# Oscillations of chemical reaction rate on nickel surface in magnetic field

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We discuss the oscillatory variation of the rate of the heterogeneous chemical reaction of carbonylation of nickel in a magnetic field. The field oscillation period is 10–50 Oe. The reaction rate is changed several fold, and the effect is strongly anisotropic.

We report here the results of the study of the dependence of the rate of the heterogeneous reaction of nickel carbonylation on the external magnetic field. A sharply pronounced anisotropic oscillatory character of the dependence is observed, and it is proposed that the observed oscillations are due to quantization of the energy spectrum of the nickel in the magnetic field.

We investigated the reaction of synthesizing nickel carbonyl $Ni(CO)_4$ from nickel and carbon monoxide at atmospheric pressure and room temperature. The reaction was carried out in a thermostated flow-through reactor, on a single-crystal (100) face with surface area 3.3 $cm^2$, which was previously polished mechanically and electrolytically. The reaction rate was determined from the content of the nickel carbonyl in the outflowing gas, by absorbing the $Ni(CO)_4$ with a solution of iodine in carbon tetrachloride, followed by photocolorimetry of the solution of the nickel dimethyloximate. The time required to measure one value of the rate (the time required to gather the outflowing gas) was 3—5 min, and the measurement error did not exceed $\pm 0.2$ $\mu g/cm^2$ min.

Figures 1 and 2 show the carbonylation reaction rates measured with monotonic variation of the external magnetic field, which was parallel to the surface, in the vicinity of 500 and 3000 Oe. The points and the solid lines correspond to an increasing field, and the crosses and dashed line to a decreasing field. To illustrate the stability of the reaction rate in time, Fig. 3 shows successive tenfold measurements of the reaction at a fixed magnetic field. Figure 1 shows by way of example the sequence of the measurement days, and the intervals between the measurements of individual sections of the curves of 3 amounted sometimes to 3—6 days.

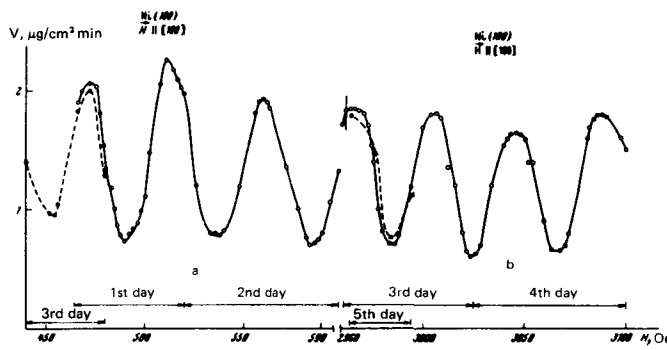


FIG. 1.

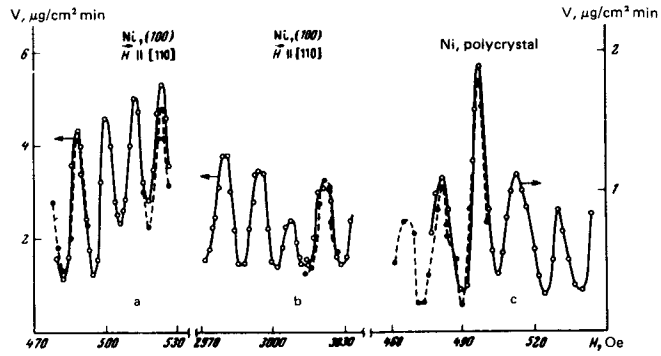


FIG. 2.

The experimental results lead to the following rather reliable conclusions: A clearly pronounced reversible and well-reproducible oscillatory dependence of the reaction rate on the magnetic field is observed. Changes in the reaction rate are observed in the range of fields where the nickel single crystal is practically magnetized to saturation. The amplitude of the change in the reaction rate is very large—in all cases $v$ varies by more than two times, and sometimes also four (Fig. 2a) and even eight (Fig. 2c) times. The curves showing the oscillations of $v$ are highly anisotropic: when the field is applied along the [100] axis, a "pure" sinusoidal $v(H)$ dependence is observed, with a period on the order of 40 Oe, and when the field is applied along the [110] axis, high-frequency oscillations appear with a period on the order of 10—15 Oe. It is possible that "beats" take place (Figs. 2b and 2c), and that two harmonics with different field dependences of the period are present (Figs. 2a, 2b). To verify this fact, however, it is necessary to perform the measurements in a wider range of magnetic fields. Finally, in first-order approximation there is no dependence of the period of the oscillations on the magnetic field. We have undertaken measurements of the oscillation frequency in two different field regions, 500 and 3000 Oe, with the special purpose of checking on the presence of periodicity in the reciprocal field. Even if the effective field in the ferromagnet is given by the induction $B = H + 4\pi I_s$ ($4\pi I_s$ for nickel is ~6000 G), the period of the oscillations should double, since $\Delta H \sim H^2$ at $\Delta H \ll H$. No such increase in the period was observed. Moreover, if we are to trust the numerical values of the averaged quantities (the statistics are of course inadequate), then we obtain changes with different signs: $\Delta H^{[100]}_{500\ Oe} = 44$ Oe, $\Delta H^{[100]}_{3000\ Oe} = 40.5$ Oe, $\Delta H^{[110]}_{500\ Oe} = 12$ Oe, $\Delta H^{[110]}_{3000\ Oe} = 14$ Oe, $\Delta H^{polycr}_{500\ Oe} = 16.4$ Oe, and $\Delta H^{polycr}_{3000\ Oe} = 10$ Oe. The order of magnitude

