An optical absorption anomaly in iron

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The optical properties of Fe(103) are investigated in the spectral range 0.06–4.9 eV at 295 and 80 °K. The plasma frequency Ω and relaxation frequency γ of the conduction electrons, and the energies of the principal features of the interband optical conductivity $\sigma(\omega)$ are determined. The electron spectrum and optical interband conductivity of ferromagnetic iron are calculated under the assumption that the matrix element for the transition probability is constant, using the Green's function method with two different model potentials, each of which yields the experimental value of 2.2 μ_B for the magnetic moment per atom. The energy dependence of the optical conductivity in the spectral range $E = 0.06$–4.9 eV is discussed. It is shown that a standard band-theory calculation gives a satisfactory account of the spectral position of the fundamental absorption band of iron at $E = 1.15$–40 eV. In the region $E = 0.2$–1.15 eV of anomalously high infrared absorption, however, agreement between the theoretical and experimental $\sigma(\omega)$ curves can be achieved only by making additional assumptions concerning the magnitude of the magnetic moment in the surface layer and the presence of surface electron states.

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It has been fairly reliably demonstrated that the energy-band theory of metals now makes it possible to calculate many of their physical characteristics, and in particular, the frequency dispersion of interband optical conductivity. Such calculations have been published in Refs. 1–5 for the 3*d* transition metals (including iron, which is investigated here). As a rule, quite satisfactory agreement between the theoretical results and the experimental data was achieved, and it became widely believed that the main difficulties in this direction had already been overcome. However, recent new detailed measurements of the optical characteristics of metals have, in some cases, revealed sharply anomalous behavior of the optical constants in the low-energy region. Below, we give a detailed discussion of an anomaly in the optical absorption of iron that was discovered in the present work.

EXPERIMENTAL DATA

1. *Specimens and measuring technique*. Fe(103) single crystals, grown by recrystallization, were ground with micropowder (grain size 5 μm) and were then polished to a mirror surface in a chloric acid electrolyte (5 wt.% $HClO_4$) at 10–12 °C at a current density of 0.5 A/cm². The removal of the cold hardened layer was monitored by x-ray diffraction.

Optical constants: the refractive index n and the absorption constant k were measured with accuracies of 2–3% and 1–2%, respectively, by the Bitti polarimetric method, using single reflection in the long-wave region ($\lambda = 0.25$–1.1 μm) and quadruple reflection in the infrared region ($\lambda = 1.1$–16 μm). The measurements of n and k in the spectral range 1.1–8 μm were made in a cryostat at 80 °K. The average numerical values of n and k are presented in Table I.

2. *Results*. From the values of n and k obtained at 295 and 80 °K we calculated the dielectric functions ε_1 and ε_2, the optical conductivity $\sigma = nk\omega/2\pi$ (ω is the circular frequency of the light wave), and the absorptivity A. The energy dependence and absolute values of A agree well with the results of direct calorimetric measurements[6] on highly pure polycrystalline specimens with electropolished surfaces, as well as with the results of Ref. 7.

The plot of σ *vs* E (Fig. 1) reveals an intense interband absorption band 1 localized in the energy region 1, 1.15–4.0 eV. The presence of this band in the optical absorption spectrum of ferromagnetic iron has been reliably established.[8-12] The differences between the results of different authors touch only on the absolute values of σ and the energy positions of some of the structural features.

According to the data of the present work, the plot of σ *vs* E for Fe(103) has a sharp peak *a* at 1.36 eV, peaks *b* and *c* at 2.10 and 2.45 eV, respectively, and bends at 2.65 (*d*), 3.02 (*e*), and 3.90 (*f*) eV. We note that the structural elements *b*, *c*, *d*, and *e* have been observed at these same energies[10] on an Fe(100) curve obtained under high vacuum conditions (10^{-8} Pa).

TABLE I. The optical constants n and k of Fe(103) at 295 °K.

