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The influence of nitrogen vacancies on the magnetic behaviour of rare-earth nitrides

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ABSTRACT

The rare-earth nitrides are ferromagnetic semiconductors with promise for spintronic devices. Their most common dopants are nitrogen vacancies (V_N), with a small enough energy of formation that they exist at of order 1% in epitaxial films. Here we report preliminary investigations of their effect on the magnetic states of two of them in the series, GdN and EuN. In the former we find an enhanced Curie temperature at very high V_N concentration, and the Eu^{2+} ions associated with V_N in the latter show strong exchange with their Eu^{3+} neighbours that might form the basis of a diluted magnetic semiconductor.

1. Introduction

The simplicity of the crystal structure adopted by the rare earth mononitrides (REN) has made them an attractive testing ground for theoretical description of strongly correlated crystalline solids [1–3]. However there has been a paucity of experimental data with which to compare theoretical results due in no small part to the propensity for *N* vacancies (V_N) and, when exposed to air, for oxide formation. Even such a fundamental issue as the conducting state, metal or semiconductor, has been subject to disagreements for nearly 50 years [1–10]. In the past 10 years there has been substantial progress in the growth and passivation of thin REN films [6–8,11–13], with the result that the role of V_N centres can be investigated.

From a historical point of view the RENs were explored extensively in the 1960s, when their crystal structure was clearly established to be of the fcc NaCl structure with lattice constants varying from ~0.48 nm (LuN) to 0.53 nm (LaN) across the series [1]. Most of them were found to be ferromagnetic in their ground state, with GdN possessing the highest Curie temperature of 70 K [5,14,15]. The magnetic responses of nearly all of them were investigated, with the single exception of the nitride of the radioactive element promethium. With a few exceptions the data available were in substantial agreement, signalling that even with their uncertain stoichiometry the materials retained the magnetic behaviour characteristic of fully stoichiometric material; the magnetic response is only a weak function of moderate concentrations of the common defects. Within another decade there were investigations of the variation of the GdN Curie temperature with V_N and oxygen levels of up to 10%, and indeed the effects were found to be relatively weak, though O was reported to significantly harden the ferromagnetic response [16,17]. In contrast with the magnetic response, the conductivity of the early materials showed substantial variation, prompting different studies to claim metallic, semi-metallic or semiconducting behaviour [1,2,6,8,12,18–20]. This variation already signals a sensitivity to unintended doping that is characteristic of semiconductors though it was not until the past 10 years that more evidence, especially optical evidence, has strengthened the case for regarding these materials as semiconductors [7,18,20]. The situation is still far from clear. However in view of their ferromagnetic ground states, and the possibility of growing technologically interesting epitaxial bilayers and superlattices among them, there is an urgency to establish their properties and the role that defects, and especially V_N centres, have on the conducting and magnetic behaviours.

2. Theoretical treatments

From a theoretical perspective the ground state has been discussed for all them within density functional theory treatments of various descriptions, and they are predicted as metals again, half metals or semiconductors depending largely on the assumed values for uncertain exchange and correlation parameters [1–3,7]. In one case, GdN, the resulting band structure has been tuned to agree with a measure of the optical band gap in both ferromagnetic and paramagnetic phases [7], with results that agree with both of these gaps and with x-ray spectroscopic investigations of states well away from the gap [18]. No other REN

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has been subjected to that level of investigation. Theoretical treatments of the magnetic response have been reported for GdN and here the 20 K T_C result is in substantial disagreement with experiments [21]. This has encouraged a proposal that T_C might be enhanced by the RKKY exchange, though in the semiconductor scenario the variable carrier density should then have prevented the observed uniformity among the reported Curie temperatures [22]. Against this background there has been one theoretical treatment of nitrogen vacancies (V_N) in GdN, establishing their formation energy of order 0.5 eV [23]. The vacancy traps one or two electrons, so it can be expected that each one dopes the conduction band with between one and two electrons.

3. Results

The growth of almost all REN films is accomplished simply by evaporating RE ions in the presence of neutral N_2 gas, with the ratio of N_2 to RE flux on the surface of at least 100. As expected for V_N donors the carriers are electrons. The exception we have so far identified is Eu, which does not react with neutral N_2 and grows only in the presence of activated nitrogen [24]. Temperatures of several hundred °C are required for epitaxial growth, and at those elevated temperatures their relatively low formation energy leads to a significant V_N concentration, and carrier densities lying in the range of 10^{20}–10^{21} cm^{-3} [8,12,25]. Deposition onto ambient-temperature substrates yields a polycrystalline film of substantially better stoichiometry, which then permits fuller investigation of the effects of V_N and carrier concentrations [6,7,11,13].

3.1. GdN—carrier-enhanced T_C

The REN that both we and others have studied most intensively is GdN. Gd lies at the centre of the RE series, and has a half-filled 4f shell with the maximum spin of 7/2 and a moment of $7\mu_B$. The Curie temperature in our films is at most weakly dependant on V_N concentration up to at least several %, in agreement with the extensive literature. However at higher V_N concentration there is a substantial enhancement of the Curie temperature; in Fig. 1 it can be seen that T_C rises to as much as 200 K in films with V_N densities estimated to be near 10%, as signalled by a carrier density, estimated from the conductivity, approaching 10^{23} cm^{-3}.

