On the observation of a magnetic phase transition in a quasi-two-dimensional system

V. D. Borman, B. I. Buttsev, B. I. Nikolaev, and V. I. Troyan

Moscow Engineering Physics Institute

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Experiments are described in which a jump in the thermal flux in highly rarefied (Kn>1) CO, N_2, and CO_2 molecular gases interacting with gold and platinum surfaces saturated with chemisorbed CO molecules is observed in a magnetic field. The observed dependence of the intensity of the field in which the jump occurs on the CO concentration in the surface can be explained if the existence of a magnetic phase transition in the chemisorbed layer is assumed.

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In the present work, in investigating the thermodynamic effect in N_2, CO_2, and CO gases interacting with platinum and gold surfaces, we experimentally observed a thermal-flux jump that can be interpreted as a consequence of a phase transition triggered by the magnetic field in the two-dimensional surface layer of chemisorbed CO molecules. Magnetic phase transitions in two-dimensional systems were theoretically predicted a long time ago, and have been investigated many times within the framework of the Ising model, but we do not know of any reports about their experimental observation.

The thermomagnetic effect (TME)[1] consists in the fact that, in the Knudsen heat-transfer regime, the thermal flux Q through a gas located in the gap between two plane-parallel plates (one plate is heated, while the other is cooled) changes by a value ΔQ upon the application of a constant magnetic field **H**. This effect is due to the dependence of the probability for inelastic scattering of the gas molecules on the surface of the solid on their orientation. In the absence of the field, the gas molecules in the gap become polarized when they interact with the surface.[1,2] As a result of the precession of the molecules in the field, there occurs a change in their polarization and, as a result, the thermal flux in the gas changes. The quantity ΔQ depends on the product of the precession frequency $\omega = \mu H/\hbar$ and the molecules' time of travel $\tau = L/\bar{v}$ (L is the distance between the surfaces). In high fields ($\omega\tau \gg 1$), there occurs total averaging of the orientation of the angular momentum of the gas molecules over angle in the plane perpendicular to the vector **H**, and the quantity ΔQ tends to a limiting value ΔQ_{sat}.

In the present work the TME is used to study surface properties. The gas molecules then perform the role of probing particles if the relation $\xi = n\bar{v}\sigma t \ll 1$ (where n is the gas density, σ is the surface area occupied by one absorbed molecule, and $t = t_0 \exp(E_a/T)$ is the mean lifetime of a molecule in the surface, E_a being the absorption energy) obtains. This relation implies that the probability for scattering of the gas molecules on an absorbed molecule is small. This is fulfilled in the experiments described below for all the employed gases interacting with Au and Pt surfaces (for a pressure $p \sim 1\times10^{-3}$ Torr, a temperature $T \sim 300$ K, and a physical-absorption energy $E_a \sim 5$ kcal/mole, the quantity $\xi \lesssim 10^{-7}$). In the case of chemisorption (of the gases CO and O_2 in Au and Pt surfaces) the molecule lifetime in the surface is much longer than the duration of the experiment, and the investigation of the TME enables us to study the inelastic, nonspherical scattering of gas molecules on a surface covered with a monolayer of absorbed molecules.

The measurements were carried out on the experimental setup described earlier in Ref. 2. In Fig. 1 we show the dependence $\Delta Q(H)$ (**H** ∥ **k**, **H** ⊥ **k**, **k** being the vector normal to the surface) in nitrogen N_2 interacting with a gold surface covered with chemisorbed oxygen molecules. The quantity $\Delta Q(H)$ goes through a maximum and, as $\omega\tau \to \infty$, tends to ΔQ_{sat}. Within the limits of experimental error, the experimental data are described by the theoretical dependence[2] (the continuous curve).

In Fig. 2 we show the dependences $\Delta Q(H)$ for N_2 interacting with a Au surface covered with a chemisorbed CO gas (Fig. 2a). This experiment was performed after the surfaces of the pickup had been saturated with CO gas. It can be seen from the figure that there occurs in a field of intensity $H_t \approx 1150$ Oe a jump in the thermal flux: $\Delta Q_t = \Delta Q_{\text{sat}}(H < H_t) - \Delta Q_{\text{sat}}(H > H_t)$. When the chemisorbed CO is partially replaced by O_2 molecules, the value of the field H_t decreases (see Fig. 2b). When the chemisorbed CO in the monolayer is completely replaced by O_2 molecules, the curve assumes a form (Fig. 2c) similar to that of the original curve (Fig. 1).

