NATURAL FREQUENCIES OF NICKEL AND NICKEL ALLOYS IN THE INFRARED SPECTRAL REGION

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Two anomalies with the same natural frequencies $h\nu_0 \cong 0.3$ and 0.8 eV as in pure nickel have been found in binary nickel-base alloys by the magneto-optical method. The relation between the signs and variation of intensity of the anomalies confirms the assumption that they are due to a single type of electronic d—s transition (L_{32}, L_2') in the two sub-bands with different spin orientation. The shift of the 0.8 eV anomaly in Ni-Cu and Ni-Al alloys is interpreted as the result of shift of the right-hand and left-hand spin sub-bands during the filling of the 3d nickel band. The order of magnitude of the anomaly shift corresponds in certain cases to spin-orbit splitting of the 3d band in nickel.

IN recent years the greatest progress in metal physics has been connected with theoretical and experimental studies of the Fermi surface. Under the influence of this progress, the more complicated but no less important problem of the complete reconstruction of the energy spectrum of the electrons in the outer energy bands of the metal has temporarily been relegated to the background. The complexity of this problem lies in the fact that the need for going outside the framework of the single-electron theory is felt here more acutely. Nonetheless, a noticeable revival has been observed most recently in investigations of states lying deep below the Fermi surface. Experimental information on these states is obtained not from transport phenomena, as in the study of the Fermi surface, but by using different optical procedures (ordinary optical spectroscopy, magneto-optics, photoelectronic emission, etc.). Since the electronic transitions or resonant excitations of electronic plasma in metals are greatly "smeared out" and are observed against a background of effects connected with carrier motion, the greatest importance is attached to perfection of the experimental techniques. A good exposition of the latest progress in the use of optical natural frequencies for the study of the energy spectrum of solids is contained in Phillips's review paper.[1]

Experimental and theoretical investigations of this kind are of particular importance for ferromagnetic metals, since the main contribution to the exchange interaction and to the spontaneous magnetization of a ferromagnet comes just from electrons located far below the Fermi level. Direct information on the natural frequencies of a ferromagnetic metal can be obtained from its magneto-optical frequency characteristics. Earlier[2], in an investigation of the magneto-optical spectra of nickel, we observed two small anomalies with natural frequencies 0.3 and 0.8 eV, which were identified with direct interband transitions in the region of definite singular points of the interband state density curve. In this paper we present the results of an experimental investigation of these anomalies in different binary alloys with electron concentration close to that of nickel.

Measurements of the equatorial Kerr effect in the infrared region of the spectrum were made with the previously described experimental setup[2] at a fixed angle of incidence of the light, equal to 80°. It is advantageous to consider separately two groups of alloys: a) alloys of nickel with iron and manganese, in which the electron concentration $n = n_{3d} + n_{4s}$ is smaller than in pure nickel (n = 10 for nickel), and b) alloys of nickel in which n > 10 (Ni-Cu, Ni-Al, etc.). In the rigid-band approximation, which we shall use henceforth, an increase in the concentration of the additive in alloys of the first group leads to a lowering of the Fermi surface, and in alloys of the second group to a rising of the Fermi surface; this displacement depends in first approximation linearly on the valence of the added element. A hypothesis was advanced in[2] that the weak anomaly in nickel at 0.8 eV, and the intense anomaly which appears at the same frequency in the ordered alloys Ni_3Fe (n = 9.5) and

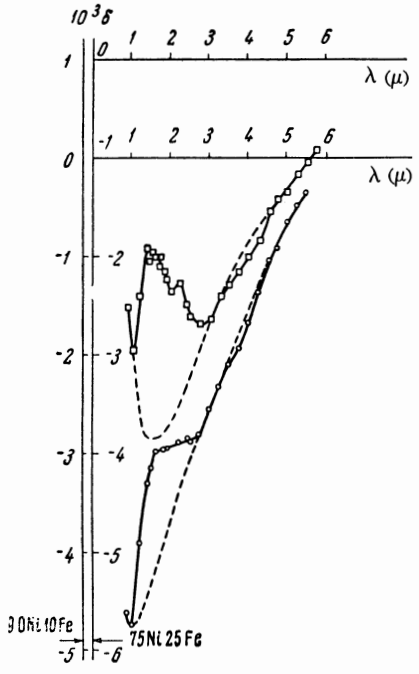

FIG. 1. Equatorial Kerr effect in the infrared region of the spectrum for disordered iron-nickel alloys: o – 90 Ni-10 Fe, □ – 75 Ni-25 Fe (atomic percentages are used here and throughout).

