

Optical spectroscopy of the Ni^{2+} -doped layer perovskites Rb_2MCl_4 ($M = \text{Cd}, \text{Mn}$): Effects of Ni^{2+} - Mn^{2+} exchange interactions on the Ni^{2+} absorption, luminescence, and upconversion properties

Oliver S. Wenger, Rafael Valiente,* and Hans U. Güdel†

Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, CH-3000 Bern 9, Switzerland

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Single crystals of Ni^{2+} -doped Rb_2CdCl_4 and Rb_2MnCl_4 are studied by polarized optical absorption and luminescence spectroscopy at 15 K. In $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$, Ni^{2+} - Mn^{2+} exchange interactions, which occur exclusively within the perovskite layers of this material, dramatically affect the absorption, luminescence, and up-conversion properties of Ni^{2+} for light polarized within the layers (σ): The Ni^{2+} ${}^3A_{2g} \rightarrow {}^1E_g$ and ${}^1A_{1g}$ ground-state-absorption (GSA) transitions are each enhanced by about an order of magnitude when compared to $\text{Ni}^{2+}:\text{Rb}_2\text{CdCl}_4$. Similarly, in $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$ the ${}^3T_{2g} \rightarrow {}^1T_{2g}$ excited-state absorption (ESA) as well as its reverse luminescence transition experience an intensity enhancement in their electronic origin region in σ polarization. One- and two-color up-conversion-excitation experiments show that, due to the in-plane exchange enhancement of the up-conversion-relevant GSA and ESA transitions in $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$, the near-infrared-(NIR) to-visible (VIS) up-conversion process at 15 K in this material is up to a factor of 55 more efficient for σ than for π -polarized excitation, and also one to two orders of magnitude more efficient than in $\text{Ni}^{2+}:\text{Rb}_2\text{CdCl}_4$ at the same temperature. The structural conditions for efficient Ni^{2+} - Mn^{2+} exchange interactions are discussed. The NIR-to-VIS up-conversion efficiency can be further enhanced by an energy-transfer step from Ni^{2+} ${}^1T_{2g}$ to Mn^{2+} ${}^4T_{1g}$, however, this occurs very inefficiently in $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$.

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I. INTRODUCTION

Together with Cr^{3+} , the Ni^{2+} ion is one of the spectroscopically most thoroughly studied transition-metal ions. Although Ni^{2+} complexes with coordination numbers from 2–7 are known, the vast majority of electronic-spectroscopic studies focuses on six and four coordinate Ni^{2+} , i.e., Ni^{2+} in (approximate) octahedral, tetrahedral, or square-planar coordination geometries.¹ Numerous studies exist in which the optical-spectroscopic properties of Ni^{2+} as a dopant ion in extended lattices have been explored. In that regard two hosts have played a major role: MgF_2 and MgO . In 1963, pulsed near-infrared laser operation of cryogenically cooled $\text{Ni}^{2+}:\text{MgF}_2$ was reported,² and this was the first example of a laser with broadband tuning capability. Later, continuous-wave laser operation of $\text{Ni}^{2+}:\text{MgO}$ was achieved at 80 K.³ In 1970, it was recognized that at cryogenic temperatures Ni^{2+} exhibits multiple emissions in MgO ,⁴ and it has since been shown to do so in a variety of materials including fluorides,^{5,6} chlorides,⁷ and bromides.⁸ Thus, among octahedrally coordinated transition-metal ions, Ni^{2+} represents one of the few exceptions to Kasha's rule,⁹ which states that luminescence is to be expected, if at all, only from the lowest excited state. As such the Ni^{2+} ion has become subject of various photon-up-conversion studies, in which its first excited state serves as a metastable energy storage reservoir, from where up-conversion to a higher excited emitting state can occur, thus leading to short-wavelength emission after long-wavelength irradiation.^{10,11} It has been recognized, however, that the efficiency of the up-conversion process in Ni^{2+} is limited by the low cross sections of the up-conversion-relevant ground-state-absorption (GSA) and excited-state-absorption (ESA) transitions, particularly in the

chlorides. This is because both transitions are spin forbidden, and spin is a relatively good quantum number in 3d-metal ions.

Since the early work of Tanabe and co-workers,^{12,13} it is known that exchange interactions between adjacent transition-metal ions in insulating solids may lead to a significant intensity enhancement of spin-forbidden d - d transitions.^{14,15} We have recently shown for Ni^{2+} -doped RbMnCl_3 that the Ni^{2+} up-conversion rate is greatly enhanced compared to the isostructural $\text{Ni}^{2+}:\text{CsCdCl}_3$.^{16,17} The aim of the present study is to get more detailed insight into the effects of Ni^{2+} - Mn^{2+} exchange interactions on the optical-spectroscopic properties of Ni^{2+} , in general, and its up-conversion characteristics, in particular. For this purpose we have chosen the isostructural compounds Rb_2CdCl_4 and Rb_2MnCl_4 . They crystallize in the tetragonal space group $I4/mmm$ with the perovskite-layer structure shown in Fig. 1.^{18,19} This structure consists of layers of corner-sharing MCl_6^{4-} octahedra, separated from each other by the Rb^+ ions, and the MCl_6^{4-} octahedra are slightly tetragonally compressed along the c axis, leading to D_{4h} symmetry at the metal site. The shortest intralayer M^{2+} - M^{2+} distance is roughly 5.1 Å in both Rb_2CdCl_4 and Rb_2MnCl_4 , whereas the shortest distance between M^{2+} ions in different layers is roughly 8.8 Å. At $T_N = 57$ K, Rb_2MnCl_4 orders antiferromagnetically in the same magnetic structure as K_2NiF_4 .²⁰ Short-range ordering of the Mn^{2+} spins within the perovskite layers persists up to temperatures of about 150 K.^{20,21} Because of its anisotropy this lattice type is eminently suited for our study. We are interested in the effect of exchange interactions between adjacent magnetic ions, and these only occur within the layers. Thus by using polarized light, we can switch the effects on and off.

