Temperature dependence of the electron paramagnetic resonance spectrum of liquid oxygen

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(Submitted 12 December 1977)
Pis'ma Zh. Eksp. Teor. Fiz. **27**, No. 2, 129–131 (20 January 1978)

The temperature dependence of the EPR spectrum of liquid oxygen was investigated in the interval 54.3–93 K. With decreasing temperature, the line width in the spectrum increases and the maximum shifts towards weaker fields. The form of the EPR spectrum of the liquid oxygen does not experience a jump in the phase transition from the liquid to the γ oxygen.

PACS numbers: 76.30.—v, 64.70.Dv

In an investigation of the spectra of electron paramagnetic resonance (EPR) of liquid oxygen in mixtures with liquid nitrogen it was noted[1] that with decreasing oxygen concentration in liquid mixtures the width of the EPR line of the liquid oxygen increases and the maximum of the line shifts towards weaker magnetic fields. This was attributed mainly to the decrease of the exchange interaction. It was assumed in the case of liquid oxygen there takes place a strong exchange narrowing of the spectral line as a result of the interaction of the oxygen molecules with one another. However, besides the exchange narrowing of the line in the liquid oxygen, the EPR spectral line should also be narrowed by a mechanism connected with an increase of the thermal motion of the molecules when the temperature is raised.[2] If it is assumed that in the temperature range from 54.3 to 99.2 K the exchange interaction does not depend on temperature, then it is of interest to be able to distinguish somehow between these two narrowing-down mechanisms, so as to be able to determine their separate contributions. This can apparently be done by measuring the change of the width and of the position of the maximum of the line in the EPR spectrum of liquid oxygen with decreasing temperature, down to the formation of the solid phase.

In the experiments we use a previously described[3] setup to obtain γ oxygen by pumping off liquid-oxygen vapor. The γ oxygen was produced in a stub of a quartz Dewar situated in the H_{012} resonator of a 3-cm-band EPR spectrometer with RF modulation of the constant magnetic field. When the pumping-off was stopped. the

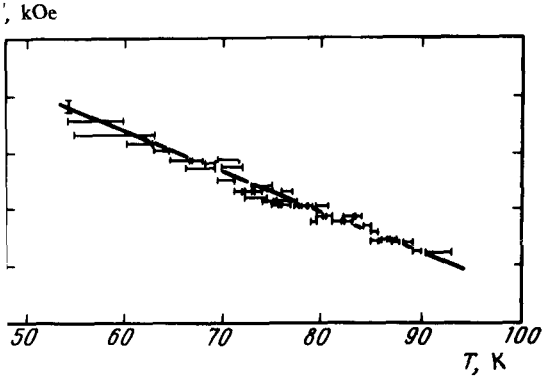
ıflux of heat from the outside melted the γ oxygen, and the produced liquid oxygen as slowly heated. The liquid-oxygen temperature could be determined from its satuıted vapor pressure.[4] The pressure was measured with a mercury manometer. At the ıme time, the EPR spectrum of the liquid oxygen was plotted on an automatic reɔrder. The saturated vapor pressures corresponding to the starting point and the end ɔint of the recorded spectrum were noted and used to determine the interval in which ıe temperature corresponding to the plotted spectrum varied. The result was the mperature dependence of the EPR spectrum of liquid oxygen in the range 54.3–93

The reduction of the plotted spectra included measurement of the nominal width ıW)—the distance between the maximum and the minimum of the derivative of the ısorption signal with respect to the field—as well as the position of the maximum of e absorption signal (the zero of the derivative) in oersteds. It turned out that with ıcreasing temperature the NW of the line in the EPR spectrum of liquid oxygen ıcreases and the maximum shifts towards weaker fields. This indicates, that besides e strong exchange narrowing of the line, there is an appreciable narrowing due to ermal motions of the molecules.

A plot of the temperature dependence of the NW is shown in Fig. 1. Within the ıits of experimental errors, this plot can be regarded as a stright line with a slope 6 ± 4)Oe/deg.

It must be noted that when the temperature is decreased the EPR spectrum of the uid oxygen is continuously deformed without undergoing, within the limits of the perimental accuracy, any discontinuity in the position of he maximum and in the minal width during the liquid—crystal phase transition.

Figure 2 shows the spectra obtained at different temperatures and normalized to a gle value of the arbitrary intensity (distance between the maximum and minimum the intensity curves).



. 1. Temperature dependence of the NW of the liquid-oxygen EPR spectrum. The horizontal bars on the e mark the range of the temperature, which changed when the liquid oxygen was heated during the of the plotting of the given EPR spectrum; the vertical bars indicate the errors in the NW ıurement.

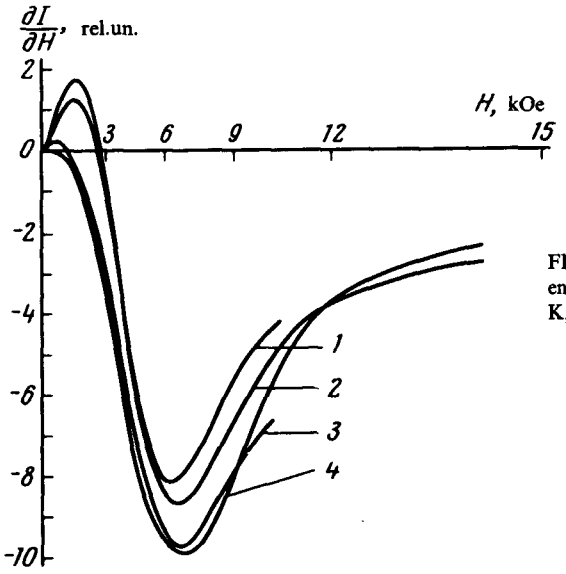


FIG. 2. EPR spectra of liquid oxygen at different temperatures: 1—$T=88$–89 K, 2—$T=162$ K, 3—$T=55$ K, 4—$T=54.3$ K (γ oxygen).

It is most probable that the recently EPR spectrum of γ oxygen[3] is the extreme form of the EPR spectrum of liquid oxygen whose temperature has been lowered to the point of the phase transition into γ oxygen.

In conclusion, the author thanks Academician I.V. Obreimov for suggesting the problem and for constant interest.

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