

EXCHANGE-COUPLED PAIRS OF TRANSITION METAL IONS
AND THEIR EFFECT ON THE OPTICAL ABSORPTION
SPECTRA OF ROCK-FORMING SILICATES*A. I. Bakhtin and V. M. Vinokurov
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(ABSTRACT)

The broad intensive absorption band in the 13,000-18,000 cm^{-1} region in the spectra of clinopyroxenes, amphiboles, micas, and other iron-bearing minerals, usually attributed to the charge transfer $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$, is interpreted here as a band of electric dipole transition in the exchange-coupled pairs $\text{Fe}^{2+}-\text{Fe}^{3+}$ from the ground state ${}^5T_2{}^6A_1$ to the excited state ${}^5T_2{}^4T_2$, produced by excitation of the Fe^{3+} ion. Position in the spectrum, high intensity, polarization, and other characteristics of this band are well explained by exchange interactions of iron ions in the pair $\text{Fe}^{2+}-\text{Fe}^{3+}$. The broad absorption band 20,000-24,000 cm^{-1} in the spectra of titanium-bearing minerals is explained by formation of $\text{Ti}^{3+}-\text{Ti}^{4+}$ exchange-related pairs. — Authors' Abstract

The optical spectra of many iron-bearing minerals (pyroxenes, amphiboles, layer- and ring-silicates, etc.) often contain a broad and intensive absorption band in the 13,000-18,000 cm^{-1} region [1-14]. This band has a number of specific properties. It appears only when the mineral contains both Fe^{2+} and Fe^{3+} ions, occupying neighboring polyhedra sharing an edge or a face. It does not appear in the spectrum when Fe^{2+} and Fe^{3+} ions are separated in the crystal structure [10]. The band is polarized and the electric vector of absorption is oriented along the metal-metal direction in the adjacent polyhedra. The extinction coefficient for the band in silicates is usually $\epsilon \cdot n \cdot (1-10)$ 1/mole \cdot cm ($f \sim 10^{-5}-10^{-4}$), two orders of magnitude higher than for the spin-forbidden transitions and comparable to the value of ϵ for spin-allowed bands. On the basis of these characteristics Canadian investigators [7, 10, 15] ascribed the intensive band in the 13,000-18,000 cm^{-1} region of the spectra of a number of iron-bearing minerals to the $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ transition.

We have attempted to analyze the characteristics of the broad intensive absorption

band in the 13,000-18,000 cm^{-1} region, usually present in the spectra of iron-bearing pyroxenes, amphiboles, micas, and some other minerals, and also of other bands from the point of view of exchange interactions of the iron-group ions in crystals.

DISCUSSION OF $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ TRANSITION

The intensive broad absorption band in the 13,000-18,000 cm^{-1} region in the spectra of pyroxenes, amphiboles, micas, and other iron-bearing minerals (Fig. 1) corresponds in position to the transitions ${}^6A_1(S) \rightarrow {}^4T_2(G)$ of Fe^{3+} ions and appears in the spectra together with other bands of Fe^{3+} ions. However, because of its characteristics, described above, this band cannot be regarded as one of the usual bands of d-d transitions in the crystal field. Its high intensity cannot be explained by low symmetry of the local crystal field, or electron vibrational and spin-orbital interactions, because there is no direct linear correlation between the intensity of the band and the concentration of Fe^{3+} . The relation between intensity and Fe^{3+} content is more complex. The intensity of the band depends on the total iron content in the sample, the ratio of Fe^{2+} and Fe^{3+} concentrations, and the position of the two ions in the structure relative to each other [7]. The band appears in the spectrum when the concentration of iron in the sample is $\sim 1\%$ and more. At lower concentrations