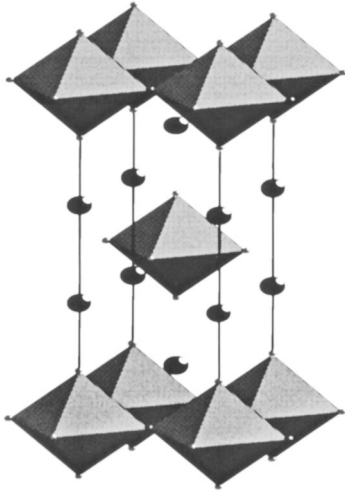


FIG. 1. Unit cell of the Rb_2MCl_4 ($M=\text{Cd}, \text{Mn}$) lattices. The octahedrons represent MCl_6^{4-} units, arranged in layers in corner-sharing geometry. The Rb^+ ions are located between these layers and they are represented by the isolated spheres.

II. EXPERIMENT

A. Crystal growth and manipulation

Single crystals of pure and Ni^{2+} -doped Rb_2MnCl_4 and Rb_2CdCl_4 were grown from the melt by the Bridgman technique.²² The nominal Ni^{2+} dopant concentrations in the melt were 0.1% and 5% in both systems, and they are assumed to be the same in the crystals. Due to their hygroscopic nature, all starting materials and the crystals were handled in an inert atmosphere. They were sealed in epoxy resin (Demotech 20), cut and polished perpendicular to the perovskite layers. For absorption or emission measurements the samples were enclosed in indium-sealed copper cells and filled with He gas for heat dissipation. Sample cooling occurred with a He closed-cycle refrigerator (Air Products Displex) for absorption measurements and with a He-gas-flow-tube technique for emission experiments.

B. Spectroscopic measurements

Absorption spectra were recorded on a Cary 5e spectrophotometer. Continuous-wave (cw) luminescence was excited using the 488-nm line of an Ar^+ laser (Spectra Physics 2060-10A). Wavelength dispersion of the sample luminescence was performed in a (3/4)-m Spex 1702 single monochromator equipped with 600-grooves/mm-gratings blazed at 750, 1250, and 1600 nm. The $\text{Ni}^{2+} {}^1T_{2g} \rightarrow {}^3A_{2g}$, ${}^3T_{2g}$ luminescence transitions were detected with a cooled red sensitive photomultiplier tube (Hamamatsu P3310-01) connected to a Stanford Research 430 photon-counting system. The $\text{Ni}^{2+} {}^1T_{2g} \rightarrow {}^3T_{2g}$, ${}^3T_{1g}({}^3F)$ luminescence transitions were detected with a liquid-nitrogen-cooled Ge detector (ADC 403L), and the $\text{Ni}^{2+} {}^1T_{2g} \rightarrow {}^3T_{1g}({}^3F)$, 1E_g , and ${}^3T_{2g} \rightarrow {}^3A_{2g}$ luminescence transitions were detected with a dry-ice-cooled PbS detector (Hamamatsu P3337). The Ge/PbS detector signals were processed using a Stanford Research 830 lock-in amplifier. The polarization of the luminescence

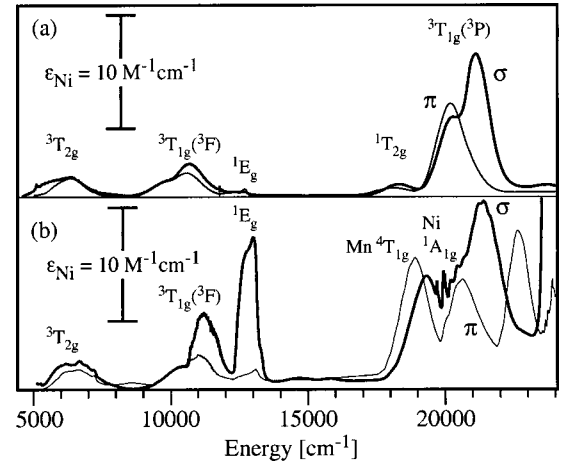


FIG. 2. Polarized 15 K absorption spectra of 5% Ni^{2+} -doped Rb_2CdCl_4 (a) and Rb_2MnCl_4 (b). Strong lines, σ polarized; faint lines, π polarized.

was selected using a Glan-Taylor analyzer behind the sample. The luminescence passed a polarization scrambler before it entered the monochromator to prevent artifacts.

For the up-conversion and excited-state-excitation experiments one or two Ar^+ -laser-pumped Ti^{3+} : sapphire lasers (Spectra Physics 3900 S) were used. Wavelength control was achieved with a step-motor-driven birefringent filter and a Burleigh WA 2100 wavemeter. The wavelength dependence of the laser power was measured on a powermeter (Coherent Labmaster E) simultaneously with the excitation scans. Typical excitation densities used for the one-color up-conversion experiments were of the order of $\sim 250 \text{ mW/cm}^2$, and about 1 mW/cm^2 for the probe beam in the two-color up-conversion experiment. The polarization of the probe laser was controlled with a polarization rotator. The $\text{Ni}^{2+} {}^1T_{2g} \rightarrow {}^3A_{2g}$ up-conversion luminescence was dispersed with a Spex 1402 0.85-m double monochromator equipped with 500-nm blazed 1200-grooves/mm-gratings and detected with a RCA C31034 photomultiplier tube.

For time-resolved experiments the $\text{Ar}^+/\text{Ti}^{3+}$: sapphire laser beams were passed through an acousto-optic modulator (Coherent 305) connected to a function generator (Stanford Research DS 345). The $\text{Mn}^{2+} {}^4T_{1g}$ lifetime in Rb_2MnCl_4 was measured after excitation with the second harmonic of a pulsed Nd^{3+} :YAG (yttrium aluminum garnet) laser (Quanta Ray DCR-3). Luminescence decay curves were recorded on a multichannel scaler (Stanford Research 430).

