netic generation under consideration and the oscillatory attenuation is to be expected.

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[1] B. Abeles, Phys. Rev. Lett. 19, 1181 (1967).

[2] G. Turner, R. L. Thomas, and D. Hsu, Phys. Rev. B 3, 3097 (1971).

[3] W. D. Wallace, M. R. Gaerttner, and B. W. Maxfield, Phys. Rev. Lett. 27, 995 (1971).

[4] Y. Goldstein and A. Zemel, Phys. Rev. Lett. 28, 147 (1972).

[5] V. F. Gantmakher, Zh. Eksp. Teor. Fiz. 42, 1416 (1962) [Sov. Phys. JETP 15, 982 (1962)].

[6] V. J. Easterling and H. V. Bohm, Phys. Rev. 125, 812 (1962).

[7] J. J. Quinn, Phys. Lett. 25A, 522 (1967).

[8] G. E. Juras, Phys. Rev. 187, 784 (1969).

One-Electron Energy Levels in Fe_3O_4

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A one-electron energy diagram is suggested for magnetite, which is consistent with recent soft-x-ray emission and absorption spectra, cathodoluminescence, and optical-absorption data.

In the $3d$ transition-metal oxides, normal bands of mainly $2p$ oxygen and $4s$ metal (M) character are separated by an energy gap E_g of about 6 eV. The $3d(M)$ electrons interact strongly with each other and with the surrounding anions, giving rise to a set of localized states or else narrow bands in the $2p(\mathrm{O})$-$4s(M)$ gap, which usually contains the Fermi level.

Optical spectroscopists represent the energy of the highly correlated d-electron manifold by a term which may include electrons in different orbital and spin states. An alternative approach is to ignore completely the collective behavior of the d electrons and construct a one-electron energy diagram, as Balberg and Pankove did for Fe_3O_4.[1] Here we wish to suggest a different one-electron energy scheme which we believe is in better agreement with the experimental data.

Two parameters determine the main features of the one-electron energy diagram. One is Δ_{cf} ($=10Dq$), the crystal-field splitting of the t_2 and e one-electron orbitals due to their covalent mixing and electrostatic interaction with the ligands. The other is Δ_{ex}, the Hund's-rule exchange splitting between spin-up and spin-down orbitals on the same cation. Other intra-atomic electrostatic interactions are ignored. Dq may be deduced directly from the optical spectrum of the ion. Limits may be set of Δ_{ex} for a $3d^n$ ion in an octahedral site for $4 \leqslant n \leqslant 7$ from a knowledge of the spin state. Essentially there is a high- or low-spin state, depending on whether Δ_{ex} is greater or less than Δ_{cf}.

According to Balberg and Pankove,[1] all the majority-spin d electrons {five spin-down electrons in the tetrahedral (A) sites and ten spin-up electrons in the octahedral [B] sites in $(\mathrm{Fe}^{3+})[\mathrm{Fe}^{2+}\text{-}\mathrm{Fe}^{3+}]\mathrm{O}_4$}[2] *lie below the top of the 2p(O) band,* and only the eleventh spin-down d electron on the octahedral sites is in the gap E_g. For this they assumed $\Delta_{\mathrm{ex}} \simeq 6$ eV, quoting a theoretical value for MnO. They interpret their cathodoluminescence data as showing that the crystal-field splitting of the $3d(B)$ spin-down orbitals lies between 2.6 and 3.2 eV; the degeneracy of the t_{2g} orbitals is partly removed by a trigonal component of the B-site crystal field, and they split into upper e_ϵ and lower a_1 orbitals.

We criticize this scheme for the following reasons: The values of (a) Δ_{ex} and (b) Δ_{cf} are far too large; and (c) it cannot explain the soft-x-ray results. Instead, we propose the scheme of Fig. 1, where *all the occupied d electron levels lie in the gap.*

(a) Exchange splitting: Calculations of the critical value of Δ_{cf} for a transition from a high- to a low-spin state are available in the literature.[3] The transitions occur when $\Delta_{\mathrm{cf}} \approx \Delta_{\mathrm{ex}}$, so the calculated values, 17 600 and 30 000 cm^{-1} (2.2 and 3.7 eV) for Fe^{2+} and Fe^{3+}, respectively, are esti-

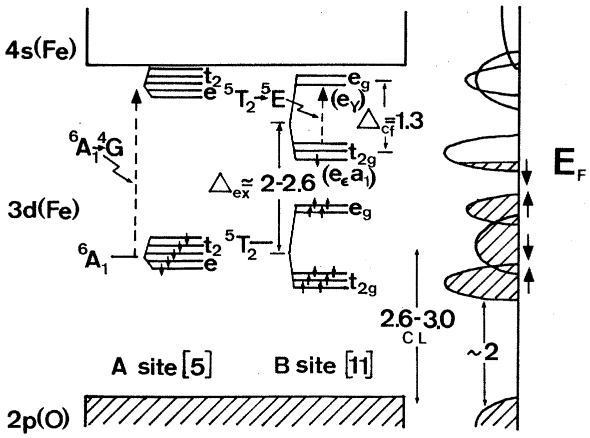

FIG. 1. Proposed one-electron energy diagram for Fe_3O_4 at room temperature. Energies marked are in eV.

