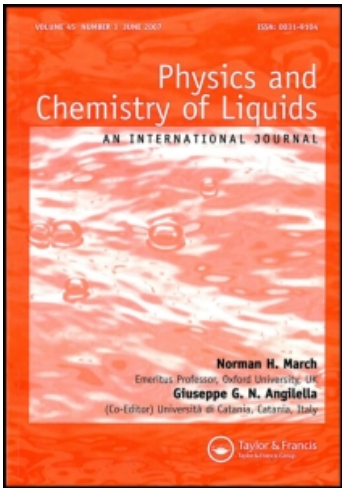

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Spin-polarized electron liquid in CrO_2 under high pressure

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Letter

Spin-polarized electron liquid in CrO_2 under high pressure

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Recent experiments on the suppression of ferromagnetism due to the spin-polarized electron liquid in half-metallic CrO_2 are combined with existing band structure calculations. A semi-empirical form of the variation of Curie temperature with pressure P for $P < 12$ GPa is thereby proposed, to be confirmed, or refined, following further high pressure experiments.

Keywords: Pressure; Spin-polarized electron liquid

There is a surprising variety of electrical and magnetic behavior among transition metal oxides having a rutile structure. Starting with MnO_2, this material is known to exhibit antiferromagnetic ordering (AFO). Also they may be insulating, as is the case for TiO_2, or metallic as for RuO_2. So far it appears that CrO_2, our main focus below, is the only member of this class of materials that is (a) metallic and (b) has ferromagnetic order (FO).

A few properties of chromium dioxide that are noteworthy are as follows: (i) CrO_2 is a metastable phase and heating at atmospheric pressure above 500–600 K leads to the formation of a stable oxide, namely Cr_2O_3; (ii) CrO_2 is used for magnetic recording, and the material production via high-pressure decomposition of CrO_3 is well established [1–3]; and (iii) tunneling experiments [4] have confirmed the half-metallic nature of CrO_2.

Our own interest in this material has been motivated by the very recent experiment of Sidorov *et al*. [3] on the influence of high pressure on the ferromagnetic transition temperature of CrO_2. In particular, the decrease in the Curie temperature T_C with applied pressure P was determined by these authors from measurements of magnetic AC-susceptibility.

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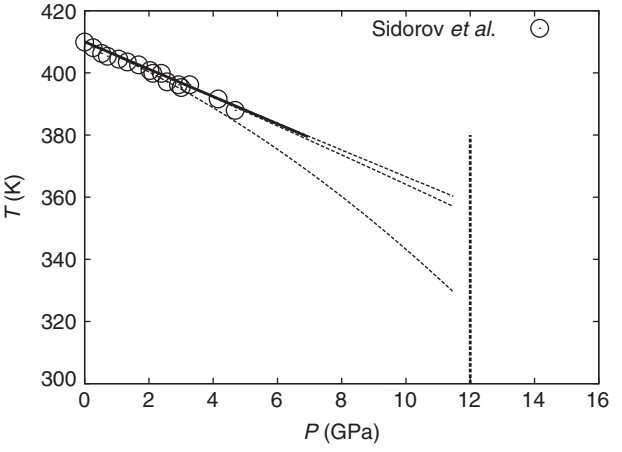

Figure 1. Curie temperature T_C as function of pressure P. Experimental points have been redrawn from [3], while vertical dashed line at $P \approx 12\,\mathrm{GPa}$ locates the phase boundary between the rutile and $CaCl_2$-type structures suggested in [3]. Solid line is then Sidorov *et al.*'s [3], linear fit satisfying equation (1), whereas dashed lines are quadratic approximants to our proposal, equation (5) below, with $P_c = 12, 50$ and $80\,\mathrm{GPa}$ (bottom to top) and $\gamma = 1/2$, again satisfying equation (1).

Figure 1 reports experimental data from [3], which were available for hydrostatic pressures $P \leq 5\,\mathrm{GPa}$. From this figure, the suppression of ferromagnetism with pressure over this range is characterized by [3]

$$\left.\frac{\mathrm{d}T_C}{\mathrm{d}P}\right|_{P=0} = -4.4\,\mathrm{K\,GPa^{-1}}. \tag{1}$$

This experimental fact [3] has been compared with the theoretical study of Matar and Demazeau [5] using the so-called augmented spherical wave–local spin density approximation (ASW–LSDA), in which band structure calculations for CrO_2 were performed at different pressures using experimentally determined lattice constants [5]. These calculations also predict such a decrease in T_C with pressure, as well as the complete disappearance of ferromagnetism at 120–150 GPa. But, as figure 1 indicates, such a prediction is not to be compared, at least directly, with experiment, since X-ray diffraction [5,6] and Raman scattering [6] measurements demonstrated that the tetragonal rutile lattice is stable for CrO_2 up to 12 GPa. Then, higher hydrostatic pressure leads to a modest orthorhombic distortion and a phase change to the $CaCl_2$-type structure [6]. Though the prediction of Matar and Demazeau [5] as to the disappearance of ferromagnetism at much higher pressures is not directly testable because of this phase transition, nevertheless their ASW–LSDA band structure calculations yield the estimate [3,5]

$$\frac{\mathrm{d}T_C}{\mathrm{d}P} \approx -\frac{T_C(0)}{P_c} = -3.4\,\mathrm{K\,GPa^{-1}}, \tag{2}$$

which is reasonably consistent [3] with the experimental slope in equation (1). Here, $T_C(0)$ is the Curie temperature at atmospheric pressure, while $P_c = 120\,\mathrm{GPa}$ is the calculated critical pressure, at which T_C vanishes [5].

