ABSORPTION OF LIGHT BY PAIRS OF LIKE AND UNLIKE TRANSITION-METAL IONS

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The absorption of light by pairs of transition-metal ions was first established by Schawlow, Wood, and Clogston[1] for chromium ions in ruby. McClure[2] has also observed pair absorption involving manganese ions in ZnS crystals, and we[3] have recently reported an analysis of the absorption by pairs of manganese ions in crystals of $KZnF_3$. We have also shown that the anomalously high intensity of some of the absorption bands in pure $KMnF_3$ is related to absorption by pairs of ions.[3] Because of the unusual nature of this mechanism for absorption of light, it is important to determine the factors responsible and the generality of this type of phenomenon. In particular, it is necessary to establish whether pair absorption is possible when the two ions are not the same. We summarize in this Letter results of our research which are related to these problems.

From a study of the concentration dependence of the spectra of various ions in fluoride crystals, we have found that absorption by like pairs can be observed in transitions to states which have the same orbital configuration as the ground state, i.e., the electronic transitions are essentially spin flips. The intensity of the pair absorption also depends on the bond angle (overlap) in the pair. It is greater in perovskite fluorides (180° bonds) than in the rutile fluorides (120° bonds) for the same metal ions. For example, the transition to the ${}^4A_{1g}$ and ${}^4E_g{}^a$ states of Mn^{2+} has a higher intensity in $KMnF_3$ (molar extinction coefficient $\epsilon = 0.61$ at 300°K) than in MnF_2 [$\epsilon(\sigma) = 0.16$; $\epsilon(\pi) = 0.20$ at 300°K)], although the intensities of the broad bands are nearly the same.

We have also found that absorption by pairs of unlike ions is possible, and in all cases so far studied, the intensity of absorption is greater than for like ion pairs. The states involved are the same as mentioned in the previous paragraph, and the same overlap conditions apply. We have studied the spectra of crystals containing Mn-F-Fe, Mn-F-Co, and Mn-F-Ni pairs, and we summarize the important features of the results here.

(a) The intensities of the transitions to the ${}^1E_g$ state of Ni^{2+} and the ${}^4A_{1g}$, ${}^4E_g{}^a$, and ${}^4E_g{}^b$ states of Mn^{2+} can be enhanced by interaction between the two ions. We have shown this from measurements of the absorption spectra of crystals of $KMn_xNi_{1-x}F_3$ $(0 \leq x \leq 1)$ in the 3000Å (${}^4E_g{}^b$), 4000Å (${}^4A_{1g}$, ${}^4E_g{}^a$), and 6500Å (${}^1E_g$) spectral regions. Figure 1 shows the 4000Å band at 20°K for crystals with $x = 1.00$, 0.96, and 0.82. In crystals for which $x = 0.01$, we find that the oscillator strength of the 4000Å band (corresponding to the ${}^4A_{1g}$ and ${}^4E_g{}^a$ states of the Mn^{2+}) is 5.6×10^{-5}. This represents an enormous enhancement over the single-ion value[3] of 1.7×10^{-8}, and also much greater than the value of 9.5×10^{-7} for $KMnF_3$.[3]

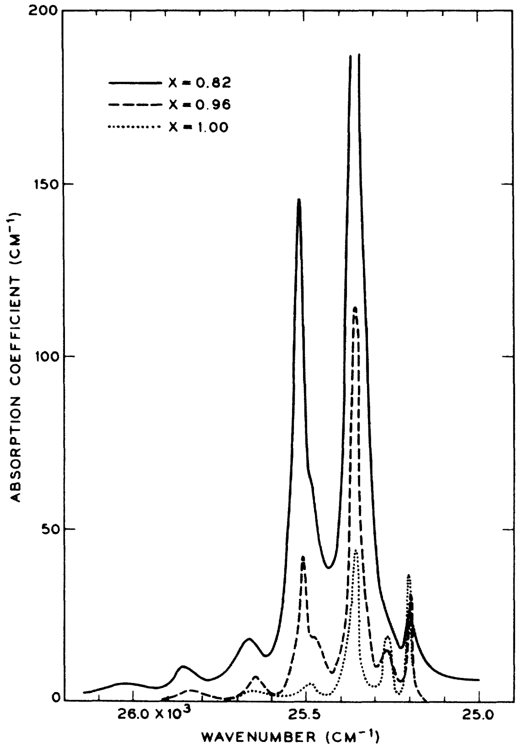

FIG. 1. 20°K absorption spectra of crystals of $KM_xNi_{1-x}F_3$ in the 4000Å region.

