)-1}{\hbar\omega-2E_k-2i\Gamma_k}. \tag{3}$$

The scattering intensity decreases in temperature with the square of the first order (Hartree-Fock) renormalization factor $\eta(T)$. u_k and v_k are the Bogoliubov coefficients. The symmetry factor f_k of the different scattering geometries was directly calculated from the nearest-neighbor interaction matrix element[14] $M_{ij}=E_iT_{ij}E_sS_i^-S_j^+$. Because of the special superexchange

mechanism[15] the nearest-neighbor scattering tensor T_{ij} only has components where dipole transitions along the nearest-neighbor directions are involved. Thus, for spins at a tetragonal site symmetry no scattering intensity in (xy) and any z polarization is predicted.

As shown in Fig. 1, a good fit to the experimental data has been obtained with $J=810$ cm^{-1} and a temperature-dependent one-magnon damping as displayed in Fig. 2 (triangles). The error bars are due to sample dependence and quality of the obtained fit to the experimental data. This one-magnon damping consists of the intrinsic magnon-magnon interaction (Fig. 2, curve *a*) and, mainly, of some additional extrinsic damping in agreement with the experimental findings. At low temperatures our calculations cannot reproduce the high-energy tail of the experiments. We assign this tail to four-magnon scattering which is completely neglected in our calculations. Usually, four-magnon scattering is expected at around twice the frequency of two-magnon scattering. Due to the additionally introduced one-magnon damping two- and four-magnon scattering can merge and form the asymmetric high-energy tail at low temperatures. This merging will not significantly change the low-order spectral moments as they have been calculated without an additional damping mechanism.[3] At higher temperatures one-magnon damping increases. This affects, in particular, the four-magnon contribution to the scattering which becomes a broad, featureless background without influence on the line shape of the two-magnon scattering. In the isotropic nearest-neighbor Heisenberg system for A_{1g} symmetry, the interaction operator commutes with the Heisenberg Hamiltonian and no scattering intensity can occur, although symmetry allows scattering from long-wavelength spin excitations. However, an anisotropy Δ and additional interaction mechanisms destroy that commutator rule and can induce A_{1g} scattering intensity. Although our theoretical treatment does not reproduce the zone center exactly, we qualitatively obtain at low energies a background in B_{1g} and A_{1g} symmetry which increases with temperature.[16] While the B_{1g} background intensity is caused by the strong damping of zone-edge scattering, the A_{1g} intensity arises mainly from zone-center excitations. Since the energy contribution to the whole Hamiltonian due to the anisotropy is quite small, the main effect should arise from additional interaction mechanisms.

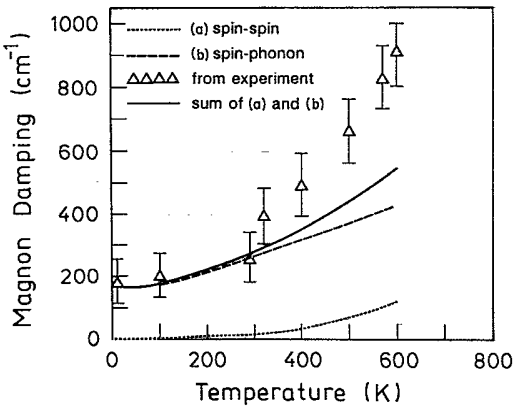

FIG. 2. Temperature-dependent damping of the zone-boundary spin excitations as obtained from the experiment (Δ) compared to contribution of intrinsic spin-spin interaction and spin-lattice interaction.

Such additional interaction could be the magnon-phonon interaction: the exchange energy J varies strongly with distance. These processes have been investigated theoretically by Cottam.[17] To first order a magnon is inelastically scattered by a phonon. In conventional antiferromagnets with spin-excitation energies less than phonon energies pseudomomentum and energy conservation of that process predicts a negligible contribution to the spin-excitation damping. In the high-T_c materials this situation has dramatically changed: the exchange energy is so high that the short-wavelength spin excitations have energies twice the maximum phonon energy. In that case pseudomomentum and energy conservation allow many phonons to contribute, a fact which increases the short-wavelength spin-excitation damping.