All luminescence spectra were corrected for the wavelength dependence of the detection system and were converted to photon counts versus energy using the procedure described by Ejder.²³

III. RESULTS AND DISCUSSION

A. Polarized ground-state-absorption spectroscopy of $\text{Ni}^{2+}:\text{Rb}_2\text{MCl}_4$ ($M=\text{Cd}^{2+}, \text{Mn}^{2+}$)

Pure Rb_2CdCl_4 is transparent up to about $40\,000 \text{ cm}^{-1}$ and thus all absorption bands in Fig. 2(a) are due to $\text{Ni}^{2+} d-d$ transitions. In first-order approximation Ni^{2+} is octahedrally

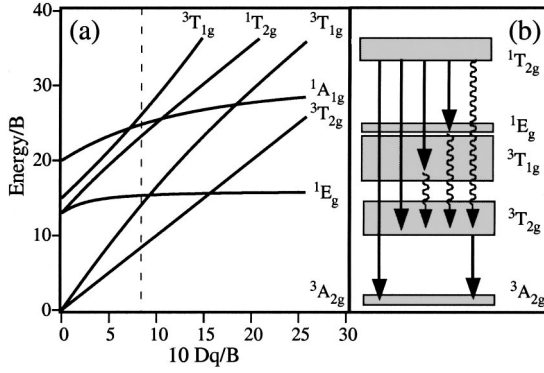


FIG. 3. (a) Tanabe-Sugano energy-level diagram for octahedrally coordinated d^8 ions. The dashed line corresponds to the crystal fields in the title compound. (b) Schematic energy-level diagram for Ni^{2+} , illustrating the Ni^{2+} luminescence transitions (straight arrows). The curly arrows represent nonradiative multiphonon-relaxation processes.

coordinated by Cl^- in Rb_2CdCl_4 and therefore the assignment of these absorption bands occurs with the d^8 Tanabe-Sugano energy-level diagram of Fig. 3(a). The vertical dashed line in Fig. 3(a) indicates the approximate ligand-field strength of Ni^{2+} in the title compounds. The oscillator strengths f in Fig. 2(a) are on the order of 10^{-5} – 10^{-4} for the spin-allowed triplet-triplet transitions and about 10^{-6} for the spin-forbidden triplet-singlet transitions. The effect of the tetragonal distortion of the NiCl_6^{4-} unit in Rb_2CdCl_4 shows up as a splitting of the T states into $E + A$ and $E + B$ components in the polarized absorption spectra of Fig. 2(a). Their polarization dependence is explained by Table I, which lists the possible enabling modes for vibronically induced electric-dipole (ED) transitions in the two polarizations $\mathbf{E} \perp \mathbf{c} (\sigma)$ and $\mathbf{E} \parallel \mathbf{c} (\pi)$ in the Rb_2MCl_4 lattices. From the polarized spectra in Fig. 2(a) and Table I we recognize that the ${}^3A_{2g}$ component of the ${}^3T_{1g}({}^3P)$ state lies energetically higher than the 3E_g component. This is in agreement with the *compressed* NiCl_6^{4-} octahedron in this lattice, see Sec. I.

In a chloride environment and octahedral coordination, Mn^{2+} is spectroscopically innocent below roughly $17\,000\text{ cm}^{-1}$. Therefore all absorption bands in Fig. 2(b) below this energy are due to Ni^{2+} . Above this energy the $\text{Mn}^{2+} {}^6A_{1g} \rightarrow {}^4T_{1g}, {}^4T_{2g}$ absorption bands are superimposed on the $\text{Ni}^{2+} {}^3A_{2g} \rightarrow {}^1T_{2g}, {}^1A_{1g}, {}^3T_{1g}({}^3P)$ bands. Although the $\text{Mn}^{2+}:\text{Ni}^{2+}$ ratio is 20:1 in this crystal, the Mn^{2+} $d-d$ absorp-

tion bands are of comparable intensity to the Ni^{2+} $d-d$ bands. This is due to the fact that all the Mn^{2+} absorption transitions seen in Fig. 2(b) are spin forbidden. Similar to the Ni^{2+} $d-d$ bands, the Mn^{2+} absorption bands have a strong dependence on the polarization of the incident light. In particular, the ${}^4T_{1g}$ band maximum redshifts by about 500 cm^{-1} between σ and π polarization, see Fig. 2(b).³⁵ The most striking and very important difference between Figs. 2(a) and 2(b) is the high intensity ($f \approx 3.6 \times 10^{-5}$) of the $\text{Ni}^{2+} {}^1E_g$ absorption band around $13\,000\text{ cm}^{-1}$ in σ polarization of $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$ (strong line). It is strongly enhanced both with respect to $\text{Ni}^{2+}:\text{Rb}_2\text{CdCl}_4$ [Fig. 2(a)] and with respect to the π spectrum of $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$ (faint line). The physical origin of this enhancement and the consequences are discussed in the following sections.

B. Exchange enhancement of $\text{Ni}^{2+} {}^1E_g$ and ${}^1A_{1g}$ ground-state absorptions in $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$

In diamagnetic hosts such as Rb_2CdCl_4 , spin prohibition is overcome by spin-orbit coupling to energetically close-by spin-allowed transitions. For $\text{Ni}^{2+}:\text{Rb}_2\text{CdCl}_4$ this leads to an essentially polarization-independent oscillator strength of about 2×10^{-6} for the ${}^3A_{2g} \rightarrow {}^1E_g$ transition, see Fig. 2(a). In the σ -polarized absorption spectrum of 5% $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$ [strong line in Fig. 2(b)] this is enhanced to 3.6×10^{-5} , i.e., by a factor of 18. For π -polarized light there is no enhancement. We attribute the enhancement in σ polarization to Ni^{2+} - Mn^{2+} exchange interactions within the perovskite layers. This is similar to the intensity enhancement of the formally spin-forbidden $d-d$ transitions of Mn^{2+} in crystals such as MnF_2 and RbMnF_3 , an effect that has first been studied systematically by Ferguson, Guggenheim, and Tanabe.¹³ Tanabe and co-workers have developed a theoretical formalism to account for such exchange effects.^{12,24} They considered a pair of ions interacting with the electric vector $\mathbf{E}$ of the incident light. This interaction can be described as follows:

$$\hat{H} = \sum_{i,j} (\mathbf{\Pi}_{a_i,b_j} \cdot \mathbf{E})(\mathbf{s}_{a_i} \cdot \mathbf{s}_{b_j}), \quad (1)$$

where i and j refer to the singly occupied orbitals of ion a and b . This transition dipole moment is spin dependent. The vector components Π_{a_i,b_j} in Eq. (1) are related to the orbital exchange parameters J_{a_i,b_j} as follows:

$$\Pi_{a_i,b_j} = \left(\frac{\partial J_{a_i,b_j}}{\partial E_{x,y,z}} \right)_{E_{x,y,z} \rightarrow 0}. \quad (2)$$

This means that the Tanabe intensity mechanism is efficient, wherever exchange interaction pathways between a and b are efficient. In contrast to Mn^{2+} , which has an unpaired electron in each d orbital, the unpaired electron density in Ni^{2+} is only located in the e_g set of d orbitals, and thus Ni^{2+} - Mn^{2+} interactions are of the σ type as illustrated in Fig. 4(a) (scheme I). In $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$ the Ni^{2+} - Cl^- - Mn^{2+} bridges are linear, and thus the main superexchange pathway involves σ -type orbitals of Cl^- , i.e., the $3s$ and $3p_z$ orbitals.²⁵

TABLE I. Vibronic selection rules for some selected electronic transitions from the ground state in D_{4h} -coordinated Ni^{2+} in Rb_2MCl_4 .

