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**Ab initio calculations of elastic properties of Ru<sub>1-x</sub>Ni<sub>x</sub>Al superalloys**I. D. Bleskov,<sup>1</sup> E. A. Smirnova,<sup>1</sup> Yu. Kh. Vekilov,<sup>1</sup> P. A. Korzhavyi,<sup>2</sup> B. Johansson,<sup>2,3</sup> M. Katsnelson,<sup>4</sup> L. Vitos,<sup>2,3</sup> I. A. Abrikosov,<sup>5</sup> and E. I. Isaev<sup>1,5,a)</sup><sup>1</sup>Department of Theoretical Physics, Moscow State Institute of Steel and Alloys, 4 Leninskii Prospekt, Moscow 119049, Russia<sup>2</sup>Department of Materials Science and Engineering, Royal Institute of Technology (KTH), SE-100 44 Stockholm, Sweden<sup>3</sup>Department of Physics and Materials Science, Division for Materials Theory, Uppsala University, P.O. Box 530, SE-751 21 Uppsala, Sweden<sup>4</sup>Department of Physics, Radboud University of Nijmegen, NL-6525 ED Nijmegen, The Netherlands<sup>5</sup>Department of Physics, Chemistry, and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden

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*Ab initio* total energy calculations based on the exact muffin-tin orbitals method, combined with the coherent potential approximation, have been used to study the thermodynamical and elastic properties of substitutional refractory Ru<sub>1-x</sub>Ni<sub>x</sub>Al alloys. We have found that the elastic constants  $C'$  and  $C_{11}$  exhibit pronounced peculiarities near the concentration of about 40 at. % Ni, which we ascribe to electronic topological transitions. Our suggestion is supported by the Fermi surface calculations in the whole concentration range. Results of our calculations show that one can design Ru–Ni–Al alloys substituting Ru by Ni (up to 40 at. %) with almost invariable elastic constants and reduced density. © 2009 American Institute of Physics. [DOI: 10.1063/1.3120543]

In comparison with  $B2$  NiAl and CoAl, isostructural RuAl has significant toughness at room temperature and maintains considerable strength at higher temperatures.<sup>1,2</sup> Also,  $B2$  RuAl has a high melting temperature (about 2300 K) and high oxidation and corrosion resistance.<sup>2</sup> The presence of  $\langle 100 \rangle$ ,  $\langle 111 \rangle$ , and  $\langle 110 \rangle$  slip vectors provides the significant plasticity for  $B2$  RuAl (Ref. 2) in a sharp contrast to Ir-based superalloys<sup>3</sup> which turned out to be quite brittle. Such outstanding mechanical properties of Ru–Al alloys allow one to consider them as attractive materials for high-temperature applications. Ruthenium, being a platinum group metal, has a high weight density, which obviously limits its applications in jet and gas turbine engines. On the other hand, NiAl and RuAl have the same crystal structure ( $B2$ ) and, according to the phase diagram,<sup>4</sup> they form a continuous (Ru,Ni)Al solid solution. In order to circuit the high-density problem, one should try the opportunity to partially substitute Ni for Ru.<sup>5,6</sup> Furthermore, there is no intermediate brittle phase between the  $B2$  phase and the disordered  $A2$  solid solution, i.e.,  $B2$  phase precipitates directly from the high-temperature  $A2$  solid solution.<sup>7</sup> A good review of the structural, physical, and mechanical properties of Ru–Al alloys can be found in Refs. 8 and 9.

Mechanical properties of materials are intimately related to the elastic constants. Accurate knowledge of the elastic stiffness and of the atomic scale phenomena behind its variation with composition promotes fundamental understanding of a wide diversity of properties that the solid solutions exhibit. In this letter we present results of our studies of the elastic constants and mechanical properties of (Ru,Ni)Al alloys and show that their peculiar concentration dependence is related to the electronic topological transition.