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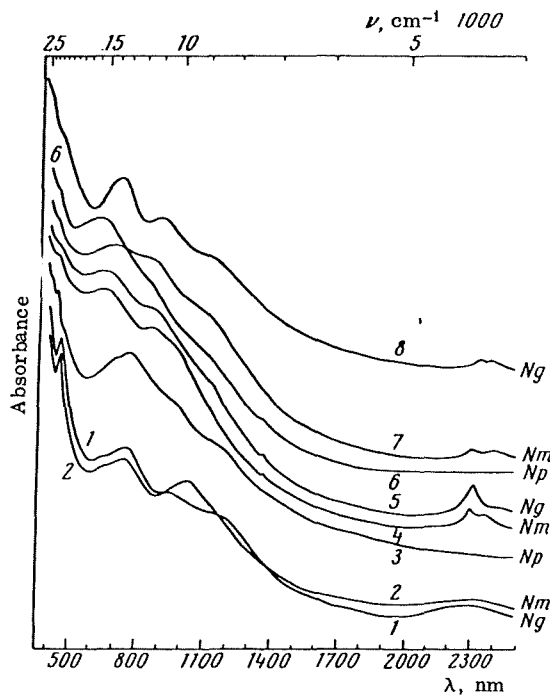


Fig. 1. Absorption spectra of diopside (1, 2), aegirine (3), hornblende (4, 5), arfvedsonite (6, 7) and phlogopite (8).

of total iron it does not appear, but instead the spectrum shows a weak band slightly shifted into the short wave region, ascribed to ${}^6A_1(S) \rightarrow {}^4T_2(G)$ transitions of Fe^{3+} ions [2, 16].

The data presented above justify the assignment of the intensive 13,000-18,000 cm^{-1} absorption band in the spectra of iron-bearing minerals to some kind of interaction between Fe^{2+} and Fe^{3+} ions. The Canadian mineralogists Faye, Manning, and others ascribe this band to the interaction $Fe^{2+} \rightarrow Fe^{3+}$, consisting, in their opinion, in transfer of an electron from Fe^{2+} to Fe^{3+} resulting from overlapping of t_{2g} orbitals of the two ions present in the adjacent polyhedra with a common edge or face. According to these authors [7, 10, 15], a charge is transferred from Fe^{2+} to Fe^{3+} . Let us examine this process. The charge transfer may be represented as follows: $Fe^{2+}(3d^6), Fe^{3+}(3d^5) \rightarrow Fe^{3+}(3d^5), Fe^{2+}(3d^6)$. It is easy to see that when the two ions occupy equivalent structural positions and are in ground state, the starting state of the pair $Fe^{2+}({}^6T_2), Fe^{3+}({}^6A_1)$ and the final state

$Fe^{3+}({}^6A_1), Fe^{2+}({}^6T_2)$ have equal energy and no absorption of light can occur. If the ions Fe^{2+} and Fe^{3+} occupy nonequivalent structural positions the energies of the starting and final states will be different but the difference will be small and the transfer of an electron will require a considerably greater activation energy than in the first case. The activation energy, according to the results of an investigation of the electrical conductivity of rock-forming silicates [17], is of the order of 0.1 eV and, therefore, cannot be responsible for optical absorption of light. This means that in the case of the $Fe^{2+}-Fe^{3+}$ pair optical absorption can occur only if the transfer of electron takes place between ions in an excited state.

Of the excited states of Fe^{2+} and Fe^{3+} ions the energy of the ${}^4T_2(G)$ state of the Fe^{3+} ion most nearly corresponds to the energy of the band in the 13,000-18,000 cm^{-1} region. It may be assumed, therefore, that the electron transfer $Fe^{2+} \rightarrow Fe^{3+}$ occurs when the Fe^{3+} ion is in this excited state. The excited state ${}^3T_1(H)$ of the Fe^{2+} ion in an octahedral field has an energy of 16,000-18,500 cm^{-1} ,

which is close it might be su participates in $\rightarrow Fe^{3+}$. How clinopyroxene band of Fe^{2+} in the 13,000-state ${}^3T_1(H)$ d transfer, its is subordinate tion shows tha 13,000-18,000 in addition to Fe^{3+} ions, to Fe^{3+} ion and, the Fe^{2+} ion. excitation of e was not consid the energy is l

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which is close to the energy of the band, and it might be supposed that this state also participates in the electron transfer $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$. However, in the spectra of most clinopyroxenes, amphiboles, and micas the band of Fe^{2+} - Fe^{3+} interaction usually lies in the 13,000-16,000 cm^{-1} region, and if the state ${}^3\text{T}_1(\text{H})$ does participate in the electron transfer, its role in most of these minerals is subordinate. Thus, even a simple examination shows that the origin of the intensive 13,000-18,000 cm^{-1} band must be ascribed, in addition to the ground states of Fe^{2+} and Fe^{3+} ions, to the excited state ${}^4\text{T}_2(\text{G})$ of the Fe^{3+} ion and, possibly, to the ${}^3\text{T}_1(\text{H})$ state of the Fe^{2+} ion. The possibility of simultaneous excitation of electrons in the pair Fe^{2+} , Fe^{3+} was not considered [18], because in this case the energy is higher than 13,000-18,000 cm^{-1} .