Initial state		Final state		Enabling modes	Enabling modes
O_h	D_{4h}	O_h	D_{4h}	for σ polarization	for π polarization
${}^3A_{2g}$	${}^3B_{1g}$	${}^3T_{2g}$	3E_g	a_{2u}, b_{2u}	e_u
			${}^3B_{2g}$	e_u	
		${}^3T_{1g}$	3E_g	a_{2u}, b_{2u}	e_u
			${}^3A_{2g}$	e_u	

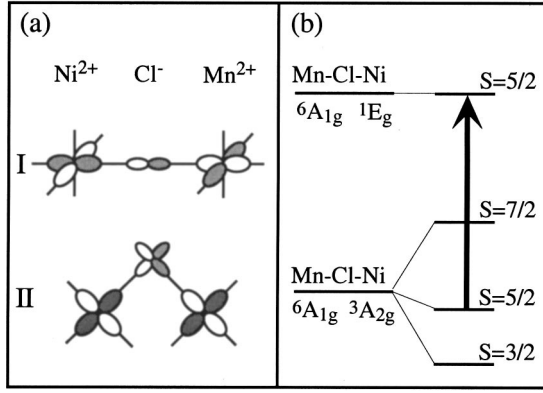


FIG. 4. (a) Molecular-orbital schemes illustrating the relevant $\text{Ni}^{2+}\text{-Cl}^-\text{-Mn}^{2+}$ exchange pathways for (I) 180° and (II) 90° bridging arrangements. (b) Schematic energy-level diagram and spin quantum numbers of the Ni^{2+} -centered ${}^3A_{2g} \rightarrow {}^1E_g$ transition in a $\text{Ni}^{2+}\text{-Mn}^{2+}$ pair.

This type of exchange interaction only occurs *within* the layers of the Rb_2MnCl_4 crystal structure, and thus the exchange enhancement of the spin-forbidden $\text{Ni}^{2+} {}^3A_{2g} \rightarrow {}^1E_g$ transition only occurs in σ polarization, see Fig. 2(b). In $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$ most of the Ni^{2+} ions have four Mn^{2+} nearest neighbors within the layer, and thus the relevant spin cluster would be a $\text{Ni}^{2+}(\text{Mn}^{2+})_4$ pentamer rather than a $\text{Ni}^{2+}\text{-Mn}^{2+}$ pair.^{26–28} For the sake of our argument there is no gain in extending our model. The pair picture is more simple and contains the essential ingredient for an understanding of the effects of $\text{Ni}^{2+}\text{-Mn}^{2+}$ exchange interactions on the optical spectra of $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$. For a $\text{Ni}^{2+}\text{-Cl}^-\text{-Mn}^{2+}$ superexchange pathway as depicted in Fig. 4(a) (scheme I), based on the well-known Kanamori-Goodenough rules,^{29,30} a dominant antiferromagnetic $\text{Ni}^{2+}\text{-Mn}^{2+}$ exchange interaction is expected. Thus, the $[\text{Ni}^{2+}({}^3A_{2g}), \text{Mn}^{2+}({}^6A_{1g})]$ pair ground state is split into pair spin levels of $S = \frac{3}{2}, \frac{5}{2}, \frac{7}{2}$ with increasing energy, as illustrated in Fig. 4(b).³¹ The relevant excited pair state is $[\text{Ni}^{2+}({}^1E_g), \text{Mn}^{2+}({}^6A_{1g})]$, and it has $S = \frac{5}{2}$. Consequently, there exists a formally spin-allowed $S = \frac{5}{2} \rightarrow \frac{5}{2}$ pair transition [see arrow in Fig. 4(b)]. It is this transition that carries the oscillator strength induced by the Tanabe mechanism. From Fig. 4(b) it follows that this exchange-induced 1E_g intensity enhancement must be thermally activated. This is what we observe in Fig. 5(a). Up to about 200 K the σ -polarized 1E_g absorption intensity of 5% $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$ increases by about a factor of 2 relative to 15 K and then slightly decreases. This is in contrast to the temperature dependence of the 1E_g absorption intensity in 5% Ni^{2+} -doped Rb_2CdCl_4 shown in Fig. 5(b). In this system the 1E_g oscillator strength is vibronically induced and increases with temperature according³² to Eq. (3):

$$f(T) = f(T_0) \coth\left(\frac{h\nu_{\text{eff}}}{2kT}\right). \quad (3)$$

A fit to the experimental data is included in Fig. 5(b) (solid line). It yields $h\nu_{\text{eff}} = 164 \text{ cm}^{-1}$ for the weighted average of

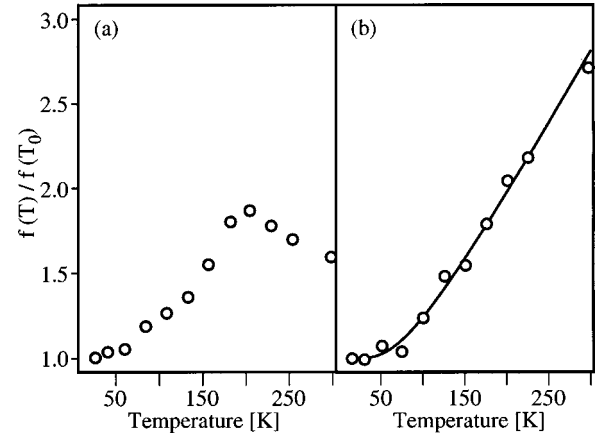


FIG. 5. Temperature dependence of the $\text{Ni}^{2+} {}^3A_{2g} \rightarrow {}^1E_g$ absorption oscillator strengths in σ -polarized spectra of (a) 5% $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$ and (b) 5% $\text{Ni}^{2+}:\text{Rb}_2\text{CdCl}_4$. The solid line in (b) represents a fit with Eq. (3) to the experimental data. The value of the fit parameter is $h\nu_{\text{eff}} = 164 \text{ cm}^{-1}$.

the ungerade enabling modes, which in view of the infrared reflectivity data of Rb_2MnCl_4 in Ref. 33 is a reasonable value.