Considering this 'hypothetical' transition near P_c and at low temperatures, the connection focussed on by Bhatia and March [7] (see also [8]) relating dT_C/dP to elementary excitations yields the analog of the Clausius–Clapeyron equation as

$$\frac{dT_C}{dP} = \frac{\Delta V}{\Delta S}: \quad P \to P_c, \tag{3}$$

where ΔV is the volume change across the phase transition from FO for $P_c < 120\,\text{GPa}$ to assumed paramagnetism for $P_c > 120\,\text{GPa}$, and ΔS is the corresponding entropy change. Both theory and experiment then suggest that ΔV and ΔS must have opposite signs. We expect the FMO phase to have lower entropy away from $T = 0$ than the paramagnetic phase, and therefore if $\Delta V = V_P - V_F$, and ΔS similarly, ΔS is positive and ΔV is therefore negative. Furthermore, from the Third Law of Thermodynamics, we expect $\Delta S \to 0$ as $T \to 0$, and since ΔV can be anticipated to remain finite at the phase transition, we find

$$\frac{dT_C}{dP} \to -\infty: \quad P \to P_c. \tag{4}$$

Though we have not a first-principles approach to data, we propose now a semi-empirical method to estimate $T_C(P)$ over a much wider pressure range than in figure 1, but we stress, in the rutile structure throughout. To accomodate the behavior of equations (3) and (4), we assume that $T_C \to \text{const} \times (P_c - P)^\gamma$ as $P \to P_C$, where $0 < \gamma < 1$. Then, with one additional parameter α, we propose the interpolation formula

$$\frac{T_C}{T_C(0)} = \frac{1}{\alpha + (1-\alpha)(1-(P/P_c))^{-\gamma}}. \tag{5}$$

To guide the representation of the data of Sidorov *et al.* [3] over the admittedly limited range of pressure indicated in figure 1, we have drawn in a linear fit of T_C *versus* P according to equation (1) given in [3] in figure 2. Since this figure indicates a critical pressure near to 90 GPa, we have fitted equation (5) to accord equation (1) for three different values of P_c, namely 80, 50, and 12 GPa. The curves shown are for $\gamma = 1/2$ and $\gamma = 1/3$ in equation (5). We suspect from the behavior for $P_c = 80\,\text{GPa}$ that if this is indeed near to the correct critical pressure for the rutile structure of CrO_2, then γ should be somewhat less than 1/2, say $\gamma = 1/3$.

To summarize, we have made proposals that suggest that the ferromagnetism in a rutile structure of CrO_2, if it could be stabilized, should be suppressed by significantly lower pressures than 120–150 GPa. We give some evidence, though semi-empirical rather than from first principles, that the critical pressure P_c may be $<80\,\text{GPa}$. Further experiments out to 12 GPa could confirm or, if necessary, refine our proposed behavior of $T_C(P)$ in equation (5).

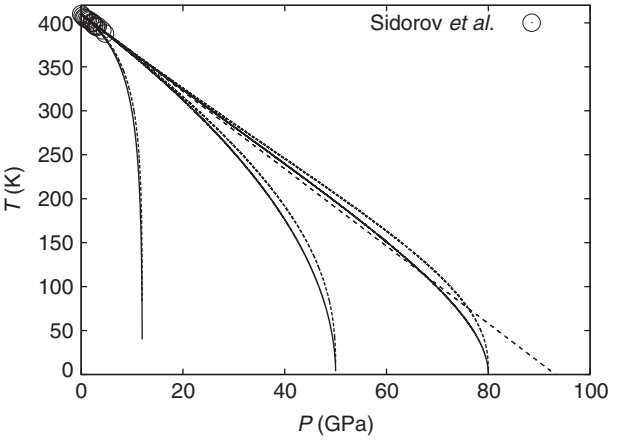

Figure 2. Plots our proposed semi-empirical dependence of T_C over pressures $P \leq 80\,\mathrm{GPa}$, equation (5), assuming that no structural phase transition occurs in this pressure range. Light dashed line is Sidorov *et al.*'s linear fit, equation (1), solid lines represent equation (5) with $\gamma = 1/2$, while dashed lines are for $\gamma = 1/3$. Different curves are for $P_c = 12, 50$ and $80\,\mathrm{GPa}$ (bottom to top).

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