THE THEORY OF EXCHANGE INTERACTIONS AND DISCUSSION OF THE ORIGIN OF THE 13,000-18,000 cm^{-1} BAND

General remarks. Much more information on the Fe^{2+} - Fe^{3+} interaction responsible for the 13,000-18,000 cm^{-1} absorption band in the spectra of iron-bearing silicates can be obtained from the theory of exchange interactions between transition metal ions in crystals [18-25]. The X-ray and Mössbauer data on these minerals show that the iron ions in them occupy adjacent polyhedra with common edges and small distances between the metal ions (3.0-3.2 Å, sometimes less). These are the conditions for the formation of Fe^{2+} - Fe^{3+} exchange-related pairs. It is known that the energy of exchange interaction in this pair is considerably less than the energy of the first excited state, and each of the ions in the pair retains its individuality to a considerable degree. As a result, the intensive absorption bands produced by the exchange interactions appear in the spectra in approximately the same regions usually occupied by the bands of isolated ions.

According to theory, there are two kinds of exchange, direct, cation-cation and indirect, cation-anion-cation exchange, in which the interaction between the paramagnetic ions takes place through the ligands. However, because of the overlap of orbitals in covalent bonding the direct exchange always involves some indirect interaction. In exchange interaction the wave functions of electrons (of the ion pair) overlap, and this increases the covalent character of bonding.

As a result, there is a correlation between the orbital and spin motions of the electrons in the exchange pair and delocalization of electron density about the ions participating in exchange, accompanied by transfer of an electron from one cation to the other with full or partial participation of the ligand orbitals. The integral of electron transition, acting between the ions of the exchange pair, acts twice, the second time in returning the pair to the ground state. The value of the integral b increases with increase in covalent bonding and is related to the covalent contribution to the crystal field D_q by the relation [27]:

$$b = 10 D_q^{\text{cov}}/3. \quad (1)$$

Polarization and intensity of electronic transitions. The action of the integrals of electron transition from cation to cation, even in indirect interaction, polarizes the transitions accompanied by absorption of light predominantly along the metal-metal direction, because this is the direction of orientation of the electric vector. The oscillator strength f of the electron transitions related to the exchange interaction and producing the 13,000-18,000 absorption band in the spectra of the iron-bearing silicates, may be estimated from the following relation [24]:

$$f \sim f_{ab}(b/\Delta E)^2 \cdot 16, \quad (2)$$

here $f_{ab} \sim f_{ac} \lambda^2$, b is the integral of transition, E the energy required for ligand \rightarrow metal transfer of an electron, f_{ac} the oscillator strength for electron transition with ligand \rightarrow metal charge transfer, and λ the covalence parameter. For the Fe^{3+} ions the value of ΔE in the octahedral field is $\sim 40,000 \text{ cm}^{-1}$ [28, 29] and the oscillator strength f_{ac} is about 10^{-1} [4, 30]. Parameter λ may be taken as 0.1. If $b \sim 10^3 \text{ cm}^{-1}$ as in [24], we get $f \sim 10^{-5}$, i.e., the intensity of the absorption bands produced by exchange interaction is of the same order of magnitude as the intensity of the spin-allowed bands. As noted above, the extinction coefficient of the 13,000-18,000 cm^{-1} band is commensurable with the extinction coefficient of the allowed bands, but this fact does not contradict its attribution to exchange interactions.

Expression (2) shows that the high intensity of the exchange interaction band is due to "borrowing" of intensity from the band of the ligand-metal charge transfer in one of the ions of the exchange pair. In intensity

borrowing the 3d functions of the metal electrons receive an admixture of wave functions of opposite configuration (2p functions of oxygen) as a result of exchange interaction. The contribution from mixing of 4p- and 3d-functions of Fe³⁺ is not large because the 4p states are 190,000 cm⁻¹ above the ground state [31]. It should be noted that the increase in the intensity of the exchange interaction bands depends on the fact that under the conditions of exchange interaction the spin of an individual ion is not a satisfactory quantum number; it is replaced by the sum of spins of the pair of ions. As a result, the spin-forbidden electron transitions in isolated ions become allowed in the presence of exchange interaction.