The 5% $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$ data in Fig. 5(a) cannot be quantitatively reproduced with our dimer model. Also a $\text{Ni}^{2+}(\text{Mn}^{2+})_4$ spin-cluster model is unable to give an accurate quantitative description of this temperature dependence. We ascribe this to the magnetic ordering of the Mn^{2+} spins in the perovskite layers of Rb_2MnCl_4 , i.e., a cooperative effect that is not accounted for by the spin-cluster model. Magnetic two-dimensional correlations are known to persist up to temperatures of around 150 K in Rb_2MnCl_4 .^{20,21} It is known that $\text{Ni}^{2+}\text{-Mn}^{2+}$ exchange interactions are stronger than $\text{Mn}^{2+}\text{-Mn}^{2+}$ interactions in analogous fluoride perovskites.^{31,34,36,37} The same must be true in the present chloride, and this is the main reason that our very simple pair model can qualitatively explain the intensity increase with temperature in Fig. 5(a).

Aside from the 1E_g intensity enhancement in $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$, there are two other direct manifestations of $\text{Ni}^{2+}\text{-Mn}^{2+}$ exchange interactions in the σ -polarized absorption spectrum of Fig. 2(b). The first is the observation of a sharp feature at about 19700 cm^{-1} , which is not present in the $\text{Ni}^{2+}:\text{Rb}_2\text{CdCl}_4$ spectrum in Fig. 2(a) which we assign to the $\text{Ni}^{2+} {}^3A_{2g} \rightarrow {}^1A_{1g}$ transition. The selective exchange enhancement of the $\text{Ni}^{2+} {}^3A_{2g} \rightarrow {}^1E_g / {}^1A_{1g}$ transitions reflects a characteristic of the Tanabe intensity mechanism, namely, transitions that correspond to a pure spin-flip in the strong-field limit [see the horizontal levels in Fig. 3(a)] are most strongly enhanced.^{12,29}

Another manifestation of the Tanabe mechanism is the intensity enhancement of the higher-energy ${}^3A_{2g}$ tetragonal component of ${}^3T_{1g}({}^3F)$ around 11000 cm^{-1} . We ascribe this to a mixing of the A_{1g} spinor component of ${}^3A_{2g}$ with the A_{1g} spinor of the $\text{Ni}^{2+} {}^1E_g$ (O_h) state. This is a well-documented intensity-gain source for the $\text{Ni}^{2+} {}^3A_{2g} \rightarrow {}^1E_g$ transition, for example, in $\text{NiCl}_2(\text{H}_2\text{O})_4$,³⁸ since it adds some triplet character to the 1E_g wave function, making the

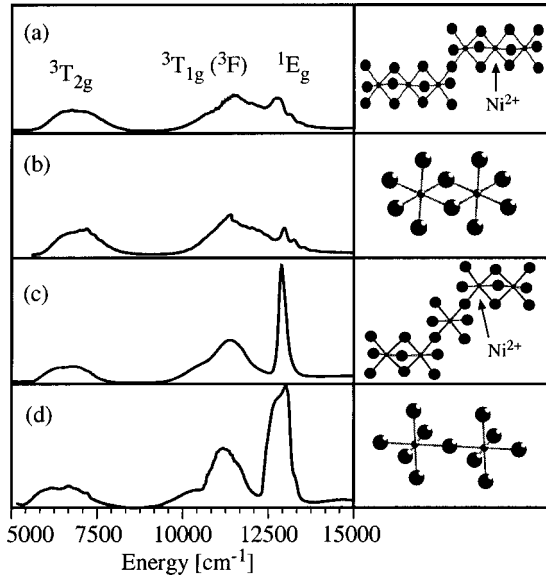


FIG. 6. Left part: 15 K absorption spectra of (a) 10% Ni^{2+} : CsMnCl_3 (axial), (b) 5% Ni^{2+} : MnCl_2 (axial), (c) 10% Ni^{2+} : RbMnCl_3 (axial), and (d) 5% Ni^{2+} : Rb_2MnCl_4 (σ polarized) in the spectral region of the Ni^{2+} ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3T_{1g}({}^3F)$, 1E_g transitions. Right part: Relevant parts of the respective crystal structures illustrating the possible Ni^{2+} - Mn^{2+} bridging arrangements in these four systems.

${}^3A_{2g} \rightarrow {}^1E_g$ transition more allowed. Our σ -polarized spectrum in Fig. 2(b), on the other hand, represents the unprecedented case, in which ${}^3T_{1g}({}^3F)$ steals intensity from the exchange-enhanced 1E_g and not vice versa.

What are the conditions for the strong enhancement of the Ni^{2+} spin-flip transitions? One important factor appears to be the Ni^{2+} -ligand- Mn^{2+} bridging geometry. Figure 6 shows the 15 K absorption spectra of the Ni^{2+} ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3T_{1g}({}^3F)$, 1E_g transitions in four different manganese host lattices: (a) 10% Ni^{2+} -doped CsMnCl_3 (axial), (b) 5% Ni^{2+} -doped MnCl_2 (axial), (c) 10% Ni^{2+} : RbMnCl_3 (axial), and (d) 5% Ni^{2+} : Rb_2MnCl_4 (σ). In these four systems the Ni^{2+} - Mn^{2+} bridging geometries are different, and this is illustrated in the right part of Fig. 6. Exchange enhancement of the 1E_g band occurs in Ni^{2+} : RbMnCl_3 (c) and Ni^{2+} : Rb_2MnCl_4 (d) but neither in Ni^{2+} : CsMnCl_3 (a) nor in Ni^{2+} : MnCl_2 (b). Comparison with the bridging geometries shows that enhancement only occurs when there is a linear Ni^{2+} - Cl^- - Mn^{2+} arrangement. This can be rationalized with the orbital pictures in Fig. 4(a). Scheme I represents an efficient σ superexchange pathway leading to strong antiferromagnetic coupling and thus strong enhancement of spin-flip transitions by the Tanabe mechanism. This structural arrangement is realized in Ni^{2+} : RbMnCl_3 and Ni^{2+} : Rb_2MnCl_4 .^{39,19} In contrast, edge- and face-sharing octahedra connect Ni^{2+} and Mn^{2+} in Ni^{2+} : MnCl_2 and Ni^{2+} : CsMnCl_3 , respectively. The relevant orbital picture for this situation is scheme II in Fig. 4(a). The relevant magnetic orbitals are orthogonal, and there is no antiferromagnetic superexchange pathway; the Tanabe mechanism cannot become active.

