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We investigate the electronic structure and magnetic properties of GdN as a function of unit cell volume. Based on the first-principles calculations of GdN, we observe that there is a transformation in the conduction properties associated with the volume increase: first from half-metallic to semimetallic, then ultimately to semiconducting. We show that applying stress can alter the carrier concentration as well as mobility of the holes and electrons in the majority spin channel. In addition, we found that the exchange parameters depend strongly on lattice constant, thus the Curie temperature of this system can be enhanced by applying stress or doping impurities.

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Electronic and transport properties of the rare-earth nitrides have long been a challenge to investigators: the nitrides are difficult to fabricate into single phase crystals and the experimental picture of their electronic structures is far from clear. Although most rare-earth nitrides have been shown to be semimetallic, there are still uncertainties about GdN. Based on the direct resistivity measurements, Xiao and Chien concluded that GdN is an insulator [1]. Nevertheless, the values they obtained for the resistivity do not rule out the possibility of a semimetallic state. Furthermore, there is no clear-cut picture emerging from a series of studies by Kaldis and co-workers in the 1970s and 1980s [2–4]. They pointed out that the specific resistivity decreased with increasing temperature, which suggests that the GdN system is semiconducting [2]. Their later experiments on better quality samples showed a very large carrier concentration of 1.9×10^{21} cm^{-3}, which is more characteristic of a semimetal [3]. Even though the optical absorption edge for GdN is about 1 eV [4], which is similar to other rare-earth nitrides, at issue is the position of the chemical potential relative to the band edges in both the spin majority and spin minority band structures.

An appealing property of GdN is that it is ferromagnetic with a large gap at the Fermi energy in the minority spin states, according to the electronic structure calculations based on the local density approximation [5–7]. At the same time, GdN is semimetallic in majority spin states with electron and hole pockets at the Fermi surface [6]. This latter property has led to some interest in GdN as a possible candidate for spin-dependent transport devices [8], exploiting the spin filter, giant magnetoresistance, or tunneling magnetoresistance effects.

An accurate description of the electronic structure of rare-earth compounds is a very challenging problem because of their unfilled $4f$ shells [9]. Calculations based on local spin density approximation (LSDA) are well known to underestimate the band gap in semiconductors. Thus LSDA and similar computational methods may not be able to correctly describe whether a highly correlated system, such as GdN, is semimetallic or semiconducting at the equilibrium volume [6]. Nonetheless, if we are interested in the trend of how the electronic and magnetic properties vary with the change of volume, we can obtain a reasonable picture for GdN from LSDA with additional Hubbard correlation terms describing on-site electron-electron repulsion associated with the $4f$ narrow bands (the LSDA + U approach) [10]. Actually, due to the fact that the f states of this system are exactly half occupied, there is no orbital moment and the anisotropic and multipole effects are minimal. As a result, GdN is the ideal material to study the magnetic exchange interactions in rare-earth nitrides [11].

In this Letter, we show that applying stress can influence significantly the electronic and magnetic properties of GdN. Using the first-principles approaches, we demonstrate that the system exhibits a nominal ''half-metallic'' band structure at the equilibrium lattice constant, and then the semimetallic and/or semiconducting character develops with increasing lattice constant. We note that the magnetic properties are also extremely sensitive to the volume variations, i.e., the exchange interactions are at first ferromagnetic, then the calculated magnitudes of exchange parameters reduce substantially with increasing volume, suggesting that the Curie temperature is reduced with an increase in lattice constant.

The first-principles band structure approach applied in this work is the full-potential linear-augmented-plane-wave plus local-orbital method [12]. In the total energy calculations, the factor $R_{MT}K_{\max}$ is chosen to be 8. We found that using as large as 4000 k points in the Brillouin zone was necessary to obtain the energy convergence up to 0.1 meV. Following previous work [13], we used a Hubbard $U = 6.7$ eV and an exchange $J = 0.7$ eV for Gd compounds in the LSDA + U scheme [10]. The calculated

density of states (DOS) of GdN agrees well with photoemission data of nitrogen covered Gd(0001) surfaces [14], as shown in Fig. 1. Given that both experiment and theory share the similar lattice structures, this suggests that our computational approach correctly represents the electronic structure of GdN.