λ, μm	n	k	λ, μm	n	k	λ, μm	n	k
0,248	0.99	2,01	0.900	3,11	4.54	2.9	4,94	10.7
0,253	1.05	2,05	0.925	3.06	4.56	3,0	5.11	11,2
0.265	1,13	2.14	0.950	3.00	4.58	3.1	5,58	11.3
0.280	1,15	2.26	1.00	2,92	4.72	3,2	5,66	11.3
0,296	1,25	2.38	1,05	2.75	4.80	3.3	5,74	11.9
0,302	1,23	2.43	1,10	3.36	4,80	3,4	5.26	11.9
0.312	1.35	2,53	1.20	3.86	5,10	3,6	5.80	12,8
0.365	1,42	3.11	1.30	3,85	5.40	3.8	6.35	13.2
0.380	1.53	3.17	1.40	4.00	5.75	4.0	6.36	13.8
0.390	1.60	3.25	1.50	4,20	6.10	4.25	6,20	14.1
0,400	1.68	3,33	1,55	4.25	6.12	4,50	6,43	15.4
0.410	1.68	3,42	1.60	4,30	6.20	4.75	6.03	15.6
0,425	1,87	3.45	1.65	4.30	6.30	5.00	6,14	16.6
0.450	2.11	3.59	1.70	4.20	6,40	5,25	6.14	17,1
0.475	2.25	3.65	1.75	4,50	6.57	5,50	5.74	18.8
0,500	2,43	3.77	1.80	4.53	6.96	5.75	5.70	19.4
0.525	2,54	3,75	1,85	4,45	6.90	6.00	5.40	21,1
0.550	2.60	3,76	1.90	4.44	7.00	6.25	5.60	20.3
0,575	2.72	3.80	1,95	4.44	7.40	7,0	6.40	22.5
0,600	2.80	3.85	2,0	4.60	7,74	8.0	7,80	24.5
0.625	2.86	3,86	2,1	4.45	7.93	9.0	8,57	26.0
0.650	2.87	3.93	2,2	4.78	8.40	10	9.20	28,5
0.675	2,89	3.97	2,3	4.50	8,94	11	10.6	29.6
0.700	2.85	4,05	2,4	4,45	9,37	12	11,1	30.0
0,750	2,81	4,15	2.5	4.44	9.46	14	10,6	36.3
0.800	2.94	4,18	2,6	4,92	9,54	15	11.0	39.0
0,850	2,95	4,33	2.8	4.85	9,83	16	13.5	42.5

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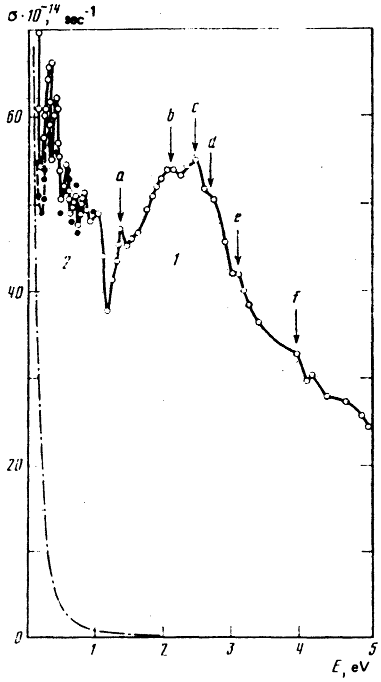

FIG. 1. Optical conductivity σ of an Fe(103) single crystal at 295 °K (○) and 80 °K (●). The dash-dot curve represents the intraband contribution.

Let us examine the optical absorption of iron in the infrared and estimate the contribution of the intraband absorption mechanism in the range $E = 0.06-1.15$ eV.

As the energy E increases, the optical conductivity σ first falls monotonically, confirming the dominance of the intraband light-absorption mechanism; then, beginning at $E = 0.196$ eV, σ rises sharply and forms the absorption band 2, which has a complex structure at its peak. By analyzing the frequency dispersion of the dielectric functions ε_1 and ε_2 in the long-wave region, we can determine the plasma frequency Ω and the relaxation frequency γ of the conduction electrons. Assuming that the light absorption at 295 °K is of Drude type, we calculated the quantities Ω^2_{eff} and γ_{eff} from the formulas $\Omega^2 = (\varepsilon_1 + \varepsilon_2^2/\varepsilon_1)\omega^2$ and $\gamma = \varepsilon_2\omega/\varepsilon_1$. Neither parameter is frequency dependent at the long wavelengths (14–16 μm); they become constant in that wavelength range with the values $\Omega^2 = (32 \pm 1.2) \times 10^{30}$ sec^{-2} and $\gamma = (0.8 \mp 0.04) \times 10^{14}$ sec^{-1}. We used these numerical values for the plasma and relaxation frequencies to estimate the intraband contribution to the optical conductivity, which, as Fig. 1 shows, is negligible even at energies as low as 0.4 eV.

Thus, the high absolute values of σ in the energy range $0.2 \leqslant E \leqslant 1.15$ eV are due mainly to interband electron transitions. If the energy of 0.196 eV at which the $\sigma(E)$ curve rises sharply is adopted as the interband absorption threshold, we must admit the presence in iron of weak subthreshold absorption in the region $0.2 \geqslant E \geqslant 0.087$ eV. The temperature shift of the absorption threshold energy amounts to 0.8×10^{-4} eV/°K.