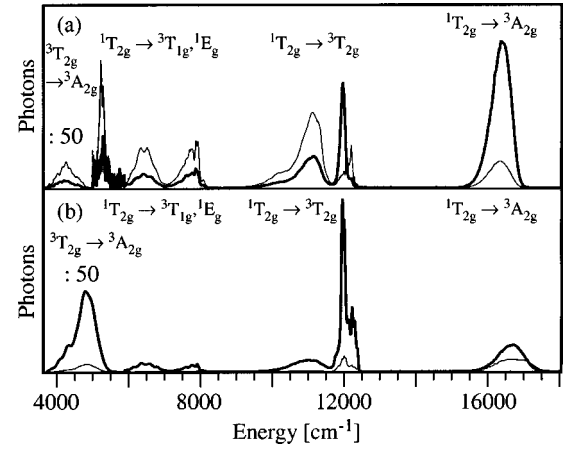


FIG. 7. Polarized 15 K survey luminescence spectra of (a) 5% Ni^{2+} : Rb_2CdCl_4 and (b) 5% Ni^{2+} : Rb_2MnCl_4 obtained after laser excitation at 20492 cm^{-1} . The strong lines represent σ -polarized spectra and the faint lines represent π -polarized spectra. In all spectra the intensity of the ${}^3T_{2g} \rightarrow {}^3A_{2g}$ luminescence transition has been scaled down by a factor of 50.

C. Exchange enhancement of the Ni^{2+} ${}^3T_{2g} \leftrightarrow {}^1T_{2g}$ absorption and luminescence transitions in Ni^{2+} : Rb_2MnCl_4

The 15 K luminescence spectrum of 5% Ni^{2+} : Rb_2CdCl_4 , shown in Fig. 7(a), was obtained after excitation into ${}^3T_{1g}({}^3P)$ at 20496 cm^{-1} , and it is a typical luminescence spectrum for Ni^{2+} in a diamagnetic halide host lattice. As schematically illustrated in Fig. 3(b), luminescence transitions from ${}^1T_{2g}$ to all lower-lying electronic states are observed. The 15-K emission branching ratios from ${}^1T_{2g}$ are given in Table II. The dominant luminescence transitions are ${}^1T_{2g} \rightarrow {}^3A_{2g}$ and ${}^1T_{2g} \rightarrow {}^3T_{2g}$, with similar integrated photon flux. As shown in Fig. 7(b), excitation of 5% Ni^{2+} : Rb_2MnCl_4 at 20496 cm^{-1} at 15 K also leads to Ni^{2+} luminescence, even though the excitation occurs into both Ni^{2+} and Mn^{2+} bands, see Fig. 2(b). There is no evidence for Mn^{2+} luminescence in this crystal at 15 K. The branching ratio from ${}^1T_{2g}$ in this crystal is very different from that in 5% Ni^{2+} : Rb_2CdCl_4 , particularly in σ polarization, see also Table II. Normalized to the ${}^1T_{2g} \rightarrow {}^3A_{2g}$ intensity, the Ni^{2+} σ -polarized ${}^1T_{2g} \rightarrow {}^3T_{2g}$ luminescence intensity is enhanced by about a factor of 5 in 5% Ni^{2+} : Rb_2MnCl_4 relative to 5% Ni^{2+} : Rb_2CdCl_4 . This enhancement mainly occurs in the electronic-origin region, indicating that it has more allowed character in the magnetic host. As for the spin-flip absorption transitions, we attribute this to an exchange enhancement

TABLE II. Normalized emission branching ratios (averaged over both polarizations) from the Ni^{2+} ${}^1T_{2g}$ state in 5% Ni^{2+} : Rb_2CdCl_4 and 5% Ni^{2+} : Rb_2MnCl_4 at 15 K.

Final state	Ni^{2+} : Rb_2CdCl_4	Ni^{2+} : Rb_2MnCl_4
${}^3A_{2g}$	0.364	0.360
${}^3T_{2g}$	0.352	0.543
${}^3T_{1g}$	0.190	0.096
1E_g	0.094	0.001

TABLE III. 15 K lifetimes of the various metastable excited states in Ni^{2+} -doped Rb_2CdCl_4 and Rb_2MnCl_4 , respectively, in crystals with different dopant concentrations.

Active ion	State	Rb_2CdCl_4		Rb_2MnCl_4		
		5% Ni^{2+}	0.1% Ni^{2+}	5% Ni^{2+}	0.1% Ni^{2+}	0% Ni^{2+}
Ni^{2+}	$^3T_{2g}$	7.4 ms ^a		8.0 ms ^a	7.8 ms ^a	
Ni^{2+}	$^1T_{2g}$	12 μs	153 μs	6 μs	41 μs	
Mn^{2+}	$^4T_{1g}$				9.8 ms	10.0 ms

^aMeasured using the method described in detail in Ref. 40.

by the Tanabe mechanism. Both $^3T_{2g}$ and $^1T_{2g}$ derive from the same electron configuration in the strong-field limit, and $^1T_{2g} \rightarrow ^3T_{2g}$ is thus a spin-flip transition, see also Fig. 3(a). The $^1T_{2g} \rightarrow ^3A_{2g}$ and $^1T_{2g} \rightarrow ^3T_{1g}$ (3F) transitions are not pure spin-flip transitions and hence they are not significantly exchange enhanced.

The exchange enhancement of the $^1T_{2g} \rightarrow ^3T_{2g}$ transition is an important finding in two respects. First, the reverse transition, i.e., $^3T_{2g} \rightarrow ^1T_{2g}$ excited-state absorption (ESA) is involved in the Ni^{2+} up-conversion process. Second, the increase in the $^1T_{2g} \rightarrow ^3T_{2g}$ luminescence-transition probability will have an influence on the Ni^{2+} $^1T_{2g}$ lifetime. In the following we discuss these two points. As listed in Table III, the Ni^{2+} $^1T_{2g}$ 15 K lifetime is 3.7 times shorter in 0.1% $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$ than in 0.1% $\text{Ni}^{2+}:\text{Rb}_2\text{CdCl}_4$. We assume that nonradiative multiphonon relaxation processes from the $^1T_{2g}$ are equally important in these two chemically very similar systems, and thus we conclude that the Ni^{2+} $^1T_{2g}$ lifetime is shortened in the magnetic lattice due to Ni^{2+} - Mn^{2+} exchange interactions. At higher dopant concentrations cross-relaxation processes dominate $^1T_{2g}$ depopulation,^{41,6} leading to additional lifetime shortenings in both systems, see Table III.