When we studied the band structure, we found that, for the theoretical lattice constant $a = 4.92$ Å [Fig. 2(a)], our LSDA + U calculations show that there exist a hole pocket at the Γ point and an electron pocket at the X point. Strong hybridization between Gd $5d$ and N $2p$ spin majority states is clearly shown around the X point, while there is no such hybridization for spin minority states, indicating GdN to be half-metallic, with a gap about 0.6 eV in the spin minority channel. As we increase the lattice constant, this system gradually develops semimetallic features in the majority states: for example, the d-p hybridization around the X point disappears and the Fermi level down shifts to the top of the hole section at the Γ point [Fig. 2(b)]. With a further increase in volume, the system eventually becomes semiconducting [Fig. 2(c)]. The exact volume at which metal-semimetal or semimetal-semiconductor transitions occurs might not be precisely determined from LSDA-based calculations. However, the trend is clear, and the predicted transitions could be observed experimentally.

We note that volume expansion or applied strain can be used to control the carrier density as well as to some degree the mobility of the carriers, as can be seen from the band dispersion curves near the Fermi energy, in Fig. 2. At larger volumes, the electron (hole) pockets become substantially shallower, meaning that the bottom (top) of the band approaches the Fermi energy and the area of the Fermi surface decreases. This is quite clear, for example, when comparing the hole pockets around the Γ point in Figs. 2(a) and 2(b), especially those Fermi-level crossing points. As a result, the density of states at the Fermi energy reduces by about 50% when lattice parameter is increased by only 5%. The decrease of dE_k/dk (tangent to the band dispersion) at Fermi level can also be seen from Fig. 2, indicating that the mobility of the holes decreases with the increase of the cell volume.

Furthermore, as also can be seen from Fig. 2, the indirect band gap of GdN can be modified by hydrostatic pressure. Based on the prediction of electron-hole-liquid theory [15], a first-order semiconductor to semimetal transition starts to take place as the indirect band gap decreases with decreasing lattice constant. Thus it is conceivable that, with proper control of the indirect gap via external pressure, it is possible to explore the ground state of this correlated electron-hole liquid, and tune experimentally the semimetal phase transition.

We have also explored the modifications of the band structure and electronic properties due to the biaxial strain, which can be produced by epitaxially growing the film on the substrate with a different lattice constant. When the

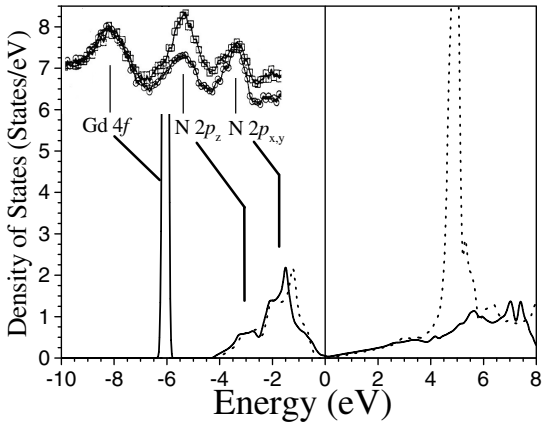

FIG. 1. Comparison between the calculated DOS (solid line, majority spin; dotted line, minority spin) at theoretical lattice constant ($a = 4.92$ Å) and the photoemission spectra for nitrogen on Gd(0001). The new photoemission features that are not attributable to the Gd(0001) substrate compare well with the calculated DOS for GdN. Features with strong N $2p$ weight are indicated. Binding energies for experiment are shifted to higher binding energies as expected with a final state spectroscopy of a correlated electron system, but the shift is roughly uniform for key features of the photoemission spectra (taken for both s and p polarized light).

