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Simultaneous Electronic Excitation of Exchange-Coupled Pairs of Manganese and Nickel Ions*

J. FERGUSON† AND H. J. GUGGENHEIM
Bell Telephone Laboratories, Murray Hill, New Jersey
AND
Y. TANABE
Department of Physics, Tokyo Institute of Technology, Tokyo, Japan

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An investigation of the ultraviolet absorption spectra of $KZn_{1-x-y}Mn_xNi_yF_3$ and $KMn_xNi_{1-x}F_3$ crystals is reported. Two regions of absorption have been found, one near 40 000 cm^{-1} and the other near 45 000 cm^{-1}, corresponding to the simultaneous electronic excitation of the Mn^{2+} to the $^4A_{1g}$, $^4E_g{}^a$ states and the Ni^{2+} to its ^1E_g state in the first case, and of Mn^{2+} to its $^4E_g{}^b$ state and Ni^{2+} to its ^1E_g state in the second. It is shown from a study of the temperature dependence of the intensity that the mechanism for the absorption of light involves exchange-coupled pairs with the selection rule $\Delta S=0$. The oscillator strengths of the lines and the temperature-dependent shifts of the absorption peaks in the spectra of the concentrated crystals can be accounted for using the theoretical model proposed earlier.

I. INTRODUCTION

In our earlier papers we discussed the absorption spectra and energy levels of a pair of exchange-coupled transition-metal ions.[1–4] We were able to propose, from an analysis of the experimental results, a mechanism for the spin-dependent absorption of light by a pair of ions which has important consequences. One, mentioned briefly in our previous paper,[4] is the simultaneous electronic excitation of both ions of an exchange-coupled pair. We have studied one system in detail to illustrate this phenomenon and we report and discuss the results here. The simultaneous electronic excitation of a pair of (rare-earth) ions was first discovered by Varsanyi and Dieke[5] and Dexter[6] has provided a theoretical interpretation of their results.

The two ions are divalent nickel and manganese in perovskite fluorides. We have also noticed parallel behavior in the corresponding rutile fluorides, but we do not consider this system further in the present work. The cubic perovskite fluorides are the same as in our previous paper,[4] i.e., solid solutions of general formula $KMn_xNi_{1-x}F_3$ and $KZn_{1-x-y}Mn_xNi_yF_3$, and we are concerned with the appearance of lines, characteristic of these solid solutions, which correspond to the simultaneous electronic excitation of the nickel ion to the ^1E_g state and the manganese to the ($^4A_{1g}$, $^4E_g{}^a$) or the $^4E_g{}^b$ state. The effects which we describe, as for the other results we have given in our earlier papers, are not limited to these transitions. They are, however, most easily detected for these particular electronic transitions because the transitions do not involve orbital changes and are simply 'spin flips'.[3]

II. RESULTS

The crystals were grown by the method outlined in our earlier papers. The absorption spectra were all recorded using a Cary model 14R spectrophotometer with the sample in a simple silica cryostat. Liquid hydrogen and liquid nitrogen were used as refrigerants and the sample temperatures were measured by copper-constantan or iron-constantan thermocouples.

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† Present address: Division of Applied Physics, CSIRO, University Grounds, Chippendale, N.S.W., Australia.

[1] J. Ferguson, H. J. Guggenheim, and Y. Tanabe, J. Appl. Phys. **36**, 1046 (1965).

[2] J. Ferguson, *et al.*, Phys. Rev. Letters **14**, 737 (1965).

[3] J. Ferguson, *et al.*, J. Phys. Soc. Japan **21**, 692 (1966).

[4] J. Ferguson, *et al.*, J. Chem. Phys. **45**, 1134 (1966).

[5] F. L. Varsanyi and G. H. Dieke, Phys. Rev. Letters **7**, 442 (1961).

[6] D. L. Dexter, Phys. Rev. **126**, 1962 (1962).

