Possible mechanisms of magnon sidebands formation in transition metal compounds

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Abstract. In this short report possible mechanisms of magnon sidebands formation in transition metal compounds are shortly discussed. Besides the well known exchange electric dipole mechanism, suggested by Tanabe, Moriya and Sugano, recently a new the exciton-magnon absorption mechanisms assisted by phonons become actual. Special attention is paid to possible contribution of phonon-assisted electric dipole exchange transition in quasi-one-dimensional antiferromagnet KCuF$_3$.

1. Introduction
The presence of the magnetic excitations in infrared (IR) absorption spectra of antiferromagnetic (AFM) insulators have been the subject of intense experimental and theoretical studies that provided information on the spin dynamics in these materials. Often, a new experimental results in such compounds required a new theoretical approach which could more precisely describe the coupling of a photon with electron spins.

Optically active spin-wave excitations had been observed first in MnF$_2$ AFM [1]. The peculiarities of the sideband structure were understood on the basis exchange-induced electric dipole (EIED) mechanism suggested by Tanabe, Moriya and Sugano [2]. It is supposed weakly allowed electric dipole (ED) transition accompanied by spin-wave excitation due to effective ED moment coming from the second order of perturbation theory with off-diagonal exchange interaction giving the correct polarization [3] as well as integrated intensity [4] dependences of the sideband peaks in MnF$_2$. Moreover, they predicted direct two-magnon emission for the pairs of magnetic ions without inversion symmetry. The theory of two-magnon absorption was successfully applied to the rutile type iron group fluorides [5].

Perkins et. al. [6] reported optical measurements for a series of undoped single-crystal copper oxides: La$_2$CuO$_4$, Nd$_2$CuO$_4$, Pr$_2$CuO$_4$, and Sr$_2$CuO$_2$Cl$_2$. For all four compounds in the case of $\mathbf{E} \parallel \mathbf{CuO}_2$ layers the absorption spectra have common feature - the low-energy peak centered near 0.4 eV, which was subsequently attributed to the simultaneous excitation of two magnons (bimagnon) and an optical phonon. These features can be explained on the basis phonon-assisted multimagnon mechanism suggested by Lorenzana and Sawatzky [7]. Optical absorption in La$_2$NiO$_4$ [8] confirmed phonon-assisted bimagnon creation scenario but fails multimagnon one concerning a broad bands on the energy range 0.4 - 1 eV in La$_2$CuO$_4$. The similar bands were observed at 1.5 eV for both La$_2$CuO$_4$ and Sr$_2$CuO$_2$Cl$_2$. Perkins et. al. [9] have concluded...
that the origin of these bands can be treated as result of the exciton-phonon (magnon) sideband transition.

Experiments on near-IR optical absorption in KCuF$_3$ at 10 K [10] revealed two sharp spectral lines MD$_1$=8508 cm$^{-1}$ and MD$_2$=9774 cm$^{-1}$ accompanied by broad multiphonon band for both $\pi$ and $\sigma$ polarizations of incoming light. Each of these lines is followed by own good resolved magnon sideband structure which disappear as temperature increase towards $T_N$. Unlike the copper oxides gives clear evidence for the MD$_1$ and MD$_2$ transitions as well as neutron scattering study [11] allowed to assign sideband absorption as simultaneous creation a bare MD$_1$ or MD$_2$ exciton and magnons.

The conventional EIED mechanism, as it turned out, can not explain the observed low-energy sideband features but can be responsible to high-energy shoulders in absorption spectrum. The suggested exchange-induced magnetic dipole (EIMD) mechanism [12] explains the basic experimental observation concerning fine structure of phonon related absorption. However, an additional possible contribution the phonon-assisted mechanism has to be discussed.

2. Exchange-induced ED and MD transitions in KCuF$_3$

The perovskite structured KCuF$_3$ crystal is a quasi 1D AFM with the Neel temperature 39 K: Cu ions along the chain (parallel to $c$ axis) suffer strong AFM exchange interaction, while the interchain exchange coupling is a weak ferromagnetic $J_{\parallel}/J_{\perp} \simeq -0.01$. Each copper ion Cu$^{2+}$ (electronic configuration 3d$^9$, S=1/2) is surrounded by a distorted octahedron. Under local crystal field and spin-orbit interaction the ground term $^2$D splits into five doublets (see Fig. 1).