The experiments performed showed that the thermal-flux jump is also observable in TME measurements in

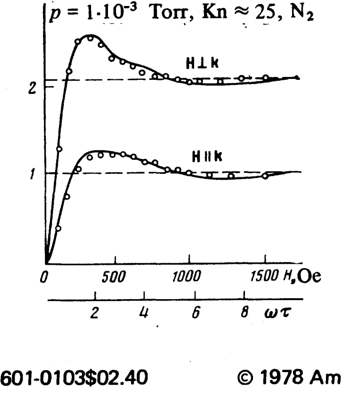

FIG. 1.

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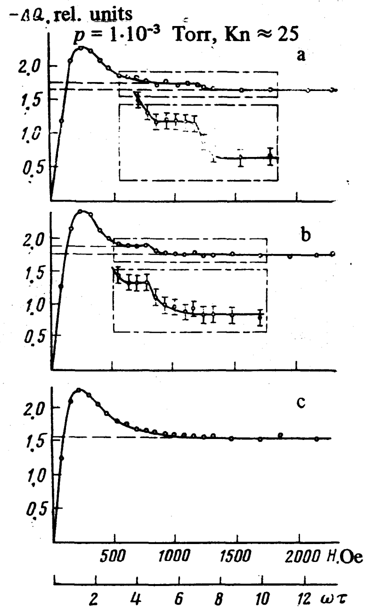

FIG. 2.

the systems N_2–Pt, CO–Pt, CO_2–Pt ($H_t = 2200$ Oe), and CO–Au ($H_t = 1150$ Oe). The Au and Pt surfaces in these measurements were saturated with chemisorbed CO molecules. Within the limits of the experimental error, the value of the quantity H_t did not change when we changed the type of gas and the pressure in the Knudsen region, and also when we changed the orientation of the field and reversed its direction. When the fraction of CO molecules in the chemical monolayer was decreased, the quantity ΔQ_t tended to decrease.

Thus, we have experimentally demonstrated that the observed change, ΔQ_t, in the thermal flux is uniquely connected with the presence of chemisorbed CO molecules in the Au and Pt surfaces, and that the quantity H_t decreases when CO molecules are replaced by O_2 molecules owing to the competing chemisorption of oxygen and the catalytic CO-oxidation reaction.[3]

It follows from the TME theory[2] that the quantity ΔQ_{sat} is determined by the character of the orientational interaction of the molecules with the surface of the solid and depends (for a fixed geometry) on the difference between the temperatures of the walls, the gas pressure, and the orientation of the field. It follows from this that the thermal-flux jump ΔQ_t may be connected with the change occurring in the orientational interaction of the gas molecules with the surface when the state of the chemisorbed CO molecules changes in the magnetic field.

Investigations carried out by Norton and Richards[4] by the method of photoelectron spectroscopy showed that, in a Pt surface, the chemisorbed CO molecules are in the form of CO^+ ions possessing spin $s = \frac{1}{2}$. The chemisorbed molecule-field interaction energy $E \sim \mu_B H \sim 10^{-17}$ erg is in this case much smaller than the chemisorption energy for CO in platinum ($E_a = 2\times10^{-12}$ erg[5]). Therefore, a field ~ 10^3 Oe cannot produce any changes in the state of the CO molecule. Moreover, if the field changed the state of the chemisorbed CO molecule, then the quantity ΔQ_t would decrease on decreasing the CO concentration in the chemisorbed layer, and the field H_t would not change, which would be at variance with the experimental data. But if we assume that there exists a collective interaction of the magnetic electrons of the chemisorbed CO molecules (e.g., via the conduction electrons of the metal), then the layer of CO molecules can be represented as a magnetically ordered structure in which magnetic-field-induced phase transitions are possible. The observed thermal-flux jump ΔQ_t is apparently connected with the fact that the phase transition is accompanied by a redistribution of the orientations of the absorbed molecules. This orientation redistribution can lead to a discontinuous change in the nonspherical inelastic scattering of the gas molecules on the surface.

Thus, the above-described experiments indicate a phase transition in the absorbed layer of molecules, among which a collective interaction exists.

It is necessary to note that the known dependence of the heat of chemisorption on the degree of occupation of the monolayer indicates the existence of a collective interaction among the chemisorbed CO molecules. Since $\mu_B H_t \sim 0.1$ K and the mean temperature of the experiment was ~ 350 K, the magnetic structure of the surface must be a complex one; for example, there can exist clusters of strongly interacting—among themselves—chemisorbed CO molecules, with weak interaction between the clusters.

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