mates of Δ_{ex}. These values are in good agreement with what one would estimate for $\Delta_{ex} = \Delta_{cf}$ ($= 10Dq$) from the Racah parameter B of the free ions.[4] The crossover point from the high-spin to the low-spin state occurs for Fe^{2+} (i.e., $^5T_2 \to {}^1A_1$) at $Dq/B = 2$, and for Fe^{3+} (i.e., $^6A_1 \to {}^2T_2$) at $Dq/B = 2.8$, respectively. Since Δ_{ex} is due to the interaction of electrons on the same cation, it should not depend to first order on the anion neighbors. The approximate validity of the above estimates has been confirmed by magnetic and spectroscopic work on several ion complexes, but the calculations of the critical value of Δ_{cf} are generally too high. The experimental work reviewed by Martin and White[5] shows that the crossover for Fe^{2+} salts occurs around 12 000 cm^{-1} (1.5 eV). Fe^{3+} is infrequently found in a pure low-spin state, and only a lower limit for Δ_{ex} can be derived from data on the high-spin ion. The value must, however, be in the range 2.5–3.7 eV, so that the average exchange splitting for $Fe^{2+/3+}$ (B) in Fe_3O_4 is 2–2.6 eV.

(b) Crystal-field splitting: Dq for Fe^{2+} on octahedral sites and Fe^{3+} on octahedral and tetrahedral sites can be deduced from optical data for other oxides. Some results are given in Table I. The ^5D term of the Fe^{2+} ion is split into $^5T_2$ and ^5E levels by an octahedral crystal field.[4] The ^5E level lies $10Dq$ higher, so that Δ_{cf} is given directly by the energy of the optical transition between these two levels. On the one-electron diagram the excitation is equivalent to promoting the sixth electron from a t_{2g} to an e_g orbital. The ^6S term of the Fe^{3+} ion is unsplit by a cubic crystal field. Dq must be deduced from the energies of the very weak $^6S \to {}^4G$ spin-flip transitions. These correspond to exciting an electron by roughly Δ_{ex}, but they cannot be properly represented on a one-electron diagram. From Table I it is clear that $10Dq$ for both Fe^{2+} and Fe^{3+} ions is much less than the 2.6–3.2 eV used in Ref. 1. For octahedrally coordinated Fe^{2+} it is 1.28 eV, and for Fe^{3+} about 2 eV. The average for B sites in Fe_3O_4 is ~1.6 eV. In any case, the crystal-field splitting is much too small to account for the cathodoluminescence peak.[1]

(c) Soft-x-ray data: As a result of the overestimate of both Δ_{ex} and Δ_{cf}, Balberg and Pankove placed the majority-spin d electrons for both A and B sites several eV into the $2p$(O) band. This was further justified on the basis of a slight shoulder roughly 2 eV to the low-energy side of the $L\alpha$ [$3d(\mathrm{Fe}) \to 2p_{3/2}(\mathrm{Fe})$] x-ray emission in Fe_3O_4.[6] Since Bonnelle found exactly the *same emission spectrum for both* Fe_2O_3 *and* Fe_3O_4, it follows that any assignment of the d levels relative to the $2p$(O) band edge must refer to the majority-spin electrons and not to the single

TABLE I. Crystal-field parameter Dq for Fe^{2+} and Fe^{3+} ions in solution and in oxide matrices.

		Dq values (cm^{-1})[a]				
		Octahedral sites			Tetrahedral sites	
	$Fe(H_2O)_6{}^{n+}$ [b]	Al_2O_3 [c]	MgO [d]	$Y_3Fe_5O_{12}$ [e]	$LiAl_5O_8$ [f]	$Y_3Fe_5O_{12}$ [g]
Fe^{3+}	1370	1650	···	1550	940	690
Fe^{2+}	1040	···	1030	···		···

[a] 1.0 eV = 8066 cm^{-1}.

[b] L. E. Orgel, in *An Introduction to Transition Metal Chemistry: Ligand Field Theory* (Methuen, London, 1966), 2nd ed., p. 47.

[c] D. S. McClure, J. Chem. Phys. 36, 2757 (1962).

[d] W. Low and M. Weger, Phys. Rev. 118, 1119, 1130 (1960).

[e] K. A. Wickersheim and R. A. Lefever, J. Chem. Phys. 36, 844 (1962).