It is known that ED transitions between $d$ levels are parity forbidden since the copper ion in the center of inversion, whereas MD transitions A$_1$-A$_4$ (in the notation of [10]) are allowed. The orbital ordering is such that two unlike copper ion positions with the ground $d_{x^2-y^2}$ and $d_{y^2-z^2}$ orbital states of a hole persist. The last one is a result of rotation the former by $\pi/2$ about the $c(z)$ axis. Using a modern conceptions of the crystal field theory we have calculated the relative probabilities of the A$_2$-A$_4$ optical transitions per two copper ion positions [13]. The calculations show that probabilities of the A$_2$(MD$_1$) and A$_3$(MD$_2$) transitions are large with respect to A$_1$, A$_4$ and, what is more, the observed relative intensities for the MD$_1$ and MD$_2$ transitions in $\pi$ and $\sigma$ polarizations coincides qualitatively with calculated one.

The first two magnon sidebands appear at 88 and 114 cm$^{-1}$ that correspond to X[$\pi/a,0,0$] and M[$\pi/a,\pi/a,0$] low-energy singularities in the magnon density of states (DOS), respectively [12]. The other sidebands is due to multimagnon processes of the X and M magnons. Besides X,

![Figure 1](image1.png)

**Figure 1.** The energy level scheme of Cu$^{2+}$ ion in KCuF$_3$. The calculated energies of the A$_2$, A$_3$ transitions are 8897 and 10097 cm$^{-1}$, respectively [13].

![Figure 2](image2.png)

**Figure 2.** Virtual process scheme of the EIMD transition [12]. Solid arrows 1, 3 correspond to a hole hopping and dashed arrow 2 is referred to MD transition.
M singularities the DOS showed a huge high-energy peaks for the $Z[0,0,\pi/2c]$ and $R[\pi/a,0,\pi/2c]$ boundary points which were not observed experimentally.

Like KCuF$_3$ in the MnF$_2$ an exciton transition is MD allowed but sidebands have ED origin. For KCuF$_3$ the Hamiltonian corresponding to absorption on the $a$ site copper ion according to EIED scenario can be written as follows

$$H_{\text{eff}}^{\text{EIED}} = \sum_b \frac{J_{\parallel ab}}{t_{ab}} < \xi | \mathbf{E} \mathbf{d} | \varphi^t > [\mathbf{S}_a^\dagger \mathbf{S}_b - 1/4], \quad (1)$$

where $J_{\parallel ab}$ is a parameter of conventional superexchange coupling between the nearest neighbors copper ions in the ground $\eta$ and $\xi$ orbital states, $t_{ab}$ is an effective hopping integral, $\mathbf{E}$ - an electric field and, $\mathbf{d}$ is dipole moment required to a hole transfer from the $b$ site to the excited $\varphi^t$ orbital state of the $a$ ion. The asterisk in (1) denotes that the spin operator for the $a$ site is not a true spin operator because it has matrix elements between different orbital states.

We found that the matrix element in (1) is nonzero when the $\mathbf{E}$ is perpendicular to the $c$ axis for the MD$_1$ exciton and hence can contributes only in $\sigma$ polarization, whereas in the case of MD$_2$ exciton it is nothing for any direction of the $\mathbf{E}$. Performing the sum over copper spins and doing the Fourier transform like it explained in papers [3, 4] one finds that intensity of magnon sideband transitions is proportional to $\sin^2(k_z c)$. This factor vanishes at X and M points of Brillouin zone and therefore becomes clear way this mechanism is not effective at 88 and 114 cm$^{-1}$ in KCuF$_3$. These facts gave us the idea about MD nature of the magnon sidebands, i.e. EIMD mechanism.

The effective Hamiltonian had been derived in [12]

$$H_{\text{eff}}^{\text{MD}} = \frac{\mu_B}{2} \sum_b \frac{J_{\parallel ab}}{|\Delta_{ab}|} < \eta | \mathbf{H} \mathbf{l}_a | \varphi^t > [\mathbf{S}_a^\dagger \mathbf{S}_b - 1/4], \quad (2)$$

where $\mu_B$ is Bohr’s magneton, $\Delta_{ab}$ is the charge-transfer energy, $\mathbf{l}_a$ - a hole orbital momentum on the $a$ site and, $\mathbf{H}$ is a magnetic field. One of the virtual process scheme is shown in Fig. 2. The derived Hamiltonian gives a correct description of relative intensities at least for the first two sidebands in $\pi$ and $\sigma$ polarizations. The calculation of the absorption coefficient showed that not all singularities in DOS in magnon spectrum are responsible for observed sideband. After summation over nearest neighbors copper ions an important form-factor is appeared. In particular for KCuF$_3$, the singularities corresponding to X,M points in magnetic Brillouin zone remain active. Whereas the singularities related to Z and R points are filtered out by $\cos^2(k_z c)$ factor.