BAND CALCULATION RESULTS

Our theoretical treatment is based on the electron spectrum of ferromagnetic iron as calculated by the Green's function method with two different model potentials, both of which yield the experimental value $2.2\mu_B$ of the magnetic moment per atom. The model parametric potential scheme used in the calculation was previously used for vanadium[2] and made it possible substantially to improve the results of an *a priori* approach[1] and to achieve quantitative agreement between theory and experiment. The initial parameters of the model for iron—the lattice constant a and the screening radii d_l for two different spin directions—are shown in Table II. The resulting dispersion curves $E(\mathbf{k})$ in directions of high Brillouin zone symmetry are shown in Fig. 2. In Fig. 3 we also show density-of-state curves for groups of bands having different spin orientations.

TABLE II. Lattice constant a and potential screening radii in iron for two spin directions (in atomic units).

	Spin up	Spin down		Spin up	Spin down
a	5.4671	5.4671	d_1	0.755	0.730
d_0	0.720	0.720	d_2	0.700	0.675

Comparison with results of a systematic study[13] (in which the results for three different potentials were analyzed in detail) shows that, on the whole, our calculations reproduce the pattern of the electron spectrum of ferromagnetic iron fairly well. The quantitative characteristics obtained in our calculations agree best with the data of Ref. 13 for the Slater-exchange model with $\alpha = 0.64$. We note that this same model was used earlier to interpret optical spectra.[4] However, that the theoretical model is capable of adequately re-

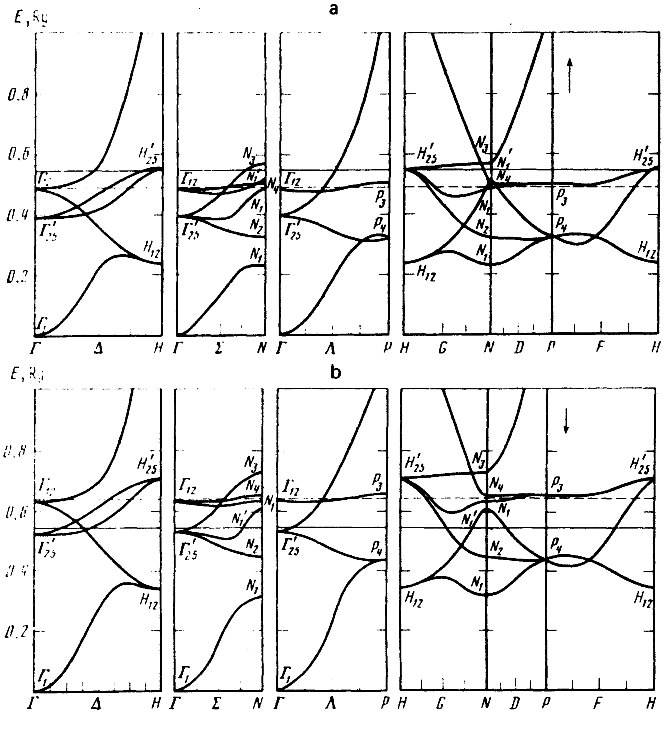

FIG. 2. Dispersion curves $E(\mathbf{k})$ for iron for the spins directed parallel ↑ (a) and antiparallel ↓ (b) to the magnetization; the solid (dashed) horizontal lines mark the position of the Fermi level in the ferromagnetic (nonmagnetic) states.

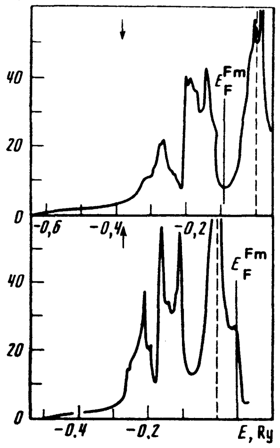

FIG. 3. Density of states in iron for two spin directions.

producing the actual situation is most convincingly confirmed by the agreement of the calculations with the recently obtained experimental value[14] of the exchange splitting at the point P of the Brillouin zone: experimental value, 1.5 eV; our result, 1.44 eV; calculated in Ref. 13, 1.52 eV.

Now let us discuss the theoretical optical conductivity curve $\sigma(E)$. Figure 4 shows the contributions to the conductivity from each of the band systems with different spin directions. Curve 3 shows the total optical conductivity due to electron transitions without spin flip, calculated under the assumption that the matrix element for the transition probability is constant. It will be seen that most of the absorption and all of its structural elements are due to a single group of bands, and a comparison with Fig. 2 permits us to conclude that the corresponding electrons have their spins directed against the magnetization. The group of bands $E(\mathbf{k})$ for electrons with the preferred spin direction is almost completely filled [Fig. 2(a)] and makes no appreciable contribution to the absorption.