[f] N. T. Melamed, F. de S. Barros, P. J. Viccaro, and J. O. Artman, Phys. Rev. B 5, 3377 (1972).

$3d(B)$ spin-down electron associated with the Fe^{2+} ion in Fe_3O_4. (Bonnelle herself remarks that these spin-down electrons behave, at room temperature, like a low-density electron gas, hardly perturbing the localized d levels, which are primarily responsible for the observed soft–x-ray emission.) The shoulder can be interpreted as the $2p(O) \rightarrow 2p_{3/2}(Fe)$ "crossover transition" between oxygen and iron atoms,[1] an idea used with success by Fischer and Baun in work on the light transition-metal oxides.[7] If it applies to iron oxides, the majority-spin electrons must be placed 2 ± 0.5 eV above the upper edge of the $2p(O)$ band.

Our one-electron diagram for Fe_3O_4, shown in Fig. 1, displays the essential feature of high-spin cations, with inverse distribution. Immense care is to be taken against indiscriminate use of this diagram. In order to remove any possible ambiguity we wish to point out that it is a pseudo one-electron scheme in which many-electron effects are incorporated in two ways: First, in the explicit way, the exchange interaction has been displayed, and second, in the implicit way, in accordance with group theoretical arguments for the possible cubic-field splittings of the d manifold (e.g., Fe^{3+} on tetrahedral or octahedral sites in the ^6S free ionic state shows none). This also permits us to indicate the simplest of the possible spectroscopic transitions. Since the extra electron on the Fe^{2+} ion can be on either of the two possible B sites, each one of them is a potential Fe^{2+} ion, and they have been lumped together in the Fe^{2+} (B site) splitting. It is further substantiated by the soft–x-ray[6] and cathodoluminescence[1] data, and the limited optical absorption spectra of Miles, Westphal, and von Hippel.[8] Five points will be discussed in turn.

(1) The identity of $L\alpha$ emission spectra of Fe_2O_3 and Fe_3O_4 requires that the $3d(A)$ spin-down electrons lie at about the same energy as the $3d(B)$ spin-up electrons, relative to the $2p_{3/2}(Fe)$ level.

(2) The $L\alpha$ peak in Fe_3O_4 is split, the two subpeaks being separated by about 1.2 eV. This splitting may be identified with the crystal-field splitting of the t_{2g} and e_g one-electron orbitals.

(3) The x-ray emission and absorption peaks are separated by 2.7 ± 0.5 eV, the absorption occurring at higher energy.[6] Since the strongest absorption takes place when $2p(Fe)$ electrons can be promoted into empty $3d(Fe)$ states, namely $3d(B)$ spin-down states or $3d(A)$ spin-up states, 2.7 ± 0.5 eV should be a measure of the exchange splitting if the Stokes shift can be neglected. This agrees well with the values given in paragraph (a).

(4) In the luminescence experiment the crystal is bombarded with 20-keV electrons, and a luminescence peak is observed at 2.6 eV, with subsidiary emission extending up to 3.5 eV. Balberg and Pankove interpreted their data as due to electrons, excited into the empty $4s(Fe)$ or $3d(B)$ spin-down e_γ bands by the bombardment, returning to the $3d(B)$ spin-down e_ϵ and a_1 levels.

Quantitative interpretations of the cathodoluminescence data must be made with caution because the optical absorption is a strongly varying function of energy in the same range. However, in Fig. 1 it seems likely that the strong luminescence is due to the cascading of low-lying $3d$ electrons into empty $2p(O)$ levels from which the electrons have been knocked out. In addition to the discussion of the crystal-field splitting in paragraph (b) which shows that the $e_\gamma \rightarrow e_\epsilon$ transition would occur below 1.3 eV, there are two other reasons to prefer this assignment. First, the $4s(Fe)$ density of states is much less than that of either $3d(Fe)$ or $2p(O)$ electrons. Second, the $4s(Fe) \rightarrow 3d(Fe)$ and $3d(Fe)$ and $3d(Fe) \rightarrow 3d(Fe)$ transitions are electric dipole forbidden to first order, and must take place by a magnetic dipole or electric quadrupole interaction, or else by a crystal-field mixing of odd parity due to lattice vibrations. These oscillator strengths are 10^{-4}–10^{-7} times that of the allowed electric dipole transitions. It places the maximum in the density of states of the majority-spin d electrons 2.6–3.0 eV above the $2p(O)$ band, in fair agreement with the interpretation of the shoulder on the $L\alpha$ x-ray peak. According to our assignment marked C.L. in Fig. 1, no cathodoluminescence should be observed below ~2 eV, and none is observed in the experiment.[1]

There are several reasons why one might not expect to see structure in the cathodoluminescence peak corresponding to the crystal-field splitting of the t_{2g} and e_g orbitals. First, Miles, Westphal, and von Hippel[8] have shown that strong absorption begins at about 2.8 eV and increases to higher energies, so that structure of the cathodoluminescence peak, expected at higher energy, may be strongly self-absorbed. Second, the crystal-field splitting of the t_{2g} and e_g orbitals (or the $^5T_2$ and ^5E levels of the Fe^{2+} ion) is influenced by lattice vibrations which could cause a rapid, nonradiative transfer between them, and would only allow radiative transfer from the lowest, t_{2g} orbital to the $2p$O level. Third, any splitting will be smeared out if the $t_{2g}(B)$ spin-up and $e(A)$ spin-down, and the $e_g(B)$ spin-up and $t_2(A)$ spin-down levels do not exactly coincide, which is what we expect.

