

Double excitation transitions in Mn^{2+} -doped alkali halides

M. Moreno, F. Rodríguez, and J. A. Aramburu

*Departamento de Óptica y Estructura de la Materia, Facultad de Ciencias,
Universidad de Santander, Santander, Spain*

F. Jaque and F. J. López

*Departamento de Óptica y Estructura de la Materia e Instituto de Física del Estado Sólido,
Consejo Superior de Investigaciones Científicas, Universidad Autónoma de Madrid,
Cantoblanco, Madrid 34, Spain*

(Received 26 May 1983)

It is shown in this work that the room-temperature excitation spectra of as-grown crystals of LiF, NaF, NaCl, KCl, and KBr doped with Mn^{2+} reveal the existence of double excitation peaks. These peaks are related to the formation of precipitated phases containing Mn^{2+} in the alkali halide lattice. In the case of LiF: Mn^{2+} the position of the [${}^4A_1(G)$, ${}^4E(G)$] and ${}^4T_1(G)$ peaks suggests an anomalously small Mn^{2+} - F^- distance for the precipitated phase.

I. INTRODUCTION

The optical properties associated with a given transition-metal cation M in an ionic lattice depend to a great extent on the MX_n complex formed by M and the n nearest anions X . Nevertheless, when the cation is not an impurity dissolved in a given host lattice, but is ordered as a component of a perfect lattice, new features can appear related to the existence of an effective exchange interaction between the cations in nearest-neighbor positions. One of the most spectacular consequences of this fact is the appearance of the so-called double excitation transitions which have been particularly observed for some Mn^{2+} compounds such as MnF_2 ,¹ $RbMnF_3$,^{1,2} $KMnF_3$,² $NaMnF_3$,³ and Rb_2MnCl_4 .⁴ Also, a double excitation has been recently observed in Mn-doped NaCl when the impurity is precipitated in a metastable phase (Suzuki phase).⁵

If we consider a pair of Mn^{2+} ions in close positions the ground-state wave function is in a first approximation $\phi_1^0\phi_2^0$, where ϕ_1^0 and ϕ_2^0 mean the ground-state wave function for each of the *isolated* Mn^{2+} ions involved in the pair. Of course, within this approximation the transition $\phi_1^0\phi_2^0 \rightarrow \phi_1^a\phi_2^b$, where both a and b are different from zero, is not allowed mainly because the coupling operator with the radiation field is a one-electron operator. However, in a further approximation each of the $\phi_1^a\phi_2^b$ states may be coupled to other $\phi_1^{a'}\phi_2^{b'}$ by means of the kinetic and Coulombic terms involved in the Hamiltonian.⁶⁻⁸

In this case one or two of the indices a' and b' are different from a and b , respectively, and then this coupling may allow the $\phi_1^0\phi_2^0 \rightarrow \phi_1^a\phi_2^b$ transition ($a \neq 0$, $b \neq 0$). In the case of Mn^{2+} pairs some of the double excitations from the ground state of the pair are not spin forbidden as it happens for every crystal-field transition arising from the ground state of the "isolated" Mn^{2+} ion. This fact, of course, facilitates the observation of double excitation transitions in manganese compounds, some of which lie beyond the highest crystal-field transition.

The main goal of this work is to demonstrate the appearance of double excitation bands in as-grown crystals of various Mn^{2+} -doped alkali halides. This fact is related to the

formation of precipitated phases containing Mn^{2+} , within the alkali halide lattice. In particular, the following alkali halide lattices doped with Mn^{2+} are investigated in this work: LiF, NaF, NaCl, KCl, and KBr.

The formation of precipitated phases was suggested in the early EPR work dealing with Mn^{2+} in alkali halide lattices.^{9,10} The EPR spectra of some of these as-grown crystals showed the appearance of an exchange-narrowed band characteristic of salts containing a paramagnetic ion not as an impurity but as a true component of the perfect lattice. Furthermore, the observation of EPR spectra associated with "isolated" Mn^{2+} ions requires quenching the as-grown crystals in order to dissolve to a large extent the precipitated phases of Mn^{2+} .^{9,10}

Owing to this we shall compare through this work the optical spectrum of every as-grown crystal with the corresponding one obtained after quenching. This comparison may support the existence of double excitation bands in the as-grown crystal and, at the same time, provide us with information about differences in Mn^{2+} -ligand distance, covalency, etc., among the precipitated phase and the "isolated" Mn^{2+} ions dissolved in the host lattice.