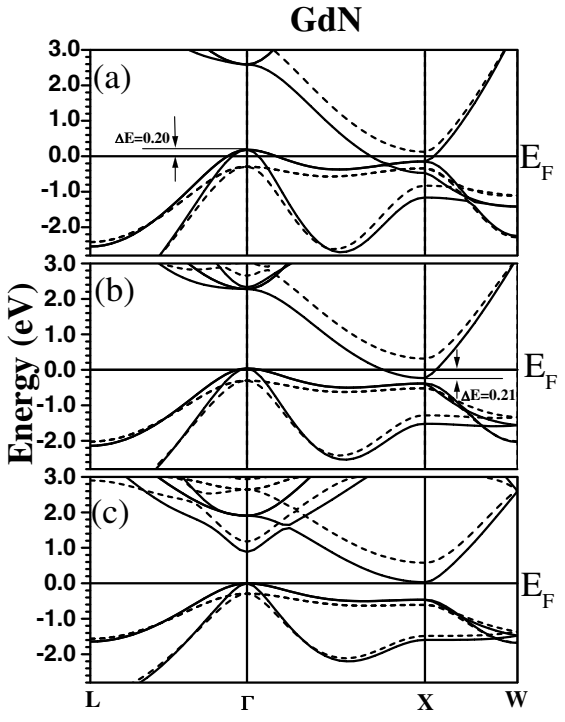

FIG. 2. Band structure of GdN in the vicinity of the Fermi energy for three volumes: (a) at the calculated equilibrium lattice parameter $a = 4.92$ Å; (b) at the lattice parameter increased by 5% ($a = 5.16$ Å); (c) at the lattice parameter increased by 14% ($a = 5.63$ Å). Solid and dotted lines represent spin majority and spin minority states, respectively. The change of conducting properties are indicated by the change of energy difference between the top (bottom) of the hole (electron) pockets and the Fermi energy.

lattice parameter of the substrate is different from that of equilibrium GdN, the lattice mismatch can produce strain. In such cases, the lattice symmetry of GdN becomes tetragonal with a c/a ratio less than 1 (larger substrate lattice constant, tensile strain) or larger than 1 (smaller substrate lattice constant, compressive strain). We performed total energy calculation on the Poisson ratio ν for GdN by applying the biaxial strain in the ab plane and observing the variation of c. Then, by comparing the biaxial strain given as

$$\frac{\Delta c/c_0}{\Delta a/a_0} = -\frac{2\nu}{1-\nu},$$

we deduced a $\nu = 0.2$, which is small compared to metals but similar to the known value of TiN. We found that the trend of band structure change, due to the biaxial strain, remains qualitatively the same as that caused by volume strain, which is expected because of the small Poisson ratio. The unit cell volume of GdN increases due to biaxial tensile stress; hence the modification of the band structure near the Fermi energy is similar to that observed during volume expansion. This may imply that the tensile stress tends to force the system to be less metallic and decreases the density of states near the Fermi surface. When applying the compressive strain, the system tends to become more metallic. Our calculations show that there is a considerable reduction in the band gap of the minority spin band structure with biaxial compressive strain. Specifically, with an in-plane compressive strain of 3%, we noticed the Fermi-level crossing of the valence bands, which renders the system no longer half-metallic.

We also found that the change in electronic structure with the applied stress significantly affects the magnetic properties of GdN, particularly, the exchange interactions. We analyzed the exchange interactions using the Heisenberg Hamiltonian:

$$H = -\sum_n J_n \sum_{i>j} \vec{S}_i \cdot \vec{S}_j,$$

where J_n are exchange parameters and n is the index of the nearest-neighbor shell. In these calculations, we limited our considerations to the third nearest-neighbor interactions, i.e., n runs from 1 to 3. The exchange parameters used in the model Hamiltonian are obtained from the first-principles band structure calculations. To do this, we carried out total energy calculations on four different magnetic ordering configurations of the fcc structure. One is ferromagnetic (FM) ordering, and the other three are antiferromagnetic (AFM) orderings, as have been described in Ref. [16], and here for convenience are called AFM_I, AFM_{II}, and AFM_{III}, respectively. According to the model Hamiltonian, the total exchange energies per magnetic lattice site of the four magnetic orderings can be explicitly expressed as

$$E_{FM} = E_0 + 6J_1 + 3J_2 + 12J_3,$$
$$E_{AFM_I} = E_0 - 2J_1 + 3J_2 - 4J_3, \qquad E_{AFM_{II}} = E_0 - 3J_2,$$
$$E_{AFM_{III}} = E_0 - 2J_1 + J_2 + 4J_3,$$

where E_0 is the reference energy. Based on these equations and the results obtained from the total energy calculations, those J parameters can be deduced accordingly. Because of the fact that the energy differences between these ordering states are generally very small, extreme care is needed in the calculations. Hence, comparisons are made only between FM and AFM energies calculated on the same structure and with the same computational parameters, to avoid any error caused by the different symmetries or shapes.