Using a pump-and-probe technique as illustrated in Fig. 8(c), the 15 K polarized excited-state-excitation (ESE) spectra of 5% $\text{Ni}^{2+}:\text{Rb}_2\text{CdCl}_4$ [Fig. 8(a)] and 5% $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$ [Fig. 8(b)] were obtained. In this experiment the energy of the

pump beam was $11\,000\text{ cm}^{-1}$, thus ensuring a sufficient $^3T_{2g}$ population without inducing up-conversion to $^1T_{2g}$ for energetic reasons. One-color up-conversion by the probe beam alone was avoided by using a low excitation density for this light source, see Sec. II B. The spectra in Figs. 8(a) and 8(b) show the polarization dependence of the 15-K $^3T_{2g} \rightarrow ^1T_{2g}$ ESE transition obtained by scanning the probe laser between $12\,000\text{ cm}^{-1}$ and $14\,000\text{ cm}^{-1}$ while monitoring the $^1T_{2g} \rightarrow ^3A_{2g}$ luminescence. The absolute intensity scales of Figs. 8(a) and 8(b) are different. In all the spectra of Fig. 8 there is a relatively sharp feature around $12\,380\text{ cm}^{-1}$, and according to previous studies we assign it to the electronic-origin region of $^3T_{2g} \rightarrow ^1T_{2g}$ at 15 K.^{17,11} Above $12\,500\text{ cm}^{-1}$ vibronic sidebands are observed. Their relative intensity is particularly high in the π spectrum of $\text{Ni}^{2+}:\text{Rb}_2\text{CdCl}_4$. In both $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$ and $\text{Ni}^{2+}:\text{Rb}_2\text{CdCl}_4$ the intensity in the $12\,380\text{-cm}^{-1}$ origin region is mainly σ polarized. There is an exchange enhancement by about a factor of 2 in the σ spectrum of $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$. This is in line with the findings from above, namely, that the reverse $^1T_{2g} \rightarrow ^3T_{2g}$ transition is exchange enhanced in σ polarization.

D. Exchange induced enhancement of the Ni^{2+} up-conversion efficiency

At 15 K excitation of the $\text{Ni}^{2+}:\text{Rb}_2\text{CdCl}_4$ and $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$ samples around $12\,500\text{ cm}^{-1}$ leads to $^1T_{2g} \rightarrow ^3A_{2g}$ up-conversion luminescence centered around $16\,600\text{ cm}^{-1}$. This is illustrated by the 15 K polarized up-conversion excitation spectra of 5% $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$, shown in Fig. 9(d), in which the luminescence at $16\,600\text{ cm}^{-1}$ is monitored. These spectra show that, depending on the excitation energy, the up-conversion luminescence is almost up to two orders of magnitude more intense for σ than for π excitation. It can be shown based on energetic arguments that up-conversion in Ni^{2+} occurs via a sequence of GSA and ESA steps. For this mechanism the up-conversion excitation spectrum is given by the product of the GSA and ESA line-shape functions.^{42,43} In our specific case the up-conversion-relevant electronic transitions are $^3A_{2g} \rightarrow ^1E_g$ GSA and $^3T_{2g} \rightarrow ^1T_{2g}$ ESA, involving rapid multiphonon relaxation from 1E_g to $^3T_{2g}$ after the GSA step, see Fig. 10. The polarized 15-K spectra of the GSA and ESA transitions in 5% $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$ are displayed in Figs. 9(a) and 9(b) respectively. The calculated products of these GSA and ESA spectra is shown in Fig. 9(c). First, we note that the agreement between the spectra in Figs. 9(c) and 9(d) is excellent, in particular, for the impor-

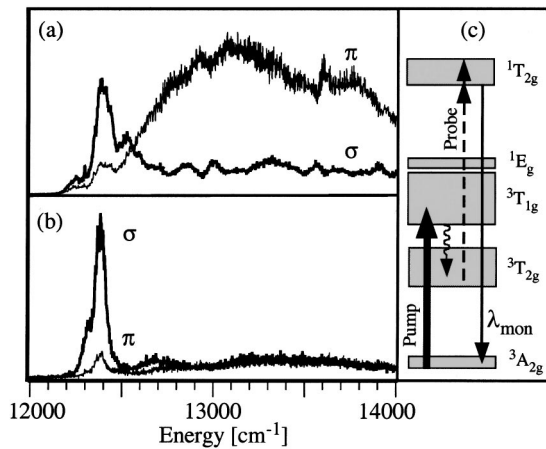


FIG. 8. Polarized 15 K Ni^{2+} $^3T_{2g} \rightarrow ^1T_{2g}$ excited-state-excitation (ESE) spectra of (a) 5% $\text{Ni}^{2+}:\text{Rb}_2\text{CdCl}_4$ and (b) 5% $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$. The scheme in (c) illustrates the principle of this measurement, and it is described in detail in Sec. II B.

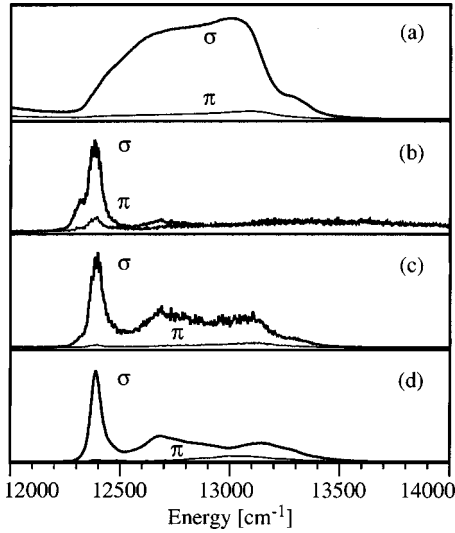


FIG. 9. (a) 15 K polarized $\text{Ni}^{2+} {}^3A_{2g} \rightarrow {}^1E_g$ ground-state-absorption (GSA) spectra and (b) 15 K polarized ${}^3T_{2g} \rightarrow {}^1T_{2g}$ ESE spectra in 5% $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$. The traces in (c) are the calculated products of the GSA and ESE spectra in (a) and (b), respectively. (d) Polarized 15 K excitation spectra of $\text{Ni}^{2+} {}^1T_{2g} \rightarrow {}^3A_{2g}$ up-conversion luminescence in 5% $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$ monitored at $16\,600\text{ cm}^{-1}$.