Our total energy calculations to evaluate the equilibrium volume ( $V_0$ ), bulk modulus ( $B_0$ ), and elastic constants have been performed in the framework of density functional

theory using the exact muffin-tin orbitals method to solve the Kohn–Sham equations. Within this approach, the individual muffin-tin potentials are allowed to overlap, which makes the extended muffin-tin orbital (EMTO) method similar in precision to full-potential methods. The combination of EMTO method with the coherent potential approximation<sup>10</sup> makes investigations of substitutionally disordered alloys possible. The exchange-correlation effects in the electron gas have been treated using the generalized gradient approximation (GGA).<sup>11</sup> Elastic constants are evaluated from the total energy  $E_{\text{tot}}$  of crystals to which volume-conserving orthorhombic [ $C'=(C_{11}-C_{12})/2$ ] and monoclinic ( $C_{44}$ ) distortions have been applied.<sup>12</sup> The two cubic elastic constants  $C_{11}$  and  $C_{12}$  are decoupled using the relation  $B_0=(C_{11}+2C_{12})/3$ . Upper-bound ( $G_H$ ) and lower-bound ( $G_S$ ) estimates of the shear modulus  $G$  for polycrystals are found according to the Hashin and Shtrikman formalism.<sup>13</sup> Besides, as it was noticed in Ref. 14, the  $G/B$  ratio can serve as an indicator of brittleness of the material.

In Fig. 1(a), we present the dependence of the lattice constant for (Ru,Ni)Al alloys on the nickel concentration. One can see a good agreement between our calculated and experimental (diamonds) (Ref. 15) lattice parameters. There is a positive deviation from the Vegard's rule for the lattice parameter of quasibinary RuAl–NiAl alloys but the dependence of  $B$  on Ni concentration is almost linear [see Fig. 1(b)]. A similar deviation from the Vegard's rule for lattice parameters was obtained independently by Gargano *et al.*<sup>16</sup> Our calculated bulk moduli for RuAl and NiAl are in agreement with the experimental data<sup>1,17,18</sup> and with the majority of theoretical calculations<sup>19–21</sup> (typical deviation is 10%–15%).

In Fig. 2, the calculated elastic constants  $C_{11}$ ,  $C_{12}$ ,  $C_{44}$ , and  $C'$ , and the shear modulus  $G$  [inset in Fig. 2(a)] for the (Ru,Ni)Al alloys are shown as a function of Ni concentration. Calculated elastic constants for NiAl are in agreement with the experimental<sup>18</sup> data but there are no reported experi-

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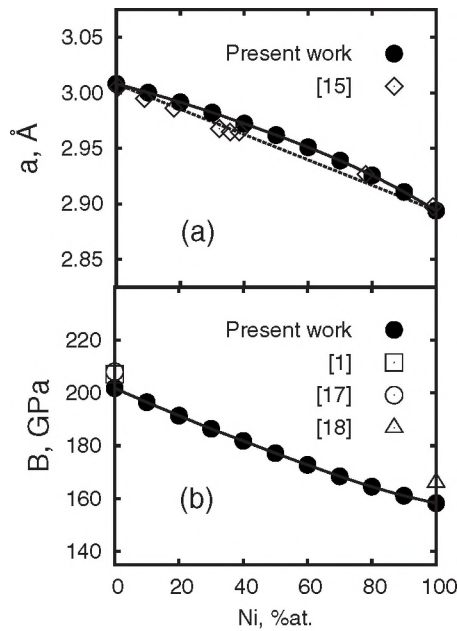


FIG. 1. Lattice constant (a) and bulk modulus (b) of  $\text{Ru}_{100-x}\text{Ni}_x\text{Al}$  superalloys as a function of Ni concentration. Dashed line refers to the Vegard's rule. Experimental lattice parameters are taken from Ref. 15.

mental elastic constants for RuAl. Our calculated elastic constants for both RuAl and NiAl agree well with most of the theoretical results<sup>19–21</sup> (the comparison with calculated and available experimental data is given in supplementary materials,<sup>22</sup> Table I).