(5) A review of the available optical absorption data taken at room temperature shows the following: (i) Absorption in the near infrared, which may be due to impurities,[9] polaron absorption,[10] or intrinsic excitation of the $3d(B)$ spin-down electron from the a_1 to the e_ϵ orbital. This splitting, not shown in Fig. 1, is about 1000 cm^{-1}.[11] (ii) A bump in the absorption at 0.8 eV,[12] which might be the excitation of the Fe^{2+} from the $^5T_2 \rightarrow {}^5E$ levels. If so, the Fe^{2+} or Fe^{3+} ion on any B site persists for long enough for separate optical spectra to be seen from each. (iii) A charge-transfer band near 2.8 eV which may be due to the majority-spin $3d(\text{Fe}) \rightarrow 4s(\text{Fe})$ transitions,[13] followed by a stronger absorption at higher energies (~5.5 eV), which is probably due to excitation across E_g.

In our view, the ensemble of soft-x-ray, cathodoluminescence, and optical-absorption data leads to a coherent and useful one-electron energy diagram, within the limitations stressed at the outset. The additional complications of finite bandwidth and possible band splitting below the Verwey transition can be incorporated into our proposed scheme.[13]

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[1] I. Balberg and J. I. Pankove, Phys. Rev. Lett. 27, 1371 (1971).

[2] Our notation differs slightly from that of Ref. 1. We denote the majority-spin electrons on A and B sites by $3d(A)$ spin down and $3d(B)$ spin up instead of $3d_\alpha$(Fe) spin up and spin down, respectively. The single minority-spin electron is $3d(B)$ spin down in our notation, and $3d_\beta$(Fe) spin up in theirs.

[3] L. E. Orgel, J. Chem. Phys. 23, 1819 (1955); J. S. Griffith, J. Inorg. Nucl. Chem. 2, 1, 229 (1956).

[4] Y. Tanabe and S. Sugano, J. Phys. Soc. Jap. 9, 766 (1954).

[5] R. L. Martin and A. H. White, *Transition Metal Chemistry* (Marcel Dekker, New York, 1968), Vol. 4, p. 113.

[6] C. Bonnelle, Ann. Phys. (Paris) 1, 439 (1966).

[7] D. W. Fischer and V. L. Baun, J. Appl. Phys. 39, 4757 (1968); D. W. Fischer, J. Appl. Phys. 40, 4151 (1959), and 41, 3561, 3922 (1970).

[8] P. A. Miles, W. B. Westphal, and A. von Hippel, Rev. Mod. Phys. 29, 279 (1957).

[9] I. Balberg and J. I. Pankove, Phys. Rev. Lett. 27, 596 (1971).

[10] D. L. Camphausen, to be published.

[11] F. Hartmann-Boutron and P. Imbert, J. Appl. Phys. 39, 775 (1968).

[12] Preliminary measurements by P. Muret of this laboratory.

[13] D. L. Camphasen and B. K. Chakraverty, in *Proceedings of the Eleventh International Conference on the Physics of Semiconductors, Warsaw, 1972* (to be published), and a more complete version to be published.

Energy Dependence of the ^{3}He Optical Potential

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A multi–data-set optical-model search code has been used to produce a set of mean geometry parameters for ^{3}He nuclei incident on medium-weight nuclei. Using this geometry, the energy dependence of the volume integrals of the real and imaginary potentials has been obtained.

The discrete potential ambiguities found in optical-model analyses of the scattering of complex projectiles[1,2] are best classified by the concept of volume integral per particle pair,[3] J_{RS}/A_PA_T, where A_P and A_T are the mass numbers of the projectile and target nuclei, respectively. This classification removes the uncertainties involved in the discussion of the real potential V_R, which depends upon the radius parameter r_R because of the continuous $V_Rr_R^n$ ambiguity. The volume integral per particle also seems to be independent of the A number of the target at a given energy for both protons[3] and complex projectiles.[4] Theoretical calculations[5] of the real well depth for helions (^{3}He nuclei) give a value 3 times that of the nucleon value at $\frac{1}{3}$ of the incident energy. These depths vary from 140 to 170 MeV depending on the geometry. In terms of volume integrals per