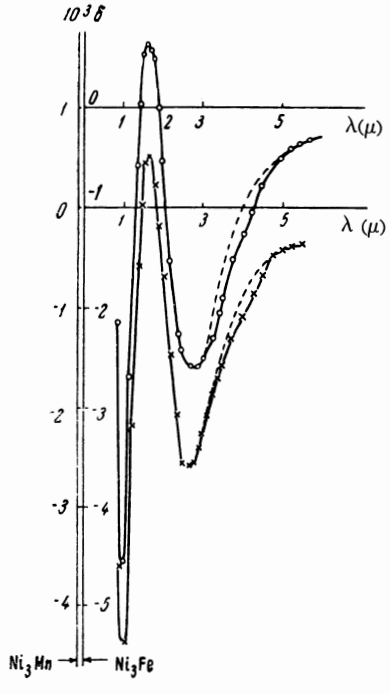

FIG. 2. Equatorial Kerr effect for ordered alloys (o – Ni_2Fe, – Ni_3Mn.

Ni_3Mn (n = 9.25) are due to interband electron transitions of the same type, i.e., they have the same origin. Measurements made by us with unordered iron-nickel alloys of intermediate concentrations have confirmed this hypothesis. Figure 1 shows curves of the equatorial Kerr effect δ for two iron-nickel alloys, from which it follows that this anomaly, with practically no change in frequency, increases in intensity with increasing iron concentration (the figure shows a plot of δ for an alloy with 20% iron, which has approximately the same form as the curve for an alloy with 25% iron). In an unordered alloy with 25% iron, the anomaly has a much more smeared form than in the ordered alloy Ni_3Fe (Fig. 2), but there is apparently no doubt that we are dealing with one and the same anomaly.

We now turn to consider the anomaly located in the 0.3 eV region. This anomaly is also observed on the δ curves for the alloys Ni_3Fe and Ni_3Mn (see Fig. 2), but in the alloys of the third group its intensity increases noticeably. Figure 3 shows curves for some of these alloys in the long-wave region.

Thus, the presence of two natural frequencies 0.3 and 0.8 eV in the magneto-optical spectra of nickel and its alloys can be regarded as a reliably established experimental fact. The relative stability of these frequencies on going over to alloys offers evidence that the appearance of the anomalies is connected not with the motion of the carriers, but with electronic transitions. It was noted in[2] that, in accordance with the model proposed by Phillips[3] for the electronic structure of nickel, such electronic transitions may be like transitions in the right-hand and left-hand spin sub-bands, ($L_{32}\downarrow$, $L_2'\downarrow$) and ($L_{32}\uparrow$, $L_2'\uparrow$). The frequencies of these transitions do not coincide with one another, owing to the difference in the parameters of the exchange splitting of the 3d and 4s bands. Figure 4 shows

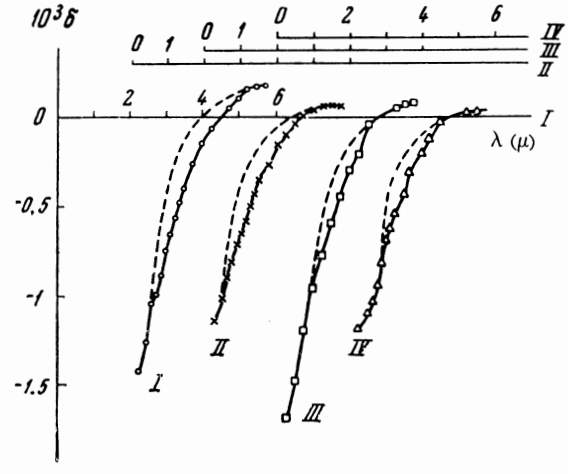

FIG. 3. Equatorial Kerr effect in the region 2.25 – 5.7 μ for nickel alloys: o – 99 Ni-1 Sn, × – 98.5 Ni-1.5 Sn, □ – 96.9 Ni-3.1 Si, Δ – 90.5 Ni-9.5 Cu.