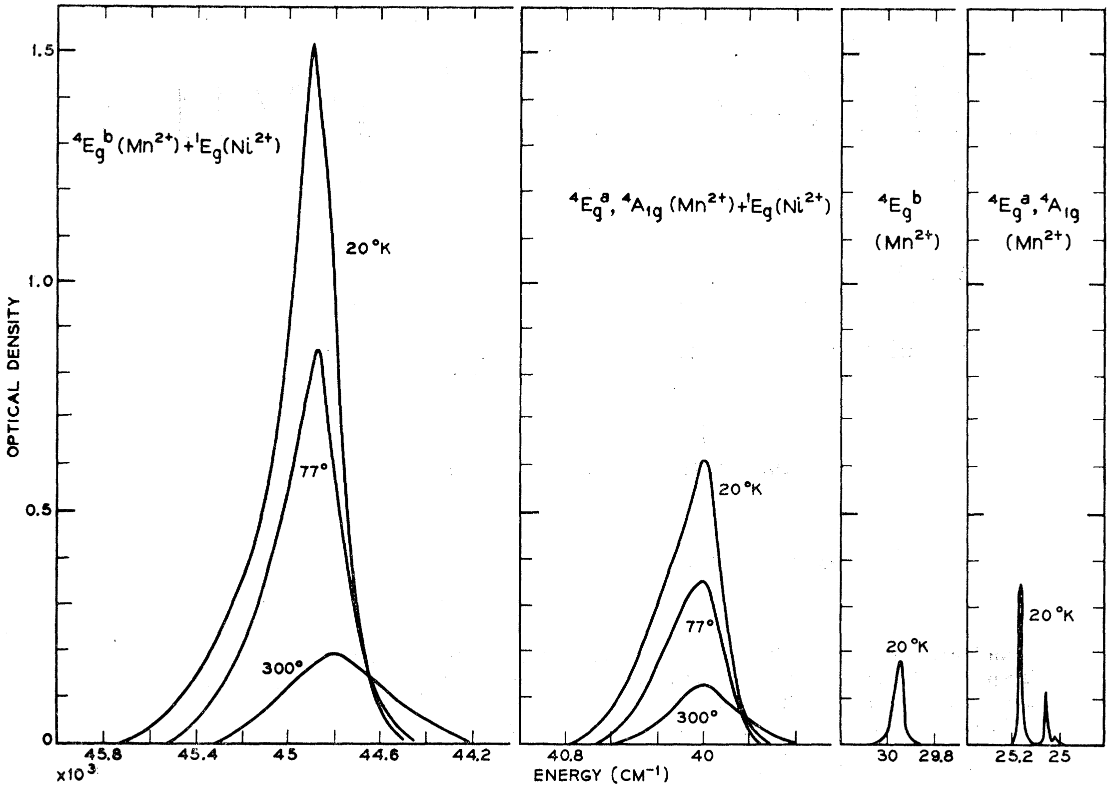

FIG 1. Absorption bands in the spectrum of a $KZn_{0.96}Mn_{0.02}Ni_{0.02}F_3$ crystal (1.75 mm thick) at various temperatures. The excited electronic states of the ion or ions are indicated.

A. $KZn_{1-x-y}Mn_xNi_yF_3$

Two crystals were prepared with the nominal concentration $KZn_{0.96}Mn_{0.02}Ni_{0.02}F_3$ and the results from each crystal were the same. The nickel and manganese ions replace the Zn ions, there is no segregation at this concentration, and all of the data can be interpreted on the assumption of a statistical distribution of the minor divalent ions. The absorption due to Mn–Ni pairs can be detected easily and from the temperature dependence studies of the intensities of the lines a value of $J=18\pm1$ cm^{-1} was obtained for the exchange energy $(J\mathbf{S}_a\cdot\mathbf{S}_b)$ for the pair of ions in their electronic ground states.[2,4] On extending these measurements farther into the ultraviolet, we found two regions of absorption which are strongly temperature-dependent. One lies at 2500 Å (40 000 cm^{-1}), the other at 2 230 Å (44 840 cm^{-1}) and both are shown in Fig. 1 together with the nickel-perturbed manganese lines near 25 000 and 29 000 cm^{-1} for comparison.

From results which are given in the next section it was established that the two lines at 40 000 and 44 840 cm^{-1} are associated with a Ni–Mn pair and the work in the present section helps define the interaction more closely. From the positions of the two lines the lower energy one can be assigned to the transition $({}^3A_{2g}\rightarrow{}^1E_g)+({}^6A_{1g}\rightarrow{}^4A_{1g}, {}^4E_g{}^a)$ and the higher energy one to $({}^3A_{2g}\rightarrow{}^1E_g)+({}^6A_{1g}\rightarrow{}^4E_g{}^b)$. The respective energies are equal, to within $\frac{1}{10}$ of 1%, to the sums of the individual excitation energies. We would not expect them to be exactly equal to sums of observed single-ion excitation energies, because the excitation energies of the two ions excited simultaneously should be slightly different from the single-ion excitations as a result of the small differences in the environments of the ions in the two cases.