stant intensity ratio between σ and π polarizations. At $12\,380\text{ cm}^{-1}$, i.e., the peak position for one-color up-conversion in $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$, the $\sigma:\pi$ ratio is 55, see Fig. 9(d). The ${}^3A_{2g} \rightarrow {}^1E_g$ GSA cross section σ_{GSA} is a factor of 10 higher for σ than for π at this energy [Fig. 9(a)], and the ${}^3T_{2g} \rightarrow {}^1T_{2g}$ ESA cross section σ_{ESA} by a factor of 6 [Fig. 9(b)]. Thus the $\sigma_{\text{GSA}}\sigma_{\text{ESA}}$ product is a factor of 60 higher for σ polarization than for π polarization, in excellent agreement with the factor of 55 found in the up-conversion experiment [Fig. 9(b)].

Our conclusion is in line with our previous studies of the Ni^{2+} upconversion rates in $\text{Ni}^{2+}:\text{RbMnCl}_3$ and

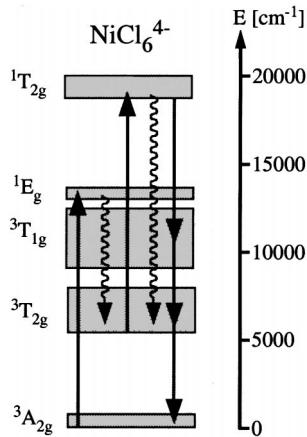


FIG. 10. Summary of the relevant radiative and nonradiative processes related to up-conversion in $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$. Solid upward arrows represent the radiative processes of GSA and ESA, and solid downward arrows represent luminescence. Curly arrows represent nonradiative multiphonon relaxation.

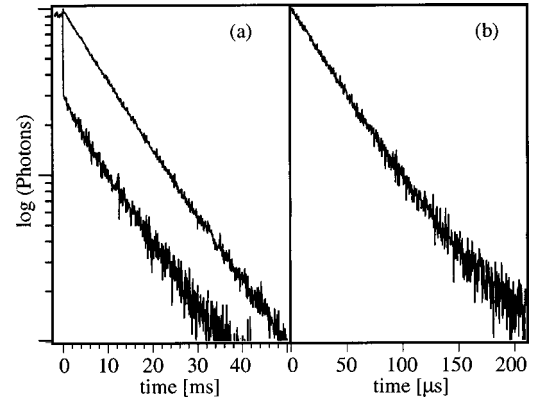


FIG. 11. (a) The upper trace shows the decay of $\text{Mn}^{2+} {}^4T_{1g} \rightarrow {}^6A_{1g}$ luminescence in a pure Rb_2MnCl_4 crystal obtained after pulsed excitation at $18\,797\text{ cm}^{-1}$ at 15 K. The lower trace is a 15 K up-conversion transient of a 0.1% Ni^{2+} -doped Rb_2MnCl_4 crystal detected at $15\,625\text{ cm}^{-1}$. Excitation occurred with square-wave pulses at $12\,380\text{ cm}^{-1}$. (b) shows the first $200\text{ }\mu\text{s}$ of the up-conversion transient in (a) on a 250 times enlarged time scale.

$\text{Ni}^{2+}:\text{CsCdCl}_3$.^{16,17} We have found a similar enhancement factor in $\text{Ni}^{2+}:\text{RbMnCl}_3$. As discussed in Sec. III C this is another lattice with linear $\text{Ni}^{2+}-\text{Cl}^{-}-\text{Mn}^{2+}$ bridging.

Finally, we note that in 0.1% Ni^{2+} -doped Rb_2MnCl_4 , excitation around $12\,380\text{ cm}^{-1}$ leads not only to up-conversion luminescence from $\text{Ni}^{2+} {}^1T_{2g}$ but also from $\text{Mn}^{2+} {}^4T_{1g}$. This manifests itself in biexponential visible up-conversion luminescence decays as illustrated in the lower trace of Fig. 11(a). There is a fast-decay component, shown on an enlarged time scale in Fig. 11(b), corresponding to the $\text{Ni}^{2+} {}^1T_{2g}$ 15-K lifetime of about $41\text{ }\mu\text{s}$ in this sample, see Table III. The slow decay component has a lifetime of 9.8 ms, in close agreement with the $\text{Mn}^{2+} {}^4T_{1g}$ 15 K lifetime in pure Rb_2MnCl_4 .⁴⁴ Energy transfer from $\text{Ni}^{2+} {}^1T_{2g}$ to $\text{Mn}^{2+} {}^4T_{1g}$ has previously been observed in $\text{Ni}^{2+}:\text{CsMnCl}_3$,¹⁷ in which essentially all the up-converted energy is emitted from Mn^{2+} . In $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$ the spectral-overlap conditions for this energy-transfer step are significantly worse, and this is why only about 0.1% of the visible up-conversion luminescence in this sample is due to $\text{Mn}^{2+} {}^4T_{1g} \rightarrow {}^6A_{1g}$.

IV. CONCLUSIONS

We summarize the effects of $\text{Ni}^{2+}-\text{Mn}^{2+}$ exchange interactions on the optical-spectroscopic properties of $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$ in Fig. 10. $\text{Ni}^{2+}-\text{Mn}^{2+}$ exchange interactions are favored by the linear perovskite-type $\text{Ni}^{2+}-\text{Cl}^{-}-\text{Mn}^{2+}$ bridging geometry, leading to an efficient antiferromagnetic superexchange pathway. Perpendicular to the perovskite layers in this lattice, the $\text{Ni}^{2+}:\text{Rb}_2\text{MnCl}_4$ system shows optical-spectroscopic properties, which are typical for a diamagnetic Ni^{2+} -doped material. For light polarized within these perovskite layers (σ) the $\text{Ni}^{2+} {}^3A_{2g} \rightarrow {}^1E_g$ GSA and the ${}^3T_{2g} \rightarrow {}^1T_{2g}$ ESA peak cross sections are higher by factors of 10 and 6, respectively, compared to π polarization. As a consequence, the up-conversion luminescence is more intense by a