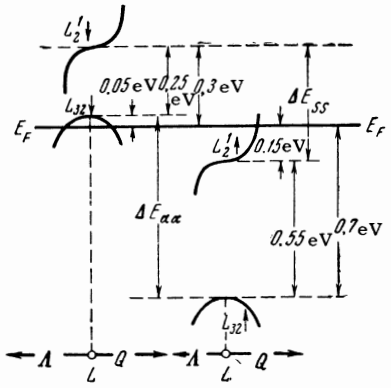

FIG. 4. Energy level scheme of ferromagnetic nickel in the vicinity of the L-point.

the energy-level scheme of nickel in the vicinity of the point L, from which it follows that identification of these transitions makes it possible to determine quantitatively the exchange-splitting parameters $\Delta E_{dd} = E(L_{32}\uparrow) - E(L_{32}\uparrow)$ and $\Delta E_{ss} = E(L_2'\uparrow) - E(L_2'\uparrow)$. It is also clear from the scheme that when the Fermi level drops, an increase should take place in the intensity of the transitions ($L_{32}\uparrow$, $L_2'\uparrow$), and when the Fermi level rises in the intensity of ($L_{32}\downarrow$, $L_2'\downarrow$). This agrees with the experimentally observed increase in the intensity of the anomalies at 0.8 and 0.3 eV in the alloys of the first and second groups. However, for a quantitative explanation of this change in the intensity it is apparently necessary to take into account the change of the oscillator strength of the electronic transitions. The correctness of the foregoing identification of the natural frequencies is qualitatively confirmed also by the difference in the signs of the anomalies at 0.3 and 0.8 eV, connected with the difference in the orientation of the spin in the corresponding energy sub-bands.

The already noted stability of the frequencies of both anomalies should apparently be observed only within certain limits. For example, within the framework of the energy level assumed above, the frequencies of the electronic transitions ($L_{32}\downarrow$, $L_2'\downarrow$) and ($L_{32}\uparrow$, $L_2'\uparrow$) should come closer together on going from the ferromagnetic to the paramagnetic state and in the limit, when ΔE_{dd} and ΔE_{ss} vanish, they should coincide. Such a situation should occur, in particular, with increasing concentration of the additive in the alloys of the second group, owing to the filling of the 3d band of nickel.

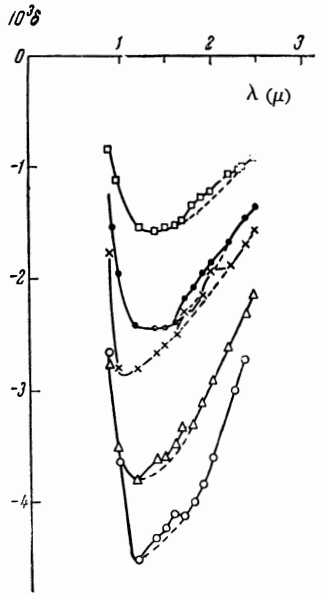

FIG. 5. Equatorial Kerr effect in the region 0.88 – 2.5 μ for nickel and its alloys: ○ – Ni, Δ – 95.25 Ni-4.75 Cu, × – 93.8 Ni-6.2Al. ● – 85.75 Ni-14.25 Cu, □ – 81 Ni-19 Cu.

Figure 5 shows the results of measurements of the anomaly at 0.8 eV in alloys of the second group. It is seen from the figure that at the increasing concentration of copper and aluminum in the alloys, this anomaly shifts towards the long-wave region, i.e., in a direction such that it comes closer to the 0.3-eV anomaly. The table lists the values of the natural frequencies of the anomalies for these alloys, obtained as the arithmetic means of the left and right edges of the anomaly (start and end of the dashed line in Fig. 5).