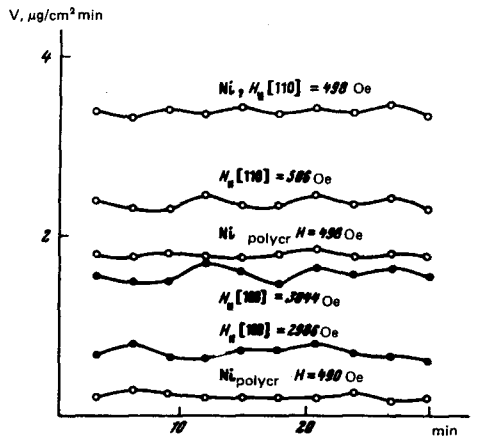


FIG. 3.

of the period of the oscillations of $v(H)$ in terms of the field, and also the fact that the oscillations are observed in the region of magnetic saturation, leads immediately to the natural attempt to explain the observed effect with the aid of the general theory of oscillatory quantum effects. But this raises at the same time two principal objections, namely, the already mentioned absence of periodicity in the reciprocal field, and the fact that the oscillations are observed at room temperature, whereas the usual explanation, that the oscillations are due to passage of the Landau level through the Fermi boundary, does not admit of the possibility of observing quantum oscillations at so high a temperature and in such relatively weak magnetic fields. We call attention therefore to the following possibility of explaining, in principle, the observed oscillation effect. The general theory of the quantization of the electronic energy spectrum of a metal indicates[1] that a very unique qunatization takes place near certain special trajectories, say trajectories with self-intersection. The levels cease to be equidistant (as called for by the periodicity of the "usual" oscillations in the reciprocal field), and the distances between them oscillate with the field. It has also been noted that inasmuch as the "new" quantum oscillations are due to oscillations of the energy itself, and not to passage of the Landau levels through the Fermi boundary, they can take place at sufficiently high temperatures.

It remains thus to assume that the rate of the chemical reaction depends on the presence or absence of a quantized level near the singular point or trajectory, a fact that determines the presence or absence of a channel via which the chemical reaction can proceed. Possible such points are the points $L$, at which there are zones with hyperbolic singularities near the Fermi level, and there is consequently a self-intersecting equal-energy conical surface, as well as points of intersections of subbands with different signs of the spin, in which the lifting of the degeneracy is determined by the orientation of the magnetization vector relative to the crystallographic axes.[2] This assumption is attractive because one can observe a qualitative correspondence between the equivalent $L$ points and the character of the observed oscillations. When the field is oriented along the [110] axis, all $L$ points are equivalent, and this corresponds to the simplest type of oscillations, while orientation of the field along the [110] axis leads to a division of the $L$ points into two groups, corresponding to low- and high-frequency oscillation harmonics.

The advantage of the considered explanation lies also in the fact that our contemporary knowledge of the band structure of nickel permits quantitative calculations of the spectrum quantization in the vicinity of any particular singular point and a comparison of theory with experiment. Other possible explanations, primarily formation of a surface electron gas as a result of chemosorption of CO on the nickel surface and a distinctive quantization of this gas by the magnetic field, or else a possible participation of the spin waves in the chemical reaction and allowance for indirect exchange interaction between the chemosorbed molecules, do not have the aforementioned advantage, since they have not been thoroughly studied.

It can be stated in conclusion that, in all probability, the observed oscillations are due to the variation of the electron energy spectrum of nickel in the magnetic field, so that the study of these oscillations uncovers a possibility of studying the electronic energy spectrum of metals and alloys at room temperature. Even more promising, however, in our opinion, is the inverse problem, namely: if we finally identify the electron-spectrum changes that cause the rate oscillations, this will be a direct method of determining the electronic mechanism of the chemical reaction. We note also that there are no grounds whatever to regard the reaction investigated by us as unique in the sense of its electronic mechanism, so that a search should be made for analogous oscillatory effects both for other types of reactions, and for other metals, alloys, and semiconductors, including nonferromagnetic ones.

[1] I.M. Lifshitz, M. Ya. Azbel', and M.I. Kaganov, Elektronnaya teoriya metallov (Electron Theory of Metals), Nauka, 1971, Part 1, Sec. 7; M. Ya. Azbel', Zh. Eksp. Teor. Fiz. 46, 929 (1964) [Sov. Phys.-JETP 19, 634 (1964)].
[2] G.S. Krinchik and E.A. Gan'shina, Zh. Eksp. Teor. Fiz. 65, 1970 (1973) [Sov. Phys.-JETP 38, No. 5 (1974)].