II. EXPERIMENTAL

The alkali halide crystals doped with manganese were grown by the Czochralski method in an inert atmosphere. Mn^{2+} was introduced in the form of MnF_2 , $MnCl_2$, and $MnBr_2$ for alkali fluorides (LiF, NaF), alkali chlorides (NaCl, KCl), and KBr, respectively. The Mn^{2+} concentration lies in the range 200–2000 ppm for every one of the systems under study. Owing to this and to the very low oscillator strengths of the crystal-field bands of Mn^{2+} we have detected the optical transitions by means of the photostimulated luminescence technique, i.e., recording the excitation spectra corresponding to the ${}^4T_1(G) \rightarrow {}^6A_1(S)$ emission whose maximum lies typically between 580 and 650 nm. The spectra were recorded using a Jobin-Yvon spectrofluorimeter model JY 3D. In order to avoid spurious signals, suitable 10-nm bandwidth Oriol filters were placed be-

fore the corresponding monochromator. All the spectra reported in this work were performed at room temperature (RT).

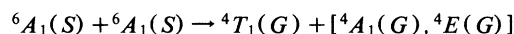
In order to support the presence of precipitated phases in our as-grown crystals we have also measured the corresponding EPR spectra at RT using a Varian E-12 X-band spectrometer. Quenching treatment was achieved by heating the samples for 30 min at 600°C and dropping them into a copper block at RT.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the excitation spectra measured at RT for both as-grown and quenched samples of NaCl:Mn²⁺. In the as-grown sample, the presence of the Suzuki phase has been confirmed by using Raman spectroscopy.¹¹

The six excitation peaks appearing at low energy have been unambiguously associated with crystal-field transitions of Mn²⁺ ions in cubic or nearly cubic symmetry.⁵ Their corresponding assignment is also given in the figure. The position of these crystal-field bands is very similar for the as-grown and quenched crystals. Nevertheless, a recent study on this system⁵ has shown that the $10Dq$ value is about 300 cm⁻¹ higher for the as-grown crystal, a fact which has been associated with a slightly smaller Mn²⁺-Cl⁻ distance in this case.

On the other hand, the excitation band peaked at 231 nm in the as-grown samples has a much higher intensity than the other ones and nearly disappears upon quenching. This band cannot be associated with any crystal-field transition whereas it has been ascribed⁵ to the double excitation



for two close Mn²⁺ ions. In fact, the energy of the transition is equal (to ~200 cm⁻¹) to the sum of the energies of the corresponding single transitions. This band has been recently related to the presence of the Suzuki phase.¹² This assignment is also supported by recent magnetic-

susceptibility measurements on as-grown samples of NaCl:Mn²⁺ performed in the 0.07–4.2-K range.¹³

For as-grown KCl:Mn²⁺ crystals we have also observed an excitation peak at 231 nm. However, the corresponding crystal-field spectrum was poorly detected because of a low Mn²⁺ concentration in the sample.

With regard to the results on KBr:Mn²⁺, they are shown in Fig. 2. In this case the most remarkable feature observed when comparing the excitation spectra corresponding with the as-grown and quenched samples is again the strong diminution in the intensity of the 236-nm peak after quenching. In a similar way to the NaCl:Mn²⁺ system this band cannot be attributed to a crystal-field transition. Thus we have assigned it to the double transition ${}^4T_1(G) + [{}^4E(G), {}^4A_1(G)]$. In fact, its energy is only ~300 cm⁻¹ higher than the sum of the energies corresponding to the single transitions involved.

The position of the crystal-field transition peaks is very similar for both situations, though the ${}^4T_1(G)$ peak (538 nm) for the quenched sample has a somewhat smaller energy than that corresponding to the as-grown crystal (530 nm).

Unfortunately, in the system KBr:Mn²⁺ the structure of the precipitated phases in the as-grown crystals has not yet been established. However, the EPR measurements show an exchange-narrowed band analogous to those observed in NaCl:Mn²⁺ and KCl:Mn²⁺, which are ascribed to Mn²⁺ precipitates.