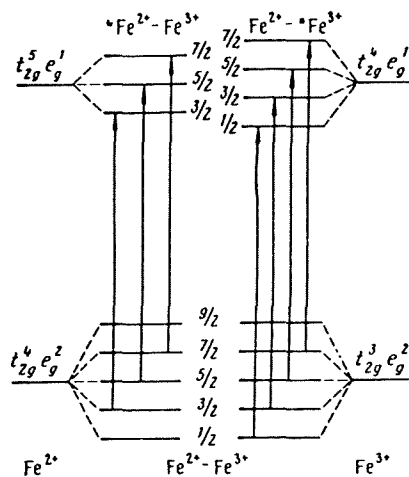


Fig. 2. Energy levels of Fe²⁺-Fe³⁺ pair in ground and excited states.

Arrows indicate possible allowed transitions.

Energy levels of Fe²⁺-Fe³⁺ pair. In describing the energy levels of exchange-related pairs a semiempirical approach is often used, based on the Hamiltonian of type: $H_{exch} = J_{ab} (S_a \cdot S_b)$, representing the principal part of exchange interactions. In this expression S_a and S_b are the total spins in ions a and b and J is the exchange integral. There are several levels for the ground state and for each of the excited states. The number of levels is given by the total spin of the ion pair, having the following values: S_a + S_b, S_a + S_b - 1, ..., |S_a - S_b|. The splitting of the levels in each state is given by relation

$$E = \frac{1}{2} J |S(S+1) - S_a(S_a+1) - S_b(S_b+1)|.$$

The values of J are usually not large but in the ions of the iron group may reach 300-400 cm⁻¹, varying substantially from one crystal to another [21, 32]. As a rule, the values of J are different for the ground and different excited states, and sometimes have different signs. The sign determines the order of levels in the exchange pair. For example, in the pair Fe²⁺-Fe³⁺ in the ground and excited states we can draw the energy level diagram shown in Fig. 2. The occupancy of levels in the ground state is regulated by Boltzmann distribution. The electron transitions are allowed between levels for which the spin of the pair does not change, i. e., the selection rule is ΔS = 0.

As can be seen in Fig. 2, as a result of exchange interaction the levels of the ground state and of each of the excited states of isolated Fe²⁺ and Fe³⁺ ions are split into several sublevels, always including pairs of

sublevels for which ΔS = 0 and between which electron transitions are allowed. Because the sublevels are close to each other in each of the states, these transitions in the optical spectra of the iron group ions are recorded as a single line shifted slightly with respect to its position in the spectrum of an isolated ion. The structure of this line is not always resolved even at 77°K. Lines of this kind are considerably more intensive than the lines of isolated ions because of removal of spin restriction and admixture of functions in a state opposite to that of the ligands connecting the cation pairs. The intensity of these lines is "borrowed" from the band of charge transfer in Fe³⁺ ions from ligand to metal.

Attribution of the 13,000-18,000 cm⁻¹ band. Maximum intensification of bands can be expected, as can be seen in Fig. 2, for the Fe³⁺ ions in Fe²⁺-Fe³⁺ pairs, since the transitions here from the lower level are spin-allowed. The intensity of the Fe³⁺ bands increases also because the energy of the ligand → metal electron transfer is much lower for Fe³⁺ than for Fe²⁺ ions. In view of this, and of the fact that the 13,000-18,000 cm⁻¹ band occupies the same position in the spectrum as the band of ⁶A₁(S) → ⁴T₂(G) transition in isolated Fe³⁺ ions, the broad absorption band in the 13,000-18,000 cm⁻¹ region may be attributed to the Fe³⁺ ions in exchange interaction with Fe²⁺

ions. This int characteristic must enquire r all the possible responding to to ⁴T₁(G), ⁴T₂(G) and other level → ⁴T₂(G) trans It should be not into the ⁴E(D) of iron-bearing very strong ba transfer in the seldom seen in ⁶A₁(S) → ⁴A₁, ⁴ masked. It is of the intensiti difference in th → ⁴T₁(G) and ⁶A₁ be explained by ⁴T₁(G) and ⁴T₂(G) interaction in fact is that the electrons of di considerable d they occur, sin of electron den orbitals [21]. rect to write th exchange inter