There is a marked difference in linewidth between the double-ion excitation lines and the single excitation lines shown in Fig. 1. However, the former are actually about the same as the linewidth of the manganese-perturbed nickel excitation to the ${}^1E_g$ state[4] not shown in Fig. 1. (The greater linewidth of the ${}^1E_g$ excitation line is simply related to the strong spin-orbit interaction between the ${}^1E_g$ state and the nearby ${}^3T_{1g}{}^a$.) The line widths of the 40 000 and 44 840 cm^{-1} lines are therefore primarily determined by the excitation of the nickel ion of the pair to the ${}^1E_g$ state and not by any other factor.

The single-ion excitations of a pair obey the selection rule $\Delta S=0$ and it is important to determine whether the same rule applies to the simultaneous electronic excitations. The ground electronic state of the pair is composed of three levels with $S=\frac{3}{2}$, $\frac{5}{2}$, and $\frac{7}{2}$, respectively.[4] In the excited state of the pair, the nickel ion is in a singlet state and the manganese ion is in a quartet state so that the only allowed transition is that from the lowest level of the ground state ($S=\frac{3}{2}$) if the selection rule $\Delta S=0$ applies. The marked temperature dependences of the two lines at 40 000 and 44 840 cm^{-1} are consistent with this scheme, and we tested it quantitatively by measuring the integrated absorption intensity of the 40 000 cm^{-1} line as a function of temperature. The results are shown in Fig. 2 along with the calculated fractional population of the $S=\frac{3}{2}$ level, based on energy separations given by the $J\mathbf{S}_a\cdot\mathbf{S}_b$ interaction term and normalized at $T=20°\text{K}$. A value of $J=17$ cm^{-1} accounts for the low-temperature results quite well but the experimental results fall consistently below the calculated curve at higher temperatures. We feel that this departure is a result of a decrease of the intrinsic transition probability brought about by an increase of the lattice parameter as the temperature is increased. The transition probability in our theory is a sensitive function of the superexchange path between the two ions, and the change of lattice parameter between 300° and 20°K would be expected to produce an observable change of the absorption intensity.

The temperature dependence of the intensity of the two-ion excitation is then consistent with our earlier work[5] and the same selection rule applies. We note from Fig. 1 that the two-ion excitation lines are more intense than the single-ion excitations. The 40 000 and 44 840 cm^{-1} lines are about 20 and 50 times, respectively, the single-ion excitations near 25 000 and 29 000 cm^{-1}. We cannot estimate accurately the absolute values of their intensities because we do not know the concentration of the Ni–Mn pairs in our samples. However, we are able to determine them from the spectra of the $\text{KMn}_x\text{Ni}_{1-x}\text{F}_3$ crystals given in the next section and we note also that the relative magnitudes of the two-ion and single-ion excitations are the same in both sets of crystals.

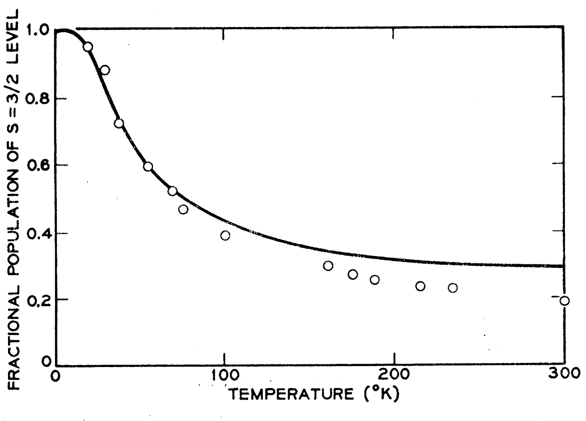

FIG. 2. Calculated fractional population of the $S=\frac{3}{2}$ level of an exchange coupled Mn-Ni pair for $J=17$ cm^{-1} (curve) and observed integrated absorption intensity of the 40 000 cm^{-1} line in the spectrum of a $\text{KZn}_{0.96}\text{Mn}_{0.02}\text{Ni}_{0.02}\text{F}_3$ crystal (circles). The experimental data and the theoretical curve have been normalized at $T=20°\text{K}$.