In fact, our elastic constants for RuAl are in excellent agreement with recent calculations of Ref. 19 carried out by means of ultrasoft pseudopotentials using a GGA exchange-correlation functional.<sup>11</sup> The difference is larger when our GGA results are compared to results obtained within the

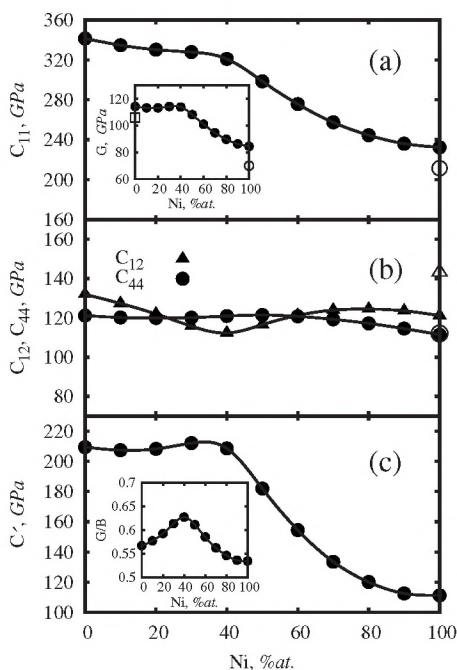


FIG. 2. Elastic constants of  $\text{Ru}_{100-x}\text{Ni}_x\text{Al}$  superalloys as a function of Ni content: (a)  $C_{11}$ , (b)  $C_{12}$  and  $C_{44}$ , and (c)  $C'$ . Shear modulus  $G$  and brittleness parameter  $G/B$  are shown on insets into panels (a) and (c), respectively. Experimental data are taken from Ref. 17 (open square) and Ref. 18 (otherwise, open triangle for  $C_{12}$  and circles).

local-density approximation<sup>21</sup> but still does not exceed 20%. We also note that our calculated  $C_{44}$  for NiAl is lower than that of RuAl in qualitative agreement with the results of FP-LMTO calculations.<sup>21</sup>

The elastic constants  $C_{11}$  and  $C'$ , as well as the shear modulus  $G$ , are found to exhibit quite different dependencies on the Ni concentration in two compositional regions [see Figs. 2(a) and 2(c), and the inset in Fig. 2(a)]. The first region comprises the concentration interval up to 40 at. % of Ni where the  $C'$  and  $G$  can be considered to be constant within the accuracy of our calculations. Around 40 at. % of Ni (a significant drop) occurs in the concentration dependencies of  $C'$  and  $G$ . The elastic constants  $C_{12}$  and  $C_{44}$  are almost constant functions of the composition with a marginal drop of  $C_{12}$  near the composition of 40 at. % and a shallow decrease of  $C_{44}$  for Ni content beyond 60%. As the Cauchy relation  $C_{12}=C_{44}$  is not fulfilled for the most of studied alloys, obviously, the interatomic forces in the alloys are not central-symmetric. For the  $\text{Ru}_{78}\text{Ni}_{22}\text{Al}$  and  $\text{Ru}_{60}\text{Ni}_{40}\text{Al}$  alloys, we found  $C_{12}=C_{44}$  and we suppose this is a subject for further studies. Moreover, we find that the Cauchy pressure  $C_{12}-C_{44}$  is negative for the (Ru,Ni)Al alloys with the Ni concentration in the range 30–60 at. % [see Fig. 2(b)]. According to Ref. 23, a negative Cauchy pressure is characteristic of systems with covalentlike contribution to atomic bonding and we suppose this type of bonding might cause the enhanced hardness of (Ru,Ni)Al alloys observed experimentally in Ref. 24. Of course, there are many other possible sources of enhancement of the alloys' hardness (such as lattice mismatch, presence of dislocations, nonstoichiometry, etc.) but we suggest that interatomic bonding should play the main role in solid solution hardening. Amazingly, the dependence of the brittleness parameter  $G/B$  on the Ni content [inset in Fig. 2(c)] is quite similar to that of the hardness of (Ru,Ni)Al alloys.<sup>24</sup>