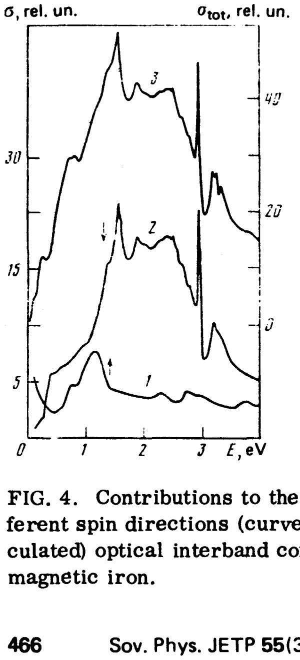

FIG. 4. Contributions to the conductivity from bands with different spin directions (curves 1 and 2) and the total (calculated) optical interband conductivity (curve 3) for ferromagnetic iron.

A comparison of the experimental (Fig. 1) and theoretical (Fig. 4, curve 3) optical conductivity curves shows that the principal absorption band in the photon-energy range $E = 1.15-4.0$ eV is similar to the band previously observed in vanadium[1] and is due to interband transitions involving d electrons. That this absorption band is wider by some 20–30% in iron is due to the presence of ferromagnetic ordering in iron, i.e. to the presence of two energy-band systems that have different spin directions and are shifted with respect to one another. This is also the cause of the somewhat smaller absolute value of the absorption in this energy region. In our opinion, therefore, a standard spin-polarized band-structure calculation provides a quite satisfactory description of the frequency dependence of the optical conductivity of iron above 1.15 eV.

DISCUSSION OF THE OPTICAL ABSORPTION ANOMALY

In the infrared region ($0.2 \leqslant \hbar\omega \leqslant 1.15$ eV), the experimental $\sigma(E)$ curve for iron, unlike those for vanadium and chromium, reveals an unexpectedly large absorption with an extremely complicated structure: many sharp peaks (Fig. 1, band 2). Even this structure and the strength of the absorption cannot be explained in terms of current ideas of the nature of the energy-band spectrum of iron without additional assumptions.

It was first necessary to estimate the contributions to the optical conductivity from electron transitions with spin flip, which could arise as a result of the spin-orbit coupling as well as from indirect interband transitions. The first effect was estimated theoretically (it cannot be estimated experimentally) by unifying the spectra of electrons with different spin directions and then calculating the optical conductivity of the unified energy-band system. In that approach, transitions with and without spin flip are treated as equally probable, and this certainly makes the effect much greater. Nevertheless, no substantial changes in the frequency dependence of the optical conductivity took place in the energy region of interest to us. The contribution from indirect interband transitions was estimated experimentally by comparing the optical constants as measured at room temperature and at liquid nitrogen temperature. The experimental curves thus obtained did not differ substantially from one another (Fig. 1).

In addition, we calculated the optical conductivity by convolution of the state density; this is valid provided the direct and indirect electron transitions are equally probable. Again we considered two cases: transitions with and without spin flip. Although the contribution from indirect transitions increases the general absorption background somewhat in the infrared region, it still does not give the necessary order of magnitude, nor can it explain the observed complex structure of the absorption. In view of that, we may suppose that indirect interband electron transitions are not the dominant factor in the enhancement of the infrared optical absorption of iron.

As we see, the absorption mechanisms discussed above cannot account for the anomalous part of the $\sigma(E)$

curve (Fig. 1, region 2). There obviously exist possible reasons of a different kind for this absorption anomaly. We shall discuss some of them below.

An active discussion of surface magnetism has recently been going on in the literature. The idea of a reduction in the surface magnetization and the appearance of "dead" magnetic layers in ferromagnetic metals was first advanced in Ref. 15 on the basis of experiments with electrolytically deposited films. It was later established[16-18] that the observed change in the magnetic moment in the surface layer of ferromagnetic metals, or its complete disappearance in the first atomic layers, is due to the chemical state of the surface, and in particular, to the chemisorption of hydrogen. However, a magnetic reconstruction of the surface layers is to be expected even for a pure surface, because of the lower coordination number of the surface atoms.

In analyzing optical data it must be borne in mind that the penetration depth δ of the light beam into the metal amounts to hundreds of atomic layers [for Fe(103), for example, $\delta = 36-60$ nm in the spectra range $\lambda = 1.15-16\,\mu$m], so the main contribution to the absorption comes from the excitation of interior electron states. However, surface effects, and in particular, surface band states, may substantially affect the optical properties.