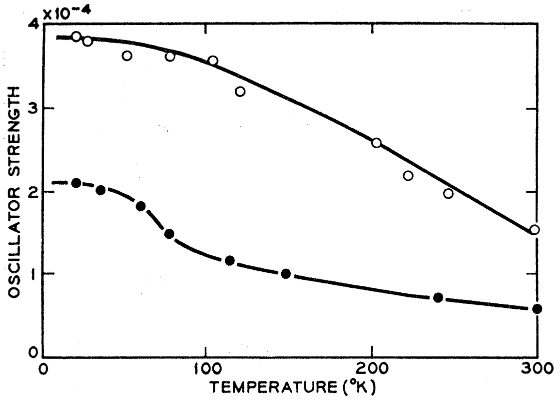

FIG. 3. Temperature dependence of the oscillator strength of the simultaneous electronic transition $({}^3A_{2g}\rightarrow{}^1E_g)+({}^6A_{1g}\rightarrow{}^4A_{1g},\ {}^4E_g{}^a)$ in $\text{KMn}_{0.005}\text{Ni}_{0.995}\text{F}_3$ (open circles) and $\text{KMn}_{0.987}\cdot\text{Ni}_{0.013}\text{F}_3$ (filled circles).

In summary, we have established the existence of two lines in the ultraviolet spectra of crystals of composition $\text{KZn}_{1-x-y}\text{Mn}_x\text{Ni}_y\text{F}_3$ which can be interpreted as the simultaneous electronic excitation of both ions belonging to a Mn-Ni pair. The linewidths are determined by the ${}^1E_g$ state of the nickel ion and the intensities of the lines are between one and two orders of magnitude large than the single excitation of the manganese ion of the pair. Both lines show a dependence on temperature which is consistent with an isotropic exchange interaction in the ground state and the selection rule $\Delta S=0$. The value of the exchange energy obtained from an analysis of the temperature dependence of the absorption intensity agrees with that obtained earlier from the single-ion excitation work[4] and also agrees with the value obtained from studies of the fluorescence of nickel in KMnF_3.[7]

B. $\text{KMn}_x\text{Ni}_{1-x}\text{F}_3$

Measurements of the ultraviolet absorption spectra (up to 48 000 cm^{-1}) of crystals of composition $\text{KMn}_x\text{Ni}_{1-x}\text{F}_3$ reveal two regions of absorption which are absent in the spectra of both pure materials (i.e., $x=0$ or 1). At room temperature, these two regions are at approximately 40 100 and 44 900 cm^{-1} and they correspond to the excitation of the $({}^1E_g+{}^4E_g{}^a,\ {}^4A_{1g})$ and $({}^1E_g+{}^4E_g{}^b)$ states, respectively. We measured the spectra of crystals with various values of x to extablish the connection between these bands and the presence of both nickel and manganese and then made more detailed studies of the crystals for which $x\approx 0.01$ and

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[7] L. F. Johnson, R. E. Dietz, and H. J. Guggenheim, Phys. Rev. Letters **17**, 13 (1966).

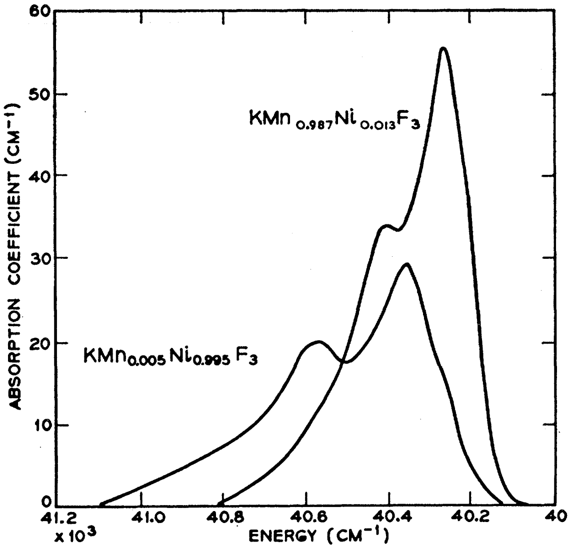

FIG. 4. Absorption spectra at 20°K showing the simultaneous electronic transition $(^3A_{2g}\rightarrow{}^1E_g)+(^6A_{1g}\rightarrow{}^4A_{1g},\ ^4E_g{}^a)$ in $\mathrm{KMn_{0.005}Ni_{0.995}F_3}$ and $\mathrm{KMn_{0.987}Ni_{0.013}F_3}$.

0.99. For crystals with these approximate compositions we can safely assume that the minor constituent has all six nearest-neighbor divalent-ion sites occupied by the major constituent, i.e., we have $\mathrm{Mn(FNi)_6}$ in one case and $\mathrm{Ni(FMn)_6}$ in the other.