The excitation spectra for LiF:Mn²⁺ and the assignment corresponding to every excitation peak are shown in Fig. 3. Clearly apparent from the figure are the significant changes induced by quenching upon the excitation spectrum of the as-grown crystals. Quenching gives rise to serious displacements on the crystal-field transition peaks and also to the near disappearance of peaks at 248 and 217 nm. Again, this fact supports the assignment of these peaks to double excitation transitions.

The energies of the peaks assigned to the double excitations ${}^4T_1(G) + [{}^4A_1(G), {}^4E(G)]$ and ${}^4T_2(G) + [{}^4A_1(G),$

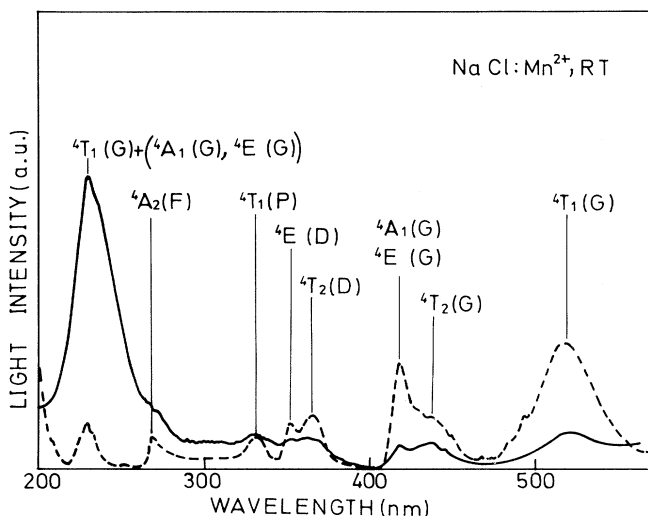


FIG. 1. Excitation spectra, measured at RT, of the Mn²⁺ emission for a sample of NaCl:Mn²⁺ containing the Suzuki phase (continuous line) and for a freshly quenched sample (dashed line).

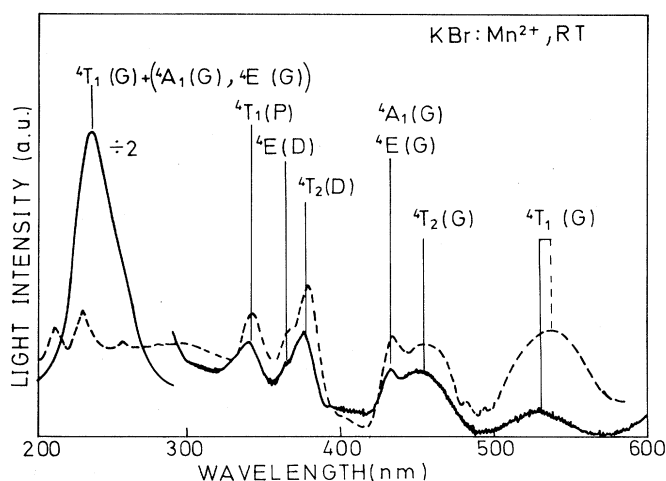


FIG. 2. Excitation spectra of the Mn²⁺ emission for as-grown (continuous line) and quenched (dashed line) samples of KBr:Mn²⁺.

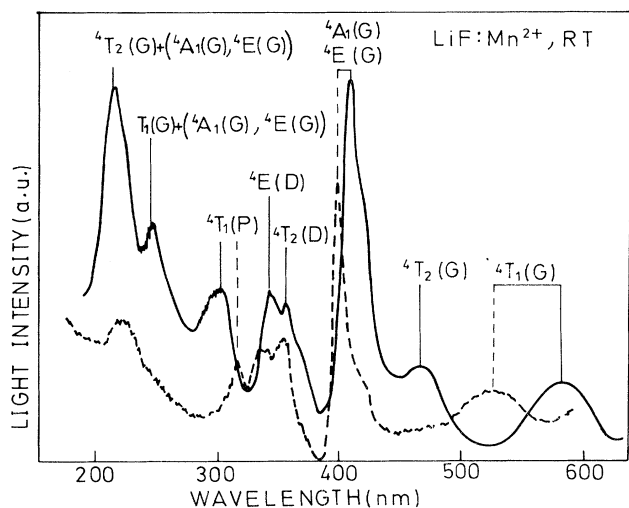


FIG. 3. Excitation spectra of the Mn^{2+} emission for as-grown (continuous line) and quenched (dashed line) samples of LiF:Mn^{2+} .