Our LSDA + U calculation gives the correct ground state for GdN, i.e., FM ordering. The J_n values are, nonetheless, quite small, which is expected from the low transition temperature. In addition, we found that these exchange parameters of GdN depend strongly on the lattice constant (Fig. 3). When the lattice constant increases, the FM J_1 increases while the value of J_2 changes sign, namely, from FM to AFM, although J_3 remains largely unchanged. Thus the FM transition temperature T_c, which is proportional to the sum of neighboring exchange energies $12J_1 + 6J_2 + 24J_3$ according the mean-field theory, is sensitive to the change of lattice constants.

It is well known that the oscillatory Rudermann-Kittel-Kasuya-Yosida–type interaction varies sensitively with the density of charge carriers. Thus, based on the above observations, we can see that the enhancement of the exchange interactions between neighboring magnetic sites, when the lattice constant decreases, is caused by the increase of the number of free charge carriers as the GdN system becomes more metallic. Actually, the strong lattice constant dependence of the GdN J parameters is a manifestation of the sensitive crystal structure dependence of the GdN electronic structure, which lies between the metal and insulator phases. Furthermore, the trend of J_2 with the

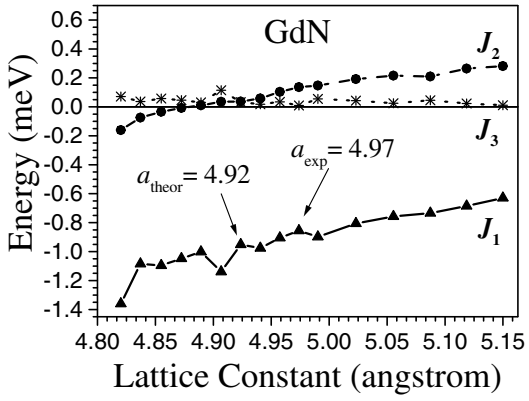

FIG. 3. Exchange parameters of GdN plotted as a function of the lattice constant; notice the strong volume dependence of J_1 and J_2.

increase of the volume implies the strengthening of an AFM superexchange interaction when the system becomes less metallic. This can be understood as a competition between the superexchange and the indirect carrier mediated exchange interactions. Usually the former is roughly proportional to t^2/U, where t is the band energy or hopping integral, and does not change too strongly when the lattice parameter increases. Whereas the later, as we already discussed, would decrease with the increase of the lattice constant. Hence this reduction causes an overall increase in the antiferromagnetic coupling between second-nearest-neighbor Gd sites. Therefore we can see that the magnetic properties of Gd nitride are strongly related to their electronic properties. Based on these findings, we expect that GdN, in which a strong AFM and FM competition exists, could be AFM [4] or an even more complicated structure such as spin glass [17] when experiencing different stress.

Monte Carlo (MC) simulations, based on the model Heisenberg Hamiltonian with *ab initio* derived exchange parameters, are used to obtain the Curie temperature. The same method has been applied successfully in the study of complex permanent magnetic materials [18]. The lattice studied in our MC simulation is a $10a \times 10a \times 10a$ fcc cell (4000 spins) with periodic boundary conditions, where a is the lattice constant. At theoretical lattice parameter ($a = 4.92$ Å) we find the Curie temperature to be about 38 K, agreed reasonably well with the experimentally observed 58 K. This agreement is quite impressive, considering the strong correlated nature of this system. One possible reason for the underestimate of T_c may arise from neglecting the correlated hopping processes in the one-electron picture, which are the higher order processes proposed by Kasuya and Li to explain the ferromagnetic exchange in GdN [19]. In addition, we found that the energy levels of $4f$ states are crucial in determining the accurate exchange parameters. Our calculation of the equilibrium structure of GdN, based on the present U parameter, gives the unoccupied $4f$ states 5 eV above E_F and occupied $4f$ states 6 eV below, which is in good qualitative agreement with the experimental situation [20], providing support for the validity of our studies of the magnetic properties of GdN.