We measured the temperature dependence of the intensities and energies of the bands in the spectra of two crystals with the following analyzed compositions:[8] $\mathrm{KMn_{0.005}Ni_{0.995}F_3}$ and $\mathrm{KMn_{0.987}Ni_{0.013}F_3}$. The results for the lower-energy band are more reliable than those for the higher-energy band because the latter lies close to the upper energy limit of our spectrophotometer. Because of this the spectra were recorded only at the fixed temperatures of 20, and 77°K and room temperature.

The temperature dependences of the bands associated with the simultaneous transition

$$(^3A_{2g}\rightarrow{}^1E_g)+(^6A_{1g}\rightarrow{}^4A_{1g},\ ^4E_g{}^a)$$

in the crystals are given in Fig. 3. The intensities have been expressed as oscillator strengths calculated on the basis of the minor ion in each case, although the transition involves a two-center electronic excitation. This has been done to bear out our assignment of the lines. At the very low temperatures we would expect the lines to have the same oscillator strength because the $\mathrm{Ni(MnF)_6}$ cluster is equivalent to the $\mathrm{Mn(FNi)_6}$ cluster in our theory for the two-ion mechanism. The two 20°K measurements of Fig. 3 are not quite the same. However, not shown in Fig. 3 are errors, arising from the uncertainties in the chemical analyses and measurements of sample thickness, which could amount to 30% for each set of measurements so that we feel that the differences between the two values for the oscillator strength at 20°K are not significant. We therefore take a value of 3×10^{-4} as a measure of the oscillator strength of this transition for a Mn–Ni pair at 20°K.

The spectra at 20°K are given in Fig. 4 and structure can be seen in both bands. Each band has a main maximum with a less intense one at slightly higher energy. The separations between these maxima are equal, within the experimental error, to the separations between the $^4A_{1g}$ and $^4E_g{}^a$ states of the nickel perturbed manganese bands in the corresponding crystals,[4] so we therefore assign the maxima to the simultaneous excitations, $^1E_g+{}^4A_{1g}$ and $^1E_g+{}^4E_g{}^a$, although we cannot say which one is which.

The bands shift with temperature in quite different ways, although the over-all shift between room temperature and 20°K happens to be about the same. The shifts are shown in Fig. 5 and it can be seen that each curve parallels the corresponding intensity curve of Fig. 4.

The data for the higher-energy band corresponding to the simultaneous excitation to the ^1E_g and $^4E_g{}^b$ states are given in Tables I and II along with the results for the lower-energy band. It can be seen that the higher-energy band is about three times as intense as the lower-energy band, a result which also agrees with

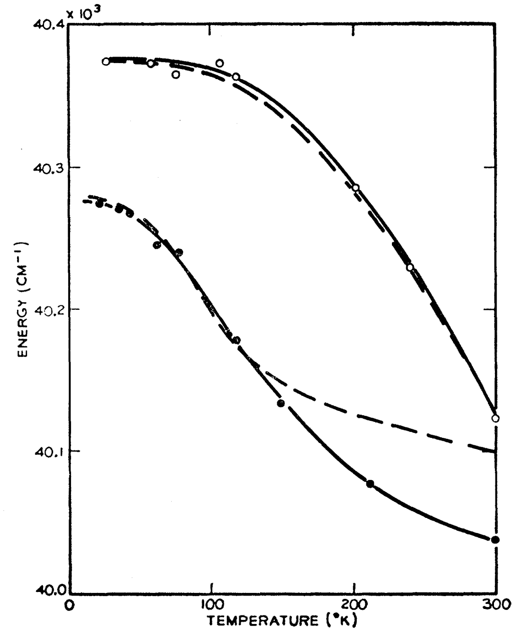

FIG. 5. Energy of the main maximum of the simultaneous electronic transition $(^3A_{2g}\rightarrow{}^1E_g)+(^6A_{1g}\rightarrow{}^4A_{1g},\ ^4E_g{}^a)$ as a function of temperature in $\mathrm{KMn_{0.005}Ni_{0.995}F_3}$ (open circles) and $\mathrm{KMn_{0.987}}$·$\mathrm{Ni_{0.013}F_3}$ (filled circles). Corresponding (dotted) curves for the single ion excitation are included from Ref. 4. These have been displaced from their actual energies to make the low-temperature values coincide with the simultaneous electronic absorption curves.

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[8] The analyses were kindly performed for us using the atomic absorption method by T. Y. Kometani of the Bell Telephone Laboratories.

TABLE I. Oscillator strengths (f) for the simultaneous electronic excitation bands in the spectra of $KMn_xNi_{1-x}F_3$ crystals at different temperatures.