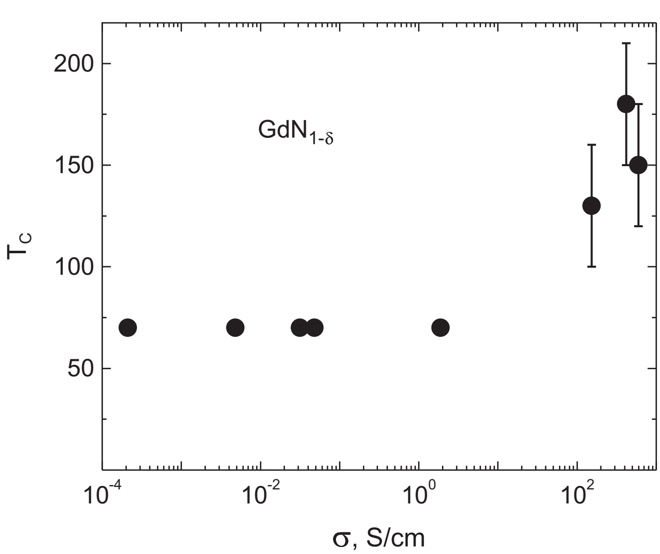

Fig. 1. Curie temperature (T_C) in K as a function of conductivity (σ). The points around 125–200 K have error bars representing the range of paramagnetic and ferromagnetic estimates of T_C.

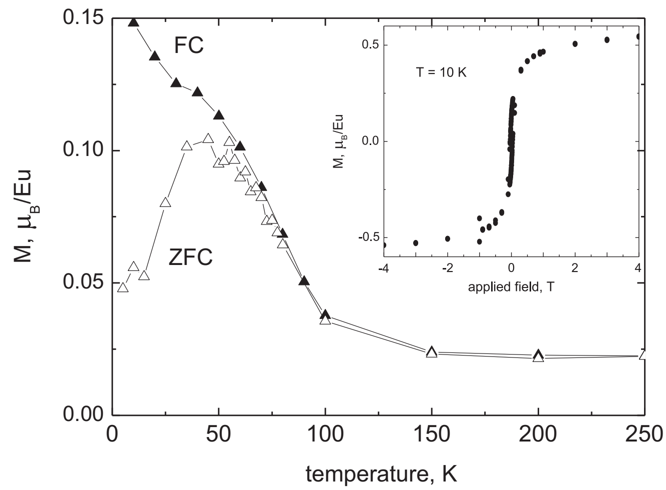

Fig. 2. Field cooled (FC) and zero field cooled (ZFC) magnetisation at 250 Oe of EuN with high V_N concentration. Inset: the magnetisation vs field at 10 K shows a saturation magnetisation that follows from about 8% of Eu in the 2+ ionisation state. The hysteresis from a coercive field of only 400 Oe is not resolved at the scale shown here.

3.2. EuN—diluted magnetic semiconductor?

As far as we have found to date the RE ions in the nitrides are in the 3+ ionisation state. However Eu, with one fewer electron than Gd, shows a propensity for a divalent state, which then bonds electrons from V_N centres as seen in XAS at the L and M edges in N-deficient EuN [26]. The $J=0$ ground state of Eu^{3+} prevents any magnetic moment alignment except a weak van Vleck susceptibility from admixtures of excited $J>0$ states, so that the very large $7\mu_B$ on each Eu^{2+} ion dominates the magnetic response at low temperature and provides an estimate of the concentration of divalent Eu and thus of V_N. The resulting material then shows similarity to diluted magnetic semiconductors (DMS), and an inter-ion exchange has been seen between Eu^{2+} and its Eu^{3+} neighbours [26]. There is some evidence of a ferromagnetic response at temperatures as high as 100 K in heavily V_N-doped EuN (Fig. 2), though we are some way from reliably establishing a ferromagnetic DMS state and relating it to the V_N concentration.

3.3. Raman signature of V_N

With the exception of EuN, where the divalent concentration can be investigated by x-ray spectroscopy, it has proven difficult to obtain an accurate direct measure of the V_N concentration. A combination of Rutherford Backscattering Spectroscopy and Nuclear Reaction Analysis can establish stoichiometry to no better than a few atomic % [12,27]. One potentially useful measure is based on the appearance of a zone-boundary phonon rendered Raman active by defects; signals from a series of EuN samples with differing V_N densities are shown in Fig. 3. The technique requires full calibration to develop it as a quantitative measure of the V_N concentration.

4. Conclusion

We have begun an investigation of the magnetic properties of rare-earth nitrides doped by nitrogen vacancies. The system explored most is GdN, with a Curie temperature that is enhanced

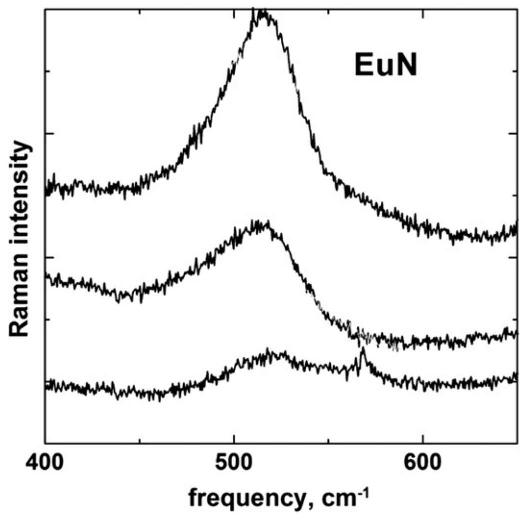

Fig. 3. Raman spectra, obtained using 633 nm excitation, from a series of EuN samples with differing V_N densities, from high (top curve) to low density (bottom curve).

from 70 K in near-stoichiometric films to as high as 200 K under very heavy doping. The second system on which we report is EuN, in which very strongly paramagnetic Eu^{2+} ions are induced by nitrogen vacancies. This system might form a diluted magnetic semiconductor at high V_N and Eu^{2+} concentration. Finally we identify the strength of the Raman signal from a zone-boundary phonon as a potential measure of V_N concentration.

Acknowledgements

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