Ordinarily, we would expect the ferromagnetic ground state to provide a stabilizing role to the spin-dependent electric conduction. Thus enhancement the Curie temperature of GdN to a practical range is quite important. As already mentioned above, one possible way is to apply stress. Moreover, doping impurities can also be an alternative: it was reported that by adding few percent of magnetic ions such as Mn, the T_c of GaN or ZnO well exceeds the room temperature range [21]; hence we believe this is a promising remedy for concern that the Curie temperature of GdN is on the low side.

In summary, we have found that there is a large lattice constant dependence of the electronic and magnetic properties in the spin-dependent band structure of GdN. This material, with a half-metallic gap of about 0.6 eV, exhibits a ferromagnetic ground state, rendering it an attractive candidate for spintronic devices. Hence we appeal strongly for experimental efforts to study this interesting compound and validate our claim.

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[1] J. Q. Xiao and C. L. Chien, Phys. Rev. Lett. **76**, 1727 (1996).
[2] G. Busch, E. Kaldis, E. Schaufelberger-Teker, and P. Wachter, Coll. Int. CNRS No. 180, Vol. I (CNRS, Paris-Grenoble, 1970), p. 359.
[3] E. Kaldis and C. Zurcher, Helv. Phys. Acta **47**, 421 (1974).
[4] P. Wachter and E. Kaldis, Solid State Commun. **34**, 241 (1980).
[5] A. Hasegawa and A. Yanase, J. Phys. Soc. Jpn. **42**, 492 (1977).
[6] A. G. Petukhov, W. R. L. Lambrecht, and B. Segall, Phys. Rev. B **53**, 3646 (1996).
[7] Walter R. L. Lambrecht, Phys. Rev. B **62**, 13 538 (2000).
[8] S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnar, M. L. Roukes, A. Y. Chtchelkanova, and D. M. Treger, Science **294**, 1488 (2001).
[9] I. N. Yakovkin, Takashi Komesu, and P. A. Dowben, Phys. Rev. B **66**, 035406 (2002).
[10] V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyzyk, and G. A. Sawatzky, Phys. Rev. B **48**, 16 929 (1993); V. I. Anisimov, J. Zaanen, and O. K. Andersen, *ibid.* **44**, 943 (1991).
[11] D. X. Li, Y. Haga, H. Shida, T. Suzuki, Y. S. Kwon, and G. Kido, J. Phys. Condens. Matter **9**, 10 777 (1997).
[12] P. Blaha *et al.*, Comput. Phys. Commun. **147**, 71 (2002).
[13] Ph. Kurz, G. Bihlmayer, and S. Blügel, J. Phys. Condens. Matter **14**, 6353 (2002).
[14] C. Waldfried, D. N. McIlroy, Dongqi Li, J. Pearson, S. D. Bader, and P. A. Dowben, Surf. Sci. **341**, L1072 (1995).
[15] R. Monnier, J. Rhyner, T. M. Rice, and D. D. Koelling, Phys. Rev. B **31**, R5554 (1985).
[16] J. Samuel Smart, *Effective Field Theories of Magnetism* (W. B. Saunders Company, Philadelphia, 1966), pp. 76–77.
[17] D. X. Li, K. Sumiyama, K. Suzuki, and T. Suzuki, Phys. Rev. B **55**, 6467 (1997).
[18] R. F. Sabiryanov and S. S. Jaswal, Phys. Rev. Lett. **79**, 155 (1997).
[19] T. Kasuya and D. X. Li, J. Magn. Magn. Mater. **167**, L1 (1997).
[20] H. Yamada, T. Fukawa, T. Muro, Y. Tanaka, S. Imada, S. Suga, D.-X. Li, and T. Suzuki, J. Phys. Soc. Jpn. **65**, 1000 (1996).
[21] J. M. Coey, M. Venkatesan, and C. B. Fitzgerald, Nat. Mater. **4**, 173 (2005).