The expected shift can be estimated quantitatively from the change in the saturation magnetization, for this would take automatically into account the shift of the sub-bands due to the filling of the 3d band of nickel and the temperature shift of the sub-bands due to the decrease in the Curie temperature of the alloy compared with pure nickel. It follows from the data of[2] that the saturation magnetization of the alloy 81Ni-19Cu at room temperature is half as large as in pure nickel. This corresponds qualitatively to the fact that the interval between the long-wave and short-wave anomalies in the 81Ni-19Cu alloy (see the table) has been reduced approximately one-half. It is also possible, although the accuracy of the experiment does not allow us to state it with assurance, that the 0.3-eV anomaly in this alloy has

Material, at.%	n	$\hbar\omega$, eV	Material at.%	n	$\hbar\omega$, eV
Ni	10	0.86	93.8 Ni — 6,2 Al	10.1860	0,65
5.25 Ni — 4.75 Cu	10.0475	0.83	81 Ni — 19 Cu	10,1900	0.61
5.75 Ni — 14.25 Cu	10.1425	0.65			

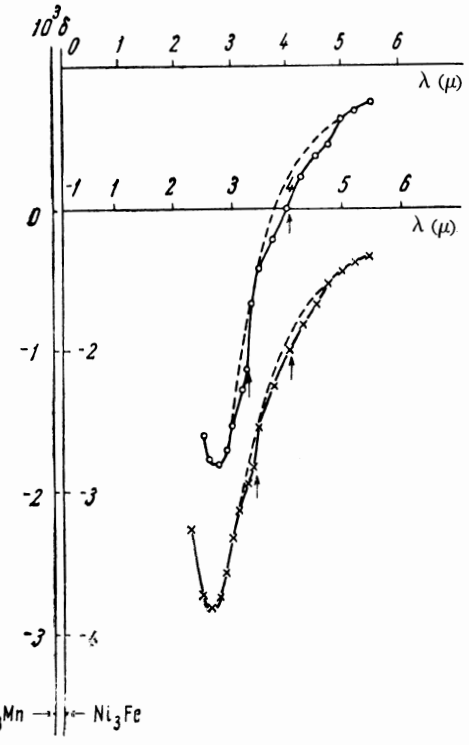

FIG. 6. Region of the 0.3 eV anomaly at increased resolution: o – Ni_3Fe, × – Ni_3Mn. The distance between the arrows corresponds to the value of the spin-orbit splitting assumed in the text.

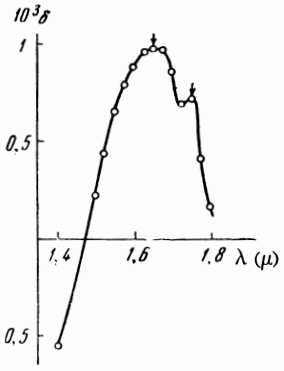

FIG. 7. Region of the 0.8-eV anomaly for an ordered alloy at increased resolution.

also shifted towards the short wave region by an amount of the order of 0.05 eV.

One more experimental result, which can be regarded as a confirmation of the proposed identification of the electronic transitions, was obtained by us in the measurement of anomalies at increased spectral resolution. It was noted in[2] that the fine structure ϵ_2' of nickel in the region of the 0.3-eV anomaly can be interpreted as being the result of spin-orbit splitting of the L_{32} level. In the ordered alloys Ni_3Fe and Ni_3Mn we were able to observe the fine structure of both anomalies directly on the δ curves. Figure 6 shows the δ curves for the alloys Ni_3Fe and Ni_3Mn in the region of the 0.3-eV anomaly, while Fig. 7 shows the δ curve for Ni_3Fe in the 0.8-eV region. The splitting of the 0.3-eV anomaly for the Ni_3Fe alloy (the distance between the two arrows on the figure) is equal to 0.07 eV, while for the Ni_3Mn alloy it is 0.06 eV; the splitting of the 0.8-eV anomaly for the Ni_3Fe alloy is 0.05 eV. At the same time, the theoretical value of the splitting of the L_{32} level, recently obtained in[5], is 0.06 eV. Within the limits of experimental accuracy we can regard the agreement between the theoretical and experimental values of the spin-orbit splitting as satisfactory. It must be noted that, in so far as we know, this is the first experimental determination of the spin-orbit splitting parameter of the d-band in a transition metal.

Thus, numerous experimental facts can be systematized and explained qualitatively on the basis of the concrete scheme of the energy levels at the upper edge of the 3d band of nickel and the mechanism of direct interband transitions. If our interpretation is true, then, as shown above, the magneto-optical effect makes it possible to determine quantitatively for a ferromagnetic metal the parameters of the exchange splitting of the 3d and 4s bands, the parameter of the spin-orbit splitting of the 3d band, and also direct observation of the displacement of the energy sub-bands with different spin orientations, leading to a decrease in the spontaneous magnetization of the ferromagnet.

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