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Analysis of the susceptibility of condensed oxygen under high pressures and in strong magnetic fields

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ABSTRACT

The temperature dependence of the magnetic susceptibility is analyzed at some constant pressures by a power-law formula using the experimental data from the literature for the $\alpha-\beta$ and $\beta-\gamma$ transitions in oxygen. A weak discontinuous (nearly continuous) transition occurring from the α to the β phase, becomes more discontinuous (weakly first order) for the $\beta-\gamma$ transition as observed experimentally, which can be explained in terms of the critical exponents deduced from our analysis.

The magnetic field dependence of the differential susceptibility is also analyzed in this study for the $\alpha-O_2$ at 4.2 K by a power-law formula using the experimental data. λ-type of observed behaviour of the differential susceptibility is discussed in terms of our analysis for the $\alpha-O_2$.

1. Introduction

Solid oxygen crystallizes in three phases at zero pressure. Below 24 K, solid oxygen is monoclinic (α-O_2) while between 24 and 44 K it is trigonal (β-O_2) [1]. Above 44 K, the solid phase of oxygen is cubic with orientational disorder (γ-O_2) [2]. As the pressure increases at room temperature, the three solid phases occur, namely,β-O_2 [3,4] at 5.46 GPa, δ-O_2 [4] at 9.3 GPa and ε-O_2 [5,6] at 9.9 GPa, and further the ε-O_2 phase transforms to the ξ phase at 96 GPa [7], as also pointed out previously [8]. At a very high pressure of 96 GPa, solid oxygen undergoes a transition to a metallic state at room temperature [9]. Those phases of O_2 molecule have been shown in the P-T phase diagrams using various experimental techniques. In particular, oxygen phase equilibria near 298 K have been described [10]. By the Raman scattering, the experimental P-T phase diagram of oxygen has been determined [3,11–13]. X-ray diffraction measurements at 298 K up to 13 GPa have provided the existence of high pressure phases [14]. Also, using the x-ray diffraction at low temperature and high pressure the T-P phase diagram of O_2 has been obtained experimentally [13,15–17]. It has been pointed out that at pressures below ~10 GPa, phase diagram of oxygen resembles closely that of other molecular crystals such as nitrogen (N_2) [18]. The phase relation among $\alpha-$, $\beta-$, $\delta-$ and $\varepsilon-$ O_2 has been revealed and the $\alpha-\delta$ phase boundry was located on a higher-temperature region than 240 K [16]. It has been pointed out that there occurs a triple point among the phases of β, δ and ε [17]. Very recently, we have calculated the T-P phase diagram of oxygen and we have predicted some thermodynamic quantities [19] using the mean field theory on the basis of the experimental data [11,12].

High pressure properties of solid O_2 have been studied for various phases as reported in the literature. Using Raman spectroscopy, the pressure dependence of intramolecular and intermolecular mode frequencies in solid oxygen has been studied [20]. The intramolecular frequency change and the volume of α-O_2 have been calculated as a function of pressure using harmonic lattice dynamics method [21]. Over a large pressure domain, X-ray diffraction [6,16,22–25], spectroscopic [8,18,26,27] and some theoretical [28–30] studies have been reported.

Magnetic properties of the oxygen molecule close to the phase transitions can be investigated. Since magnetic exchange interactions can be responsible for the structural transition [31–34], the temperature and pressure dependence of the magnetic parameters can be studied both experimentally and theoretically. Magnetization and susceptibility of condensed oxygen have been measured under high pressures and in strong magnetic fields [35]. Since the oxygen molecule possesses a magnetic moment, its magnetic properties, in particular, magnetic orientations in solid α- and β-O_2 have been studied [34]. It has been pointed out that the non-magnetic interactions favour the β-O_2 structure over the monoclinic α-O_2 which is stabilized by magnetic interactons [2]. It

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has also been stated that the magnetic ordering in the β phase stabilizes this phase, lowers the transition temperature since the β phase has short-range order [2]. The monoclinic α phase is stable at temperatures T≤ 18 K and antiferromagnetic order is predicted as the magnetic correlations appear to be long ranged [36]. The $\alpha-\beta$ transition occurs at $T_C = 17.75 \pm 0.2$ K accompanied by a magnetic transition with a correlation length $l_C = 8 \pm 1$ Å at 8 K which decreases rapidly with increasing temperature [36]. However, $\alpha-\delta$ transition involves no magnetic change [36] where δ-O_2 is magnetically disordered [37]. It has been argued that not only the $\alpha-\beta$ transition but also the $\alpha-\delta$ transition is actually driven by magnetic forces [38]. From the infrared absorption spectroscopy study of the magnetic properties of solid oxygen, it has been pointed out that a magnetic ordering occurs with increasing temperature from the nonmagnetic ε phase at low temperatures to the magnetic δ phase at high temperatures [17]. It has also been observed that phase transition occurs from the antiferromagnetic δ-O_2 to the nonmagnetic ε-O_2 [39].

In this study, we analyze the experimental data [35] for the magnetic susceptibility of solid oxygen as a function of temperature at some constant pressures using a power-law formula. We also analyze the experimental data [35] for the differential susceptibility as a function of field strength of α-O_2 at T = 4.2 K by means of power-law formula as we have analyzed the susceptibility in layered structures very recently [40,41]. The critical exponents for the susceptibility at various temperatures (at constant pressures) are deduced for the $\alpha-\beta$ and $\beta-\gamma$ transitions of oxygen. Also, the critical exponents are deduced for the differential susceptibility at various field strength (T = 4.2 K) for the α-O_2. Values of the critical exponents, are interpreted to explain the nature of the $\alpha-\beta$ and $\beta-\gamma$ transitions in O_2.