${}^4E(G)$ are only about 300 cm^{-1} higher than the sum of the energy corresponding to the single transitions. Differences of this kind should be ascribed not to exchanging effects but rather to coupling through lattice distortion as it was first noted by Stokowski, Sell, and Guggenheim¹ in their work on RbMnF_3 and MnF_2 .

It should be remarked here that the excitation spectrum corresponding to the as-grown sample of LiF:Mn^{2+} , besides their differences with that observed after quenching, shows some new features not observed up to now for the $(\text{MnF}_6)^{4-}$ complex in ionic lattices. One of the most salient features is the position of the assigned $[{}^4A_1(G), {}^4E(G)]$ peak for the as-grown sample which is located at 410 nm, although it lies at 400 nm for the quenched crystal.

In fact, the position of this peak, for MnF_2 ,¹⁴ KMnF_3 ,¹⁵ RbMnF_3 ,¹⁶ NaMnF_3 ,³ NH_4MnF_3 ,¹⁷ CsMnF_3 ,¹⁸ $\text{KZnF}_3:\text{Mn}^{2+}$,¹⁵ $\text{KMgF}_3:\text{Mn}^{2+}$,¹⁹ $\text{ZnF}_2:\text{Mn}^{2+}$,²⁰ $\text{CaF}_2:\text{Mn}^{2+}$ and $\text{CdF}_2:\text{Mn}^{2+}$,²¹ lies in the 395–400-nm region. In the same way, the energy of the first excitation peak ${}^4T_1(G)$ (16700 cm^{-1}) of the as-grown LiF:Mn^{2+} crystal is smaller than that measured for any system involving the $(\text{MnF}_6)^{4-}$ cluster. Also, the ${}^4T_1(G)$ peak energy is about 2200 cm^{-1} higher for the quenched than for the as-grown LiF:Mn^{2+} crystal.

On the other hand, the room-temperature EPR spectrum for the as-grown LiF:Mn^{2+} crystal consists only of an exchange-narrowed band with a peak-to-peak width $\Delta H_{pp} = 285\text{ G}$. Owing to this we believe that the excitation spectrum of the as-grown LiF:Mn^{2+} crystal corresponds to a precipitated phase containing Mn^{2+} , though the structure of such a precipitated phase is not yet known. The features of the crystal-field spectrum commented above would indicate that, under the assumption that Mn^{2+} is surrounded by six F^- anions, the $\text{Mn}^{2+}\text{-F}^-$ distance R in the precipitated phase must be unusually small. Taking as a guide the case of Mn^{2+} -doped fluoroperovskites, the lowest R values are found for $\text{KMgF}_3:\text{Mn}^{2+}$ and $\text{KZnF}_3:\text{Mn}^{2+}$ having $R = 2.07$ and $R = 2.08\text{ \AA}$, respectively, at room temperature.^{22,23} Thus we believe that R is smaller than 2.07 \AA for the LiF:Mn^{2+} as-grown sample. In fact, if R decreases $10Dq$

tends to increase and the first ${}^4T_1(G)$ peak is displaced towards lower energies. At the same time the unusual position of the $[{}^4A_1(G), {}^4E(G)]$ peak, with respect to the 395–400-nm region where it is normally observed for $(\text{MnF}_6)^{4-}$ clusters in ionic lattices, would be consistent with a significant increase of the covalency due to the decrease of R . As is known, an increase in the covalency gives rise to a reduction in the effective Racah parameters and then to a displacement of the $[{}^4A_1(G), {}^4E(G)]$ peak towards lower energies.²⁴ In connection with this, the calculations by Emery, Leble, and Fayet²⁵ for the $(\text{MnF}_6)^{4-}$ complex indicate that the covalency parameter f_σ shows a flat minimum around the equilibrium distance, but it increases further upon decreasing R . Also, recent experimental data on CdTe:Co^{2+} under pressure point out that when R decreases more than about 0.015 \AA the covalency of the Co–Te bond increases.²⁶

The results concerning NaF:Mn^{2+} can be seen in Fig. 4. In this case also the intensity of the 230-nm peak marked ${}^4T_1(G) + [{}^4E(G), {}^4A_1(G)]$ strongly decreases upon quenching and, at the same time, a somewhat different crystal-field spectrum appears. The differences between the excitation spectra before and after quenching are qualitatively similar to those observed for LiF:Mn^{2+} , but less drastic. For instance, the ${}^4T_1(G)$ peak observed after quenching is only 440 cm^{-1} above the corresponding as-grown crystal. However, the position of the $[{}^4A_1(G), {}^4E(G)]$ peak is placed at 406 nm for the as-grown crystal though it lies at 397 nm after quenching.