For the Cu—O—Cu superexchange of the CuO_2 planes we find that, by symmetry, only modulations of the Cu—Cu distance can contribute to the first-order magnon-phonon interaction (first derivative of J). Only in the $RBa_2Cu_3O_6$ materials the z motion of the oxygen can contribute by a small amount ($\sim 1\%$) because of the slight out-of-plane position of the oxygen. In order to estimate the contribution of the Cu motions to the zone-edge magnon damping, we consider a CuO_2 plane with only one Cu—O stretching spring constant. For that we can simplify the result of Cottam[17] if we consider only phonon creation processes

$$\Gamma \sim \left(\frac{a}{\pi}\right)\frac{4\pi S^2\hbar}{DM_{cv}\omega_0}(\nabla J)^2[1+n(T,\omega')]\,. \tag{4}$$

Comparing our model calculation with measured frequencies in the zone center,[15] we obtain $\omega_0 \sim 200$ cm^{-1} for the longitudinal acoustic frequency at the zone boundary. The magnon group velocity D at energies 200 cm^{-1} lower than at the zone boundary is taken from the calculated magnon dispersion with $D \sim 1000$ cm^{-1} per (π/a). Averaging over the Brillouin zone ω' was determined to be $\sim 0.8\omega_0$. The most critical parameter is the change of the exchange energy with Cu—O distance ∇J. Within the three-band Hubbard model the exchange J can be expressed[18] by t_{pd}, ϵ_{pd}, U_{pd}, and U_d with values[19] of 1.3, 3.6, 1.2, and 10.5 eV, respectively. An exchange energy of 0.136 meV is calculated, quite close to the experimental value. Assuming a Cu—O distance dependence of the hopping integral[20] $t_{pd} \sim r^{-7/2}$ and $U_{pd} \sim r^{-1}$ for the intersite Coulomb potential a value of $\nabla J = 0.946$ eV Å^{-1} is predicted. Scaling down to the exchange of 810 cm^{-1} found in our experiments we obtain $\nabla J = 5640$ cm^{-1} Å^{-1}. The only available experimental data are exchange energies from different cuprates[21] which give a ∇J in the range of 2500–6000 cm^{-1} Å^{-1}. From our measurement of zone-edge spin-excitation damping at $T=0$, a coupling constant $\nabla J \sim 5000$ cm^{-1} Å^{-1} is required in quite good agreement with the experimental estimates as well as with theoretical predictions. With that value the temperature dependence of the magnon-phonon interaction induced damping has been calculated (Fig. 2, curve *b*) and togeth-

er with the intrinsic spin-spin interaction (Fig. 2, solid line) most of the one-magnon damping found experimentally can be explained. It is not surprising that at higher temperatures the magnon damping increases stronger than calculated because of the neglect of higher-order magnon-phonon interactions and, maybe, an underestimate of the intrinsic magnon-magnon interaction. The difference between experiment and calculation, however, is in the same range as for phonon lifetimes in much better known substances such as Si and Ge.[22] Since this phonon-induced damping mechanism does not directly scale with J it is possible to observe the same halfwidth for La_2CuO_4 and $RBa_2Cu_3O_6$. However, our calculations of the magnon damping are only a rough estimate and there can also be contributions of other effects. We thus conclude that spin-lattice interaction is strong enough to significantly contribute to the spin-excitation damping in the high-T_c materials and can explain the temperature-dependent spin-excitation lifetime, which we found to range from 29 fsec ($T=10$ K) to 5.8 fsec ($T=600$ K).

We are indebted to many colleagues for valuable discussions and H. Hirt, M. Siemers, and P. Wurster for excellent technical help. We thank B. Friedl and U. Hohenester for assistance in some of the experiments and calculations and R. Reisser for magnetic susceptibility measurements. This work has been supported by the Alexander von Humboldt Foundation, the Austrian Science Foundation, the Bundesminister für Forschung und Technologie, and the European Community.

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