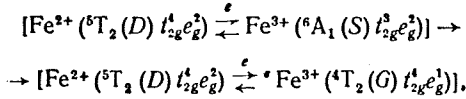
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ions. This interpretation explains all the characteristics of this absorption band. We must enquire now into the reason why, of all the possible bands of the Fe^{3+} ions corresponding to transition from ${}^6\text{A}_1(\text{S})$ level to ${}^4\text{T}_1(\text{G})$, ${}^4\text{T}_2(\text{G})$, ${}^4\text{A}_1$, ${}^4\text{E}(\text{G})$, ${}^4\text{T}_2(\text{D})$, ${}^4\text{E}(\text{D})$ and other levels, the band of the ${}^6\text{A}_1(\text{S}) \rightarrow {}^4\text{T}_2(\text{G})$ transition has the highest intensity. It should be noted that the bands of transition into the ${}^4\text{E}(\text{D})$ and ${}^4\text{T}_2(\text{D})$ states in the spectra of iron-bearing silicates are masked by a very strong band of ligand \rightarrow metal charge transfer in the polyhedra of Fe^{3+} ions and are seldom seen in the spectra (Fig. 1). The ${}^6\text{A}_1(\text{S}) \rightarrow {}^4\text{A}_1$, ${}^4\text{E}(\text{G})$ band also is strongly masked. It is difficult to judge, therefore, of the intensities of these bands. As for the difference in the intensity of the ${}^6\text{A}_1(\text{S}) \rightarrow {}^4\text{T}_1(\text{G})$ and ${}^6\text{A}_1(\text{S}) \rightarrow {}^4\text{T}_2(\text{G})$ bands, it may be explained by the different contribution of ${}^4\text{T}_1(\text{G})$ and ${}^4\text{T}_2(\text{G})$ states to the exchange interaction in the $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ pair. The fact is that the exchange interaction of the electrons of different ions depends to a considerable degree on the orbitals in which they occur, since the angular dependence of electron density is different for different orbitals [21]. Therefore, it is more correct to write the Hamiltonian of isotropic exchange interaction in this form:

$$H_{\text{exch}} = \sum_{i,j} J_{ai bj} (S_{ai} S_{bj}),$$

where summation is performed for the orbitals of ions momentarily occupied by the electrons in transit. A detailed examination of exchange interactions in the orbital degenerate states must take into account the orbital moments of the electrons in the interacting ion pair. However, a qualitative estimate can be obtained by considering only the orbital symmetry of levels in the interacting pair. It follows from symmetry considerations that the ground state ${}^5\text{T}_2(\text{D})$ of ion Fe^{3+} can interact only with the ${}^4\text{T}_2(\text{G})$ state (of all possible states of ${}^4\text{G}$ terms of the Fe^{3+} ion) because these states have the same symmetry. Therefore, the strongest exchange interaction in excited state in the pair $\text{Fe}^{2+}-\text{Fe}^{3+}$ caused by excitation of the Fe^{3+} ion can be expected for the ${}^4\text{T}_2(\text{G})$ state. This evidently explains the great intensity of the ${}^6\text{A}_1(\text{S}) \rightarrow {}^4\text{T}_2(\text{G})$ transition band of Fe^{3+} ions in exchange interaction. The ${}^6\text{A}_1(\text{S}) \rightarrow {}^4\text{T}_1(\text{G})$ band is much less intensive and in the spectra of pyroxenes, and micas is usually overlapped by the intensive spin-allowed band of the Fe^{3+} ions (Fig. 1).