3. Phonon-assisted EIED mechanism

Like in paper [12] let us consider two exchange interacting Cu$^{2+}$ (3d$^9$) ions at the $a$ and $b$ sites with the ground $\eta$ and $\xi$ orbital states, respectively. One of the virtual process scheme on which we focus here is illustrated on Fig. 3. Firstly, the spin up of the hole from the $a$ center jumps to the $b$ center (arrow 1), while the spin down on the $b$ center via phonon induced effective $t_{\xi\lambda}$ hopping integral, excites the $a$ center to the electron-phonon product $|\lambda >= |\varphi^t > |\text{ph} >$ state (arrow 2), then due to coupling with electric field the phonon disappear and the spin down transfer to the $\varphi^t$ state (arrow 3). The effective Hamiltonian for all possible spin configurations of the two centers can be obtained in third order of perturbation theory.

The perturbation here is a phonon coupling to the electric field $\mathbf{E}$

$$F_{ph} = |e| \sum_{\lambda,\varphi^t} a_\lambda^+ < \lambda | \mathbf{E} \mathbf{u}_F | \varphi^t > a_{\varphi^t} + \text{h.c.}, \quad (3)$$
Figure 3. Spatial distribution of the ground $\eta$, $\xi$ (blue) orbital states and excited $\varphi'$ (red) orbital state in the $x = 0$, $y = 0$, $z = 0$ position of copper ions along the chain. Inset: virtual process scheme of the phonon-assisted EIED transition.

where $e$ is an electron charge and $u_F$ is vibration coordinate of fluorine bridge ion. Like in paper [12] using the canonical transformation method for $S$ operator one has

$$S = \sum_{\xi,\rho} \frac{t^\xi_{\rho'}}{|\Delta^\xi_{\rho'}}|b^\xi_a - \sum_{\rho,\xi'} \frac{t^{\rho}_{\xi'}}{|\Delta^{\rho}_{\xi'}}|a^\rho_b b^\xi_{\rho'}.$$

(4)

Here, summation is running over $\rho = (\eta, \lambda)$. The case of $\rho = \eta$ corresponds to conventional hopping between the ground states of copper ions (left hand side on Fig. 3), whereas the case of $\rho = \lambda$ is responsible to excitation the $a$ ion due to an effective $t^\xi_{\lambda} = \frac{\partial}{\partial u} u$ hopping integral as a result of displacement of the fluorine ion away from $c$ axis (right hand side on Fig. 3).

Using (3) and (4) for the effective Hamiltonian corresponding to absorption on the $a$ center we get

$$H^{\text{ph-ED}}_{\text{eff}} = |e| \sum_b \frac{t_{ab}}{|\Delta_{ab}|} \langle \lambda | E u_F | \varphi' \rangle \frac{t_{ba}(\lambda)}{|\Delta_{ba}(\lambda)|} [S^a S^b - 1/4].$$

(5)

Performing sum over neighbors copper ions and doing Fourier transform one arrives to form-factor $\cos(k_z c)$. Therefore, the singularities in DOS of magnon excitations, corresponding to X,M points in magnetic Brillouin zone are also active in this mechanism. Besides, from Fig. 3 it is clear that it contributes to total integral intensity when the external electric field perpendicular to the $c$ axis, i.e. in the $\sigma$ polarization.

4. Conclusion

We shortly have discussed the microscopic models of magnon sidebands transitions in low dimensional transition metal compounds. Two important points have been emphasized. Important role plays the $k$-dependent form-factor, which can filter out the contribution of exchange electric dipole mechanism for low frequency peaks in magnon density of state. Instead it the magnetic exchange dipole mechanism becomes relevant. Second - for correct description
of the origin of the magnon sideband transition the relative intensity analysis in different polarizations is very useful. The effective transition operator of phonon-assisted electric dipole mechanism has been derived. We found that it makes an additional contribution to low frequency magnon sideband in KCuF$_3$ in $\sigma$ polarization only.

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