These results suggest that for NaF:Mn^{2+} the quenching gives rise to a higher $\text{Mn}^{2+}\text{-F}^-$ distance as for LiF , but the location at 406 nm of the $[{}^4A_1(G), {}^4E(G)]$ peak in as-grown samples cannot be associated with an unusually small value of R , as for LiF , because the ${}^4T_1(G)$ transition appears at the same position as that for KMnF_3 and $\text{KZnF}_3:\text{Mn}^{2+}$.¹⁵

IV. FINAL REMARKS

The preceding results indicate that the excitation spectra of as-grown crystals of LiF , NaF , NaCl , KCl , and KBr

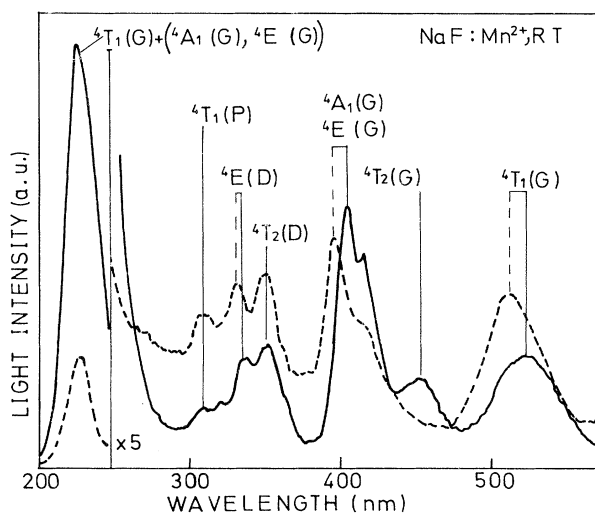


FIG. 4. Excitation spectra of the Mn^{2+} emission for as-grown (continuous line) and quenched (dashed line) samples of NaF:Mn^{2+} .

doped with Mn^{2+} show the presence of peaks which are associated with double excitation transitions because of the following reasons:

(1) The energy of the assigned double transitions is always equal ($\sim 300 \text{ cm}^{-1}$) to the sum of the energies of the corresponding two single transitions.

(2) The intensity of each one of the assigned double excitation peaks experiences a drastic decrease upon quenching which is known to give rise to the appearance of a large amount of "isolated" Mn^{2+} ions in the alkali halide host crystal. This is consistent with changes more or less significant induced by quenching on the position of crystal-field peaks.

(3) These peaks cannot be associated with charge-transfer transitions from the nearest anions to Mn^{2+} . In fact, recent experimental data point out that the first of these bands is placed at 172 nm for LiCl:Mn^{2+} while it lies at 207 nm for LiBr:Mn^{2+} .²⁷ In regards to the position of the first charge-transfer peak associated with $(\text{MnF}_6)^{4-}$, it should be around 120 nm following Jørgensen's optical electronegativity scale.²⁸ In this way a small peak observed at about 113 nm for MnF_2 has been ascribed to the first charge-transfer transition.²⁹

As the position of charge-transfer bands is mainly governed by the nature of the central ion and the corresponding ligand, neither its position nor the disappearance upon quenching can be reconciled with a charge-transfer assignment for our peaks.

The appearance of double excitation transitions should not be necessarily related to the presence of microcrystals containing a precipitated phase. Indeed, such transitions,

which require the existence of at least two Mn^{2+} ions in close positions, could also appear when dimers or other small aggregates are formed. However, in NaCl:Mn^{2+} it has been recently proved¹² that the 231-nm peak is only related to the presence of the Suzuki phase and not to the existence of such small aggregates formed, to a large extent, at RT about 100 h after quenching.

In the other hosts studied in the present work an analysis similar to that made for NaCl:Mn^{2+} has not yet been performed. However, the results on NaCl:Mn^{2+} , as well as the existence of exchange-narrowed EPR bands for the as-grown crystals investigated along this work, support our assumption that the double excitation bands observed in the present systems are mainly related to the formation of precipitated phases containing Mn^{2+} , rather than to dimers or other small aggregates.