Thus, the physical cause of formation of the intensive absorption band in the 13,000-18,000 cm^{-1} region in the spectra of these minerals is much more complex than the simple transfer of charge $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$. Its mechanism can be shown schematically as follows:



This represents excitation of Fe^{3+} ion into ${}^4\text{T}_2(\text{G})$ state and simultaneous transfer of an electron from Fe^{2+} to Fe^{3+} and back with the aid of overlapping t_{2g} orbitals. The process is simplified by the identical configuration of sub-shell t_{2g} in both ions. The electron transition and the resulting absorption of light is conveniently shown thus: $({}^6\text{T}_2^6\text{A}_1) \rightarrow ({}^6\text{T}_2^4\text{T}_2)$.

Shift of the band, covalence and parameter of exchange. As noted above, the absorption bands produced by exchange interaction occupy essentially the same regions as the bands of isolated ions. There is, however a slight shifting of the bands, caused mainly by an increase in the degree of covalent bonding in the exchange ion pairs as compared with isolated ions. Covalent bonding decreases the effective charges of the ions and increases the average radius of the 3d-orbitals by delocalization of electrons (nephelocetic effect). As a rule, increase in the degree of covalent bonding increases the crystal field parameter D_q [30] by increasing term $\langle r^4 \rangle$ and decreases the parameters B and C, and this explains the shifting of the bands of exchange coupled ion pairs. The intensity of exchange interactions is different in the different states of the ion pair and, therefore, the degree of covalence of the ion pair in the ground and different excited states also is different. For this reason, the largest shift will occur in the level with the strongest exchange interaction. In the $\text{Fe}^{2+}-\text{Fe}^{3+}$ pair this level is ${}^4\text{T}_2(\text{G})$ of the Fe^{3+} ion. In the Fe^{3+} ions increase of D_q and decrease of B and C shift ${}^4\text{T}_2(\text{G})$ in the same direction, towards the region of lower energies. This probably explains the shift of the ${}^5\text{T}_2^6\text{A}_1 \rightarrow {}^5\text{T}_2^4\text{T}_2$ absorption band in the $\text{Fe}^{2+}-\text{Fe}^{3+}$ pair, positioned in the 13,000-18,000 cm^{-1} region, into the long wave region. In the isolated Fe^{3+} ions the corresponding band is usually in the 15,000-18,000 cm^{-1} region [4, 5, 30]. If it is assumed that the shift is determined by the covalent contribution to D_q , then a rough estimate of the electron

transition parameter can be made from expression (1). As suggested earlier, it is of the order of 10^3 cm^{-1} . Using equation $J = -2b^2/\Delta E$, proposed by Anderson and cited in [30], we get a rough estimate of the exchange interaction parameter $J \sim -50 \text{ cm}^{-1}$ in the $\text{Fe}^{2+}-\text{Fe}^{3+}$ pair in the ${}^5\text{T}_2\text{T}_2$ state, which is of the same order of magnitude as the J parameter for other pairs of the iron group ions in crystals [21]. The negative sign is used because of the anti-ferromagnetic character of $t_{2g}-t_{2g}$ exchange, predominant in the minerals under discussion [22].

ON THE ORIGIN OF 20,000-24,000 cm^{-1} ABSORPTION BAND IN THE SPECTRA OF TITANIUM-BEARING MINERALS

The optical spectra of titanium-bearing minerals, in whose structure titanium occupies neighboring polyhedra sharing a vertex, edge or face, often contain a broad absorption band in the 20,000-24,000 cm^{-1} region [5, 8-12]. The extinction coefficient of this band is close to that of the spin-allowed absorption bands [12]. Because of the high intensity of the band and polarization in the metal - metal direction, Faye, Manning et al., attributed it to $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$ charge transfer, by analogy with the $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ transfer investigated by them earlier. This analogy and the examination of exchange interactions $\text{Fe}^{2+}-\text{Fe}^{3+}$ suggest that the broad 20,000-24,000 cm^{-1} band in the spectra of titanium-bearing minerals is produced by exchange reactions in $\text{Ti}^{3+}-\text{Ti}^{4+}$ pairs. The Ti^{3+} ion has one 3d electron, giving a ${}^2\text{D}$ term, which splits in the octahedral field into two levels (lower ${}^2\text{T}_2$ and upper ${}^2\text{E}$), and the transitions between these levels produce a broad absorption band in the 20,000 cm^{-1} region. The next excited state of the Ti^{3+} ion, ${}^2\text{A}_1(\text{S})$, is more than $\sim 80,000 \text{ cm}^{-1}$ above the ground state and, therefore, does not appear in optical spectra. The Ti^{4+} ion ($3d^0$) does not give absorption bands in the optical region, because its first excited state is more than $400,000 \text{ cm}^{-1}$ above the ground state ${}^1\text{A}_1(\text{S})$ [31]. In the crystal field Ti^{3+} and Ti^{4+} ions are characterized by intensive bands of ligand \rightarrow metal charge transfer, in the near-ultraviolet region at 37,000 and 40,000 cm^{-1} respectively [30, 33]. Therefore, the 20,000-24,000 cm^{-1} band may be assigned to the ${}^2\text{T}_2 \rightarrow {}^2\text{E}^1\text{A}_1$ transition in the exchange-coupled pair $\text{Ti}^{3+}-\text{Ti}^{4+}$ from the ground to excited state, attained by the Ti^{3+}