1. Now let us consider the first possibility. The optical conductivity plot that we obtained for iron for the hypothetical case of zero magnetic moment per atom shows a very large absorption precisely in the low-energy region. On this basis we may assume that, under the conditions of the experiment, a nonmagnetic state is formed, at least in the part of the surface layer of the iron being analyzed. We have calculated the optical conductivity of iron with the magnetic moment μ per atom ranging from zero to 2.2 μ_B. A typical curve for $\mu = 1.2\,\mu_B$ is shown in Fig. 5. In this case one can actually see the anomalously large absorption with a complex structure in the low-energy region of the spectrum. A detailed analysis shows that the contribution to the absorption in the interval $0 < E < 1.0$ eV comes from both groups of energy bands, i.e. the filling of the electron states [the raising of the Fermi level in Fig. 2(b)] and the freeing of those states [the lowering of the Fermi level in Fig. 2(a)] contribute comparably to the effect. When the magnetic moment is decreased further ($\mu < 1.2\,\mu_B$) the absorption in this part of the curve increases sharply, but when the magnetic moment is increased ($\mu > 1.2\,\mu_B$), it falls. It may be assumed that in the actual situation the magnetic moment of the atoms in individual atomic layers decreases from layer to layer as the surface is approached until it reaches a low (perhaps zero) value, the transition region being only about ten atomic layers thick.

2. The second possible reason for the anomalously high infrared absorption in iron is a modification of the electron energy spectrum $E(\mathbf{k})$ near the Fermi level with virtually no change in the magnetic moment. If electron traps (surface band states, defects, impurities) capable of entrapping conduction electrons are formed in a surface layer of the same extent, the filled energy bands will be depleted, i.e. the Fermi surface will be effectively lowered. A recent calculation of the band structure of a thin ferromagnetic Fe(001) film (9 atomic layers thick)[19] showed that the Fermi level in the band system $E(\mathbf{k})$ with allowance for surface electron states actually shifts downwards by 0.046 Ry.

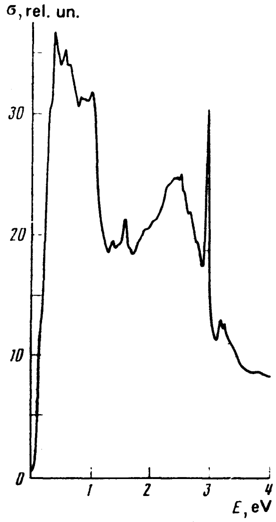

FIG. 5. Optical interband conductivity of iron for the case $\mu = 1.2\mu_B$.

The optical conductivity curve $\sigma(E)$ that we calculated on the basis of the band spectrum with a 0.042 Ry shift of the Fermi level (this corresponds to a change in the electron concentration per atom by approximately unity) is shown in Fig. 6. We see that such an effect also increases the interband contribution to the conductivity and leads to an increase in the optical absorption at low energies. We note that enhanced absorption in the energy range 0.2–1.0 eV also takes place at other (smaller) values of the Fermi-level shift. Since anomalous absorption is also observed in a number of other (paramagnetic) transition d metals (e.g. iridium[20]), it is possible that the predominant factor in producing such absorption is precisely the concentration effect.

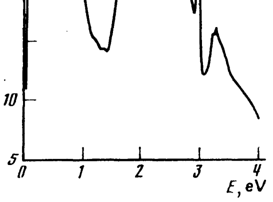

FIG. 6. Optical absorption of iron with a reduced conduction-electron concentration (Fermi energy shifted by 0.042 Ry).

Thus, a theoretical analysis of the new experimental data on the optical conductivity of ferromagnetic iron obtained in the present work has shown that a standard spin-polarized band calculation satisfactorily explains the energy dependence of the fundamental absorption band σ_{exp} in the spectral region $E = 1.15–4.0$ eV. Agreement with experiment in the low-energy range 0.2–1.15 eV is achieved by assuming that the magnetic moment is lower in part of the surface layer being analyzed or by assuming that states that act as electron traps and lower the Fermi level are produced in the surface layer. The latter mechanism will give rise to a considerable effect in materials in which the Fermi level lies close to the peaks of the density of states $N(E)$, since it is in precisely those cases that a relatively small change in the Fermi energy will result in a considerable change in the structure of the interband transition in the region near the Fermi level. This probably also accounts for the fact that the anomalous absorption discussed here is observed in transition d metals.

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