Below, in section 2 we give our analysis and results. In sections 3 and 4, our discussion and conclusions are given, respectively.

2. Analysis and results

We analyzed here the temperature dependence of the magnetic susceptibility at constant pressures for the low temperature − low pressure phases of α, β and γ in oxygen. The analysis was performed using the experimental data [35] according to the power-law formula

$$\chi = \chi_0 \left(\frac{T - T_C}{T_C}\right)^{-\gamma}, \; T > T_C \tag{1}$$

and

$$\chi' = \chi'_0 \left(\frac{T_C - T}{T_C}\right)^{-\gamma'}, \; T < T_C \tag{2}$$

In Eqs. (1) and (2), $\gamma(\gamma')$ is the critical exponent for the magnetic susceptibility and $\chi_0(\chi'_0)$ is the amplitude. T_C denotes the critical temperature. We analyzed the experimental data [35] for the $\alpha-\beta$ (T_C= 23.4 K at P = 0) and $\beta-\gamma$ (T_C= 43.3 K at P = 0) transitions of solid oxygen at constant pressures of 0, 0.1, 0.2, 0.3 and 0.5 GPa. By taking the logarithms of both sides in Eqs. (1) and (2), we get

$$\ln \chi = \ln \chi_0 - \gamma \ln\left(\frac{T - T_C}{T_C}\right) \tag{3}$$

and

$$\ln \chi' = \ln \chi'_0 - \gamma' \ln\left(\frac{T_C - T}{T_C}\right) \tag{4}$$

Thus, by plotting $\ln \chi(\chi')$ against $\ln \varepsilon$ where $\varepsilon = |T - T_C|/T_C$ is the reduced temperature the values of the critical exponent $\gamma(\gamma')$ and the amplitudes $\chi_0(\chi'_0)$ can be deduced. We did this analysis above (Eq. (3)) and below (Eq. (4)) T_C for the $\alpha-\beta$ and $\beta-\gamma$ transitions of oxygen, and we deduced the $\gamma(\gamma')$ and $\chi_0(\chi'_0)$ values with the uncertainties in the temperature intervals close to T_C for constant pressures indicated, as given in Tables (1) and (2), respectively. We note that since the uncertainties in the values of some $\gamma(\gamma')$ and $\chi_0(\chi'_0)$ are very small as we deduced, they are not given in Tables (1) and (2). We plot $\ln \chi(\chi')$ against $\ln \varepsilon$ above and below T_C in Figs. (1) and (2), respectively, for the $\alpha-\beta$ transition at constant pressures studied in solid oxygen. Figs.(3) and (4) give our plots of $\ln \chi(\chi')$ against $\ln \varepsilon$ above and below T_C, respectively, for the $\beta-\gamma$ transition at the same constant pressures in solid oxygen. In these figures, we give the uncertainties in the susceptibility $\chi(\chi')$, which we determined from our power-law analysis (Eqs. (3) and (4)) for the $\alpha-\beta$ and $\beta-\gamma$ transitions above ($T > T_C$) and below ($T < T_C$) the transition temperature of solid oxygen. We extracted the T_C values at those constant pressures as given in Tables 1 and 2 using the experimentally determined P-T phase diagram [35]. When we used the power-law formula (Eqs. (1) and (2)) for the temperature dependence of the susceptibility $\chi(\chi')$, we determined the values of the critical exponent $\gamma(\gamma')$ by fixing the critical temperature T_C for the $\alpha-\beta$ and $\beta-\gamma$ transitions within the temperature intervals at constant pressures for oxygen (Tables 1 and 2). Thus, variation of the susceptibility with the temperature was not influenced by the value of T_C at constant pressures in our analysis for this molecular system.

We also analyzed here the magnetic field dependence of the susceptibility of the $\alpha-$ O_2 at 4.2 K using the experimental data [35]. According to the power-law formula,

$$\Delta\sigma/H = K|B - B_C|^{-\kappa} \tag{5}$$

where $\Delta\sigma/H$ is the differential susceptibility, with the critical exponent κ, and the amplitude K, B is the field strength, our analysis was performed above and below the critical fild strength B_C. Table 3 gives the values of the critical exponent κ and the amplitude K with the uncertainties within the interval of the field strength B at 4.2 K for the $\alpha-$ oxygen. In Table 3, since the uncertainties in the values of some κ and K are negligible as we extracted, they are not given. In Figs.(5) and (6) above and below B_C, respectively, we plot in a log-log scale of the differential susceptibility against B-B_C according to

$$\ln(\Delta\sigma/H) = \ln K - \kappa \ln|B - B_C| \tag{6}$$

As Eqs. (3) and (4), Eq. (6) also represents a straight line with the slope which gives the critical exponent κ. We also analyzed the P-T phase diagram of oxygen for its $\alpha-\beta$ and $\beta-\gamma$ and $\gamma-$ liquid transitions using the experimental data [35] according to a linear variation of the pressure with the temperature as

$$P = a + bT \tag{7}$$

where a and b are constants. In Table 4, we give the values of a and b(=dP/dT) which were extracted from the experimental P-T data [35] for the transitions within the temperature and pressure intervals studied for O_2.

3. Discussion

In our first analysis of the magnetic susceptibility as a function of temperature above the transition temperature T_C for the $\alpha-\beta$ transition in oxygen, we obtained negative values (about 0.1) for the critical exponent γ according to Eq. (1) at constant pressures from 0 to 0.5 GPa, as given in Table 1. As the temperature lowers below T_C, those exponent values were all positive (nearly 0.1) for