ion. The intensity of the band is evidently "borrowed" from the charge transfer band produced by the ligand \rightarrow metal transfer in the Ti^{3+} and Ti^{4+} polyhedra, positioned close to the 20,000-24,000 cm^{-1} band. The ${}^2\text{T}_2^1\text{A}_1 \rightarrow {}^2\text{E}^1\text{A}_1$ band is shifted into the short wave region relative to the ${}^2\text{T}_2 \rightarrow {}^2\text{E}$ band of isolated Ti^{3+} ions as a result of an increase in the D_q parameter by the covalent contribution D_q^{COV} , produced by the exchange interaction $\text{Ti}^{3+}-\text{Ti}^{4+}$. The parameter of electron transition b can be estimated from the magnitude of the shift and formula (1). It is $\sim 10^3 \text{ cm}^{-1}$, a reasonable value for the iron group ions.

EXCHANGE INTERACTIONS AS THE CAUSE OF BORROWING OF INTENSITY BY THE SPIN-FORBIDDEN BANDS OF Fe^{2+} IONS

A number of authors have noted the high intensity of spin-forbidden absorption bands of Fe^{2+} ions with extinction coefficients sometimes as high as 5 l/mole·cm in the spectra of iron-bearing minerals [7, 9, 13, 34]. The high intensity of these bands is usually attributed to the charge transfer $\text{Fe}^{2+} \rightarrow \text{Ti}^{3+}, \text{Ti}^{4+}$. In the light of the discussion presented here the intensification of the spin-forbidden absorption bands of Fe^{2+} ions may be explained by formation of exchange-coupled Fe^{2+} ions with $\text{Ti}^{4+}, \text{Ti}^{3+}, \text{Fe}^{3+}$, and Fe^{2+} ions. This results in an increase in the degree of covalent bonding, and the intensity is borrowed from the ligand \rightarrow metal charge transfer bands. The $\text{Ti}^{4+}, \text{Ti}^{3+}$, and Fe^{3+} ions are very suitable participants in this process, first, because they have high valences and, therefore, can contribute considerably to covalent bonding (especially if they replace an ion of lower valence), and, second, they have low energy bands of the ligand \rightarrow metal transfer, making their intensity more easily "borrowed". Moreover, the symmetry of the ground state A_1 of Ti^{4+} and Fe^{3+} ions is readily interchangeable with the symmetry of other states, especially in the fields of low symmetry characteristic of minerals, and this makes the exchange interactions quite effective.

SUMMARY

Our investigation shows that many unusual features of the optical spectra of iron and titanium-bearing minerals can be explained by exchange interactions in the pairs of iron group ions in the structure of these minerals.

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New experim
uranium oxide
occurs in these
lead is determ
Abstract.

It has become
natural uranium
uraninite or pitch
minerals with
Pb as the essential
position: U⁶⁺,
U⁴⁺, and Pb, the
(radiogenic lead)
direct proof that
the crystal structure
positions indicate
crystallochemistry
U⁶⁺, Pb, Th)C

Very important
recommendations
tion. For example
states that lead
replaces U⁴⁺ in
ionic radii being
ment decrease
and in Wasserberg
mineral can be
of parameter a
that variation of
content of isomorphous
and even constant

Many attempts
mine the mode of
lead in the natural
[4] compared with
fraction reflected
lead with those
concluded that the
ture of uraninite
in the form of

*Trans. from
1978.