Temperature (°K)	$KMn_{0.987}Ni_{0.013}F_3$		$KMn_{0.005}Ni_{0.995}F_3$	
	$f(^1E_g+^4A_{1g}, ^4E_g{}^a)$	$f(^1E_g+^4E_g{}^b)$	$f(^1E_g+^4A_{1g}, ^4E_g{}^a)$	$f(^1E_g+^4E_g{}^b)$
20	2.1×10^{-4}	7.6×10^{-4}	3.9×10^{-4}	1.2×10^{-3}
77	1.5×10^{-4}	4.9×10^{-4}	3.6×10^{-4}	1.1×10^{-3}
300	0.6×10^{-4}	2.1×10^{-4}	1.5×10^{-4}	0.5×10^{-3}

the relative intensity of these bands in the simple pair spectrum given in the previous section. The higher-energy band also has a larger temperature shift of the band maximum. However, this merely parallels the relatively greater shift of the $^4E_g{}^b$ band over the $^4A_{1g}$, $^4E_g{}^a$ band in the single-ion excitation in the same crystals[5] so that no new feature is present.

III. DISCUSSION

We shall be concerned in this section with two aspects of the experimental results, namely, the intensity of the simultaneous excitation in dilute crystals and the temperature-dependent shift of the absorption peaks in concentrated crystals.

It is rather difficult to go beyond an order of magnitude argument in discussing the first aspect, so that our purpose here is to point out that the mechanism assumed in our earlier papers[4] is not inconsistent with the observed oscillator strength $f\sim10^{-4}$ which is an order-of-magnitude larger than the value for the single-ion excitation of the Mn–Ni pair reported in the previous paper.[4]

Our mechanism led to the following interaction between the spins of the ions A and B and the electric field

$$\mathcal{H}'=\sum_{ij}(\boldsymbol{\pi}_{aibj}\cdot\mathbf{E})(\mathbf{s}_{ai}\cdot\mathbf{s}_{bj}), \tag{1}$$

so that the effective transition moment between the ground states $A(^{2S_a+1}\Gamma_a\gamma_a)B(^{2S_b+1}\Gamma_b\gamma_b)$ and the excited states $A(^{2S_a'+1}\Gamma_a'\gamma_a')B(^{2S_b'+1}\Gamma_b'\gamma_b')$ with the resultant spin S is given by Eq. (34) of Ref. 3

$$\begin{aligned}P_S&=\langle S_a\Gamma_a\gamma_aS_b\Gamma_b\gamma_bS\,|\,\mathcal{H}'\,|\,S_a'\Gamma_a'\gamma_a'S_b'\Gamma_b'\gamma_b'S\rangle/E_z\\&=P(if)(-)^{S_a+S_b'-S}W(S_aS_bS_a'S_b';S1),\end{aligned} \tag{2}$$

where

$$\begin{aligned}P(if)=\sum_{ij}\pi_{aibjz}\langle S_a\Gamma_a\gamma_a\,||\,\mathbf{s}_{ai}\,||\,S_a'\Gamma_a'\gamma_a'\rangle\\\times\langle S_b\Gamma_b\gamma_b\,||\,\mathbf{s}_{bj}\,||\,S_b'\Gamma_b'\gamma_b'\rangle.\end{aligned} \tag{3}$$

The total intensity of the transition is determined by $P(if)$, because we have

$$\begin{aligned}&[(2S_a+1)(2S_b+1)]^{-1}\sum(2S+1)P_S{}^2\\&\qquad=\frac{P(if)^2}{(2S_a+1)(2S_b+1)}\times\frac{1}{3},\end{aligned} \tag{4}$$

which follows from the normalization of the Racah coefficients[9]

$$\sum_e(2e+1)(2f+1)W(abcd;ef)^2=1. \tag{5}$$

$P(if)$ takes different expressions depending upon the initial and final states. For example, we found

$$(1/\sqrt{10})(21/10)^{1/2}(2\sum_{(\xi\eta\zeta)j}\pi_{\xi j}-3\sum_{(uv)j}\pi_{uj}) \tag{6}$$

for the single-ion excitation $Mn(^6A_{1g})Mn(^6A_{1g})\rightarrow Mn(^4A_{1g})Mn(^6A_{1g})$, if we write π_{ij} in place of π_{aibjz}.[10] Summation with respect to j is taken over all the singly-occupied orbitals, that is, ξ, η, ζ, u, and v in the present case. When Mn is excited to the $^4E_g{}^{a,b}u$ state instead of $^4A_{1g}$, we have