Finally, we want to point out that this kind of experiment can provide useful information about local differences among the metastable phase and the quenched crystal. In this way the results obtained for NaCl:Mn^{2+} , LiF:Mn^{2+} , and NaF:Mn^{2+} clearly suggest that R is smaller for the precipitated phase than for the quenched crystal, this effect being particularly significant in the case of LiF:Mn^{2+} .

Further work along this line is currently in progress.

ACKNOWLEDGMENTS

Financial support by the Comisión Asesora para la Investigación Científica y Técnica is gratefully acknowledged.

- ¹S. E. Stokowski, D. D. Sell, and H. J. Guggenheim, *Phys. Rev. B* **4**, 3141 (1971).
²J. Ferguson, *Prog. Inorg. Chem.* **12**, 159 (1970).
³J. P. Srivastava and A. Mehra, *J. Chem. Phys.* **57**, 1587 (1972).
⁴B. Ghosh and R. K. Mukherjee, *Phys. Status Solidi (b)* **106**, 699 (1981).
⁵F. Rodríguez, M. Moreno, F. Jaque, and F. J. López, *J. Chem. Phys.* **78**, 73 (1983).
⁶K. I. Gondaira and Y. Tanabe, *J. Phys. Soc. Jpn.* **21**, 1526 (1966).
⁷Y. Tanabe, T. Moriya, and S. Sugano, *Phys. Rev. Lett.* **15**, 1023 (1965).
⁸D. S. McClure, in *Optical Properties of Ions in Solids*, edited by B. Di Bartolo (Plenum, New York, 1975).
⁹G. D. Watkins, *Phys. Rev.* **113**, 71 (1959).
¹⁰T. P. P. Hall, W. Hayes, R. W. H. Stevenson, and J. Wilkens, *J. Chem. Phys.* **38**, 1977 (1963).
¹¹J. M. Calleja, A. Ruiz, F. Flores, V. R. Velasco, and E. Lilley, *J. Phys. Chem. Solids* **41**, 1367 (1980).
¹²A. de Andrés, J. M. Calleja, F. J. López, F. Jaque, F. Rodríguez, and M. Moreno, *Radiat. Eff.* (in press).
¹³J. A. Aramburu, J. C. Gómez Sal, M. Moreno, F. Rodríguez, and F. Jaque (unpublished).
¹⁴J. W. Stout, *J. Chem. Phys.* **31**, 709 (1959).
¹⁵J. Ferguson, H. J. Guggenheim, and Y. Tanabe, *J. Phys. Soc. Jpn.*

- 21**, 692 (1966).
¹⁶A. Mehra and P. Venkateswarlu, *J. Chem. Phys.* **47**, 2334 (1967).
¹⁷P. J. Alonso, V. M. Orera, F. Palacio, and R. Alcalá, *Phys. Status Solidi (b)* **109**, K81 (1982).
¹⁸A. V. Malakhovskii and G. G. Vasil'ev, *Fiz. Tverd. Tela (Leningrad)* **24**, 585 (1982) [*Sov. Phys. Solid. State* **24**, 328 (1982)].
¹⁹H. U. Güdel, *Chem. Phys. Lett.* **36**, 328 (1975).
²⁰D. T. Palumbo and J. J. Brown, Jr., *J. Electrochem. Soc.* **118**, 1159 (1971).
²¹P. J. Alonso and R. Alcalá, *J. Lumin.* **22**, 321 (1981).
²²M. T. Barriuso and M. Moreno (unpublished).
²³A. Leblé, dissertation (Université du Maine, France, 1982) (unpublished).
²⁴D. Curie, C. Barthou, and B. Canny, *J. Chem. Phys.* **61**, 3048 (1974).
²⁵J. Emery, A. Leble, and J. C. Fayet, *J. Phys. Chem. Solids* **42**, 789 (1981).
²⁶J. Gardavsky, A. Werner, and H. D. Hochheimer, *Phys. Rev. B* **24**, 4972 (1981).
²⁷S. Hirako and R. Onaka, *J. Phys. Soc. Jpn.* **51**, 1255 (1982).
²⁸C. K. Jørgensen, *Prog. Inorg. Chem.* **12**, 101 (1970).
²⁹H. Adachi, S. Shiokawa, M. Tsukada, C. Satoko, and S. Sugano, *J. Phys. Soc. Jpn.* **47**, 1528 (1979).