We suggest that the unusual behavior of the elastic constants of (Ru,Ni)Al originates from the electronic topological transitions. Indeed, we have plotted the Fermi surfaces for intermetallics RuAl, and NiAl, as well as for  $(\text{Ru}_{100-x}\text{Ni}_x)\text{Al}$  alloys with  $x=20, 40, 60, 80$  at. % Ni, as cross sections by (001) and (110) planes (Fig. 3). More detailed information on the Fermi surface evolution as a function of Ni content is provided as a supplementary material.<sup>22</sup> One can see that the Fermi surface topology changes very abruptly at a composition of about 40 at. % Ni (several parts of the Fermi surface of RuAl located near the  $\Gamma X$  and  $\Gamma M$  lines disappear in the electronic structure of the  $(\text{Ru}_{40}\text{Ni}_{60})\text{Al}$  alloy while a new electron sheet starts to gradually appear). A similar explanation was proposed in Ref. 25 for a similar kind of behavior of  $C'$  in bcc Be.

For B2 RuAl we have also calculated the Grüneisen parameter  $\gamma$  (which describes anharmonicity of a crystal). The calculated value is about 1.69 for RuAl. As compared to NiAl with  $\gamma=1.42$ , RuAl turns out to be more anharmonic, presumably due to less covalent bonding in RuAl. Nevertheless, our estimate of the high-temperature linear expansion coefficient of RuAl is  $\alpha=8.5 \times 10^{-6} \text{ K}^{-1}$  in agreement with experimental results of Tryon *et al.*<sup>26</sup>  $\alpha=8.1 \times 10^{-6} \text{ K}^{-1}$ . This value is lower than the  $\alpha$  for Ni, NiAl, commercial alloy CMSX-3, and Ni(Pt)Al, and is very close to the value of  $\alpha$  for  $\text{Al}_2\text{O}_3$  at a highly desirable operating temperature around 1400 °C.

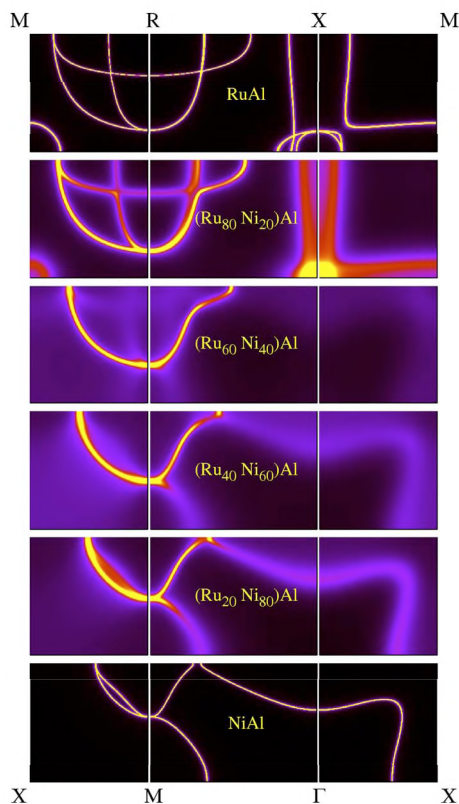


FIG. 3. (Color online) Evolution of the Fermi surface cross sections by the (001) and (110) planes with the Ni concentration for intermetallics RuAl, NiAl and  $(\text{Ru}_{100-x}\text{Ni}_x)\text{Al}$  alloys. Abrupt changes of the Fermi surface topology occur near the concentration of 40 at. % of Ni.

In summary, we have calculated thermodynamic and elastic properties of refractory (Ru,Ni)Al alloys with high melting temperature. The observed peculiarities in elastic constants of the alloys are explained as a result of electronic topological transitions occurring upon the increase of Ni content. We have shown that there is optimal concentration range up to 40 at. % of Ni for alloying of RuAl by Ni where the elastic constants of (Ru,Ni)Al alloys do not change considerably. High elastic constants in combination with reduced density and high melting temperature allow us to suggest that (Ru,Ni)Al alloys are promising refractory materials for gas turbine and jet engine technology.

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