$$\begin{aligned}(1/\sqrt{2})(21/10)^{1/2}\{-\alpha\sum_j(2\pi_{\zeta j}-\pi_{\xi j}-\pi_{\eta j})\\+\sqrt{3}\beta\sum_j(\pi_{uj}-\pi_{vj})\},\end{aligned} \tag{7}$$

where $\alpha=2/\sqrt{7}$ and $\beta=(3/7)^{1/2}$ for $^4E_g{}^a$ and $\alpha=(3/7)^{1/2}$ and $\beta=-2/\sqrt{7}$ for $^4E_g{}^b$. For the excitation to $^4E_g{}^{a,b}v$,

TABLE II. Energies of the simultaneous electronic excitation-band maxima in the spectra of $KMn_xNi_{1-x}F_3$ at different temperatures.

Temperature (°K)	$KMn_{0.987}Ni_{0.013}F_3$		$KMn_{0.005}Ni_{0.995}F_3$	
	$^1E_g+^4A_{1g}, ^4E_g{}^a$	$^1E_g+^4E_g{}^b$	$^1E_g+^4A_{1g}, ^4E_g{}^a$	$^1E_g+^4E_g{}^b$
20	40 275 cm^{-1}	45 250 cm^{-1}	40 370 cm^{-1}	45 470 cm^{-1}
77	40 240 cm^{-1}	45 180 cm^{-1}	40 365 cm^{-1}	44 360 cm^{-1}
300	40 040 cm^{-1}	44 860 cm^{-1}	40 120 cm^{-1}	44 960 cm^{-1}

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[9] G. Racah, Phys. Rev. **62**, 438 (1942).

[10] $(-)^{S-S'}$ in (36) of Ref. 4 is to be replaced by $(-)^{S'}$.

we obtain

$$(1/\sqrt{2})(21/10)^{1/2}\{-\sqrt{3}\alpha\sum_j(\pi_{\xi j}-\pi_{\eta j})-\sqrt{3}\beta \times\sum_j(\pi_{(uv)j}+\pi_{(vu)j})\}, \quad (8)$$

where we have taken into account the effect of an orbital jump which has been neglected so far. The latter effect may be expressed by adding terms like $(\boldsymbol{\pi}_{ai'ibj}\cdot\mathbf{E})(s_{ai'\leftarrow i}\cdot s_{bj})$ to (1). [See Eq. (41) of Ref. 11].

For the single-ion excitation $\mathrm{Mn}(^6A_{1g})\mathrm{Ni}(^3A_{2g})\rightarrow \mathrm{Mn}(^4\Gamma\gamma)\mathrm{Ni}(^3A_{2g})$, we have only to replace

$$(21/10)^{1/2}\sum_j\pi_{ij} \text{ by } (3/2)^{1/2}(\pi_{iu}+\pi_{iv}) \quad (9)$$

in the above expressions. In the case of the simultaneous excitation $\mathrm{Mn}(^6A_{1g})\mathrm{Ni}(^3A_{2g})\rightarrow\mathrm{Mn}(^4\Gamma\gamma)\mathrm{Ni}(^1E_gu)$ we are now interested in, we replace

$$(21/10)^{1/2}\sum_j\pi_{ij} \text{ by } -(\sqrt{3}/2)(\pi_{i(uv)}+\pi_{i(vu)}). \quad (10)$$

When Ni is excited to the $1E_gv$ state, we must replace

$$(21/10)^{1/2}\sum_j\pi_{ij} \text{ by } (\sqrt{3}/2)(\pi_{iu}-\pi_{iv}). \quad (11)$$

We have seen in the previous paper[4] that we can understand the oscillator strength $(f-10^{-5})$ of the single-ion excitation Mn–Ni→Mn*–Ni using reasonable assumptions. Although the f value for the simultaneous Mn–Ni→Mn*–Ni* is an order-of-magnitude larger than this, it is not too large to make the present mechanism untenable, because as we see in (9) and (11) π_{iu} and π_{iv} enter there with different signs and we can imagine that they happen to cancel each other in (9) while they add up in (11). If they were of comparable magnitude, it would be quite possible for (11) to be ten times as large as (9) and this would lead to a difference of a factor 10^2 in the f value. Besides, we do not actually know how large $\pi_{i(uv)}$ will be, although we feel that they are likely to be smaller than π_{iu} or π_{iv}.