There is a corresponding enhancement of the transition to the ^1E_g state of the Ni^{2+} ion. This transition has an oscillator strength of 7.7×10^{-6} in crystals of $\mathrm{KMn_{0.99}Ni_{0.01}F_3}$, to be compared with 1.3×10^{-6} in $\mathrm{KNiF_3}$ and 0.28×10^{-6} in $\mathrm{KMg_{0.99}Ni_{0.01}F_3}$, all at 20°K.

We have also studied the spectra of crystals of $\mathrm{KZnF_3}$ containing small amounts of both Ni^{2+} and Mn^{2+}. In these crystals the 4000 and 3300Å bands contain lines due to both Mn-F-Mn and Mn-F-Ni pairs, the latter being more intense. In the 4000Å region we observe three lines associated with Mn-F-Ni pairs, at 25 162.8, 25 054.3, and 25 029.2 cm^{-1}. If we assume an isotropic exchange interaction of the form $JS_a \cdot S_b$ as for the Mn-F-Mn pairs,[3] then the energy levels of the pair Mn-F-Ni are shown in Fig. 2 for both ground and excited states of the Mn^{2+}. We have measured the temperature dependence of the intensities of the lines at 25 054.3 and 25 029.2 cm^{-1}, and we find a value of $J = 18 \pm 1\ \mathrm{cm}^{-1}$ for the ground state. The corresponding value in the excited state is then $J' = 8 \pm 1\ \mathrm{cm}^{-1}$. The excited state of the Mn^{2+} is either $^4A_{1g}$ or $^4E_g{}^a$. The other line at 25 162.8 cm^{-1} must correspond to pair absorption with the Mn^{2+} ion in the other excited state, and because only one line is observed, the value for the exchange interaction in the ground and excited states must be the same or very nearly the same.

(b) The transitions to the $^2T_{1g}$ and $^2T_{2g}$ states or Co^{2+} near 17 400 cm^{-1} are stronger in crystals of $\mathrm{KMnF_3{:}Co}$ than in $\mathrm{KCoF_3}$.

(c) The spectra of crystals of $\mathrm{KZnF_3}$ containing small amounts of Fe and Mn show strong enhancement of the 4000 and 3300Å bands of the manganese. The intensities are again greater than for the Mn-F-Mn pairs.

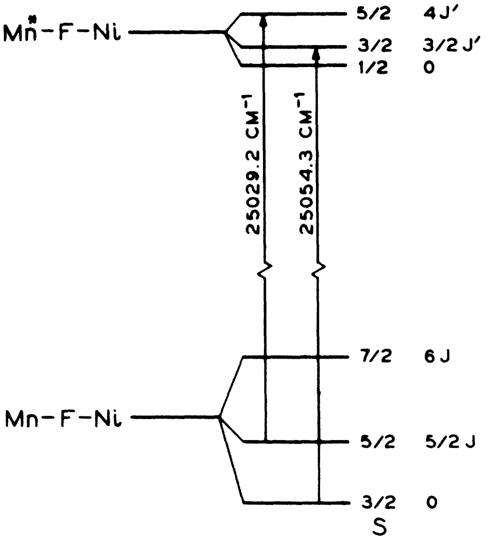

FIG. 2. Energy-level scheme for a pair of manganese and nickel ions. The upper set corresponds to the manganese ion in an excited quartet state. The observed transitions are indicated by vertical lines.

These results show that pair absorption is possible not only for like but also for unlike ions, and it is even more effective for the latter. If the same mechanism[3] as that for like ions is assumed, this means that the interaction between the electric field and the paramagnetic ion pair is stronger when the two ions are unlike. This is not surprising, because the analysis of the theoretical expression for the coupling constant in the symmetrical case reveals that most of the large contributions cancel for reasons of symmetry, whereas this is not the case for unlike pairs. However, full understanding of this effect, which is closely related to superexchange interaction, awaits further theoretical and experimental studies which are in progress.

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[1] A. L. Schawlow, D. L. Wood, and A. M. Clogston, Phys. Rev. Letters 3, 271 (1959).

[2] D. S. McClure, J. Chem. Phys. 39, 2850 (1963).

[3] J. Ferguson, H. J. Guggenheim, and Y. Yanabe, J. Appl. Phys. 36, 1046 (1965).