We shall now discuss the second problem briefly. Our interpretation of the absorption bands corresponding to single-ion excitation in the concentrated materials has been that they are actually spin-wave side bands of the exciton lines which we cannot observe because of their low intensity.[3,4] These absorption bands are, therefore, to be treated as such as we have done in the case of spin-wave sidebands in MnF_2.[12,13,14] For a qualitative understanding, however, we may use the molecular-field approximation, and this was done in the previous paper.[4] We shall also follow the previous treatment in the discussion of the shift of the peak corresponding to the simultaneous excitations.

When $X\sim0$, the magnetic shift of the absorption Mn–Ni→Mn*–Ni* will be given by

$$\begin{aligned}W_{\mathrm{Mn}^*-\mathrm{Ni}^*}=&-J_{\mathrm{Mn}^*-\mathrm{Ni}}(z-1)(S_{\mathrm{Mn}}-1)\langle S_{\mathrm{Ni}}\rangle\\&+J_{\mathrm{Mn-Ni}}(z-1)S_{\mathrm{Mn}}\langle S_{\mathrm{Ni}}\rangle\\&-J_{\mathrm{Ni}^*-\mathrm{Mn}}(z-1)(S_{\mathrm{Ni}}-1)\langle S_{\mathrm{Ni}}\rangle\\&+J_{\mathrm{Ni-Ni}}(z-1)S_{\mathrm{Ni}}\langle S_{\mathrm{Ni}}\rangle\\&-J_{\mathrm{Mn}^*-\mathrm{Ni}^*}(S_{\mathrm{Mn}}-1)(S_{\mathrm{Ni}}-1)\\&+J_{\mathrm{Mn-Ni}}S_{\mathrm{Mn}}S_{\mathrm{Ni}}. \quad (12)\end{aligned}$$

Similarly, for $x\sim1$, we find

$$\begin{aligned}W_{\mathrm{Mn}^*-\mathrm{Ni}^*}=&-J_{\mathrm{Mn}^*-\mathrm{Mn}}(z-1)(S_{\mathrm{Mn}}-1)\langle S_{\mathrm{Mn}}\rangle\\&+J_{\mathrm{Mn-Mn}}(z-1)S_{\mathrm{Mn}}\langle S_{\mathrm{Mn}}\rangle\\&-J_{\mathrm{Ni}^*-\mathrm{Mn}}(z-1)(S_{\mathrm{Ni}}-1)\langle S_{\mathrm{Mn}}\rangle\\&+J_{\mathrm{Ni-Mn}}(z-1)S_{\mathrm{Ni}}\langle S_{\mathrm{Mn}}\rangle\\&-J_{\mathrm{Mn}^*-\mathrm{Ni}^*}(S_{\mathrm{Mn}}-1)(S_{\mathrm{Ni}}-1)\\&+J_{\mathrm{Mn-Ni}}S_{\mathrm{Mn}}S_{\mathrm{Ni}}. \quad (13)\end{aligned}$$

Since $S_{\mathrm{Ni}}=1$, we notice that (12) and (13) are identical, respectively, to (11) and (9) of the previous paper[4] apart from the slightly different notation for J. The same remark as given before applies with respect to the temperature-dependent shift. We can understand the fact that the shift of the absorption band for $x\sim0$ takes place over a wider temperature range than that for $x\sim1$. We can also see why the peak of the band for $x\sim0$ is observed on the shorter wavelength side of that for $x\sim1$. We can indeed predict that the peak will shift at low temperatures by about 100 cm^{-1} when x increases from 0 to 1 in agreement with the observation, using (12), (13), and the values of the exchange integrals determined before.[4]

In order to confirm (12) and (13), we have also shown in Fig. 5 the temperature dependence of the absorption peak corresponding to the single-ion excitation $\mathrm{Mn}(^6A_{1g})\mathrm{Ni}(^3A_{2g})\rightarrow\mathrm{Mn}(^4E_g{}^a)\mathrm{Ni}(^3A_{2g})$ in $\mathrm{KMn_{0.04}Ni_{0.96}Fe_3}$ and $\mathrm{KMn_{0.96}Ni_{0.04}F_3}$ reported in the previous paper.[5] We see that the agreement is not bad when $x\sim0$. However, it is not so good when $x\sim1$ for reasons which we do not yet understand.

In conclusion, we may say that we understand the simultaneous excitation of a Mn–Ni pair in dilute crystals and the temperature-dependent shift of the peak of the simultaneous excitation in concentrated materials in terms of the mechanism proposed for the interpretation of the single-ion excitation of the exchange-coupled pair.

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