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Calculated Surface-Energy Anomaly in the 3d Metals

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Local-spin-density theory and a Green's-function technique based on the linear muffin-tin orbitals method have been used to calculate the surface energy of the 3d metals. The theory explains the variation of the values derived from measurements of the surface tension of liquid metals including the pronounced anomaly occurring between vanadium and nickel in terms of a decrease in the *d* contribution caused by spin polarization.

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The surface energy of the 4*d* and 5*d* transition metals estimated from the measured surface tension of liquid metals exhibits a parabolic variation with atomic number [1,2]. The maximum value occurs for the element in the middle of the series and corresponds approximately to the case of a half-filled *d* band. In sharp contrast to this, the surface energy in the 3*d* series exhibits a pronounced *minimum* at the central element manganese, and also the values for the other magnetic elements chromium, iron, and cobalt are anomalously low when compared to the 4*d* and 5*d* series. To our knowledge there has so far been no theoretical explanation of these anomalies. In this Letter we shall therefore present calculations which reproduce the essential features of the experimentally observed behavior and support a simple explanation of the anomaly.

The surface energy E_S is defined as the energy required to transform a bulk atom into a surface atom with a corresponding increase in the surface area, or equivalently, as half the energy needed to cut an infinite crystal along one plane into two separated semi-infinite pieces. It was early recognized [1] that the surface energy was approximately proportional to the cohesive energy E_{coh} and that the relationship $E_S \cong 0.2E_{\text{coh}}$ was obeyed at the same level of accuracy by the 3*d* as well as by the 4*d* and 5*d* transition metals. One might therefore assume that the anomaly which occurs in both E_S and E_{coh} at the middle of the 3*d* series has the same physical origin. That this is *not* the case and that the irregular behavior of the 3*d* surface energy is purely a solid-state effect are the main points of the present paper.

The cohesive energy is defined as the energy gained in the transformation of a free atom into a bulk atom. Hence, while the surface energy involves only condensed atoms in different environments, the cohesive energy also invokes the free atomic state. Now, the total energy of a free atom is greatly affected by the spin-pairing energy of the *d* electrons [3] which attains its maximum for a half-filled *d* shell [$d^5(^6S_{5/2})$] and as a result the cohesive energy of the 3*d* metals exhibits a cusplike behavior close to the manganese [4,5]. The atomic spin-pairing effect is also present in the 4*d* and 5*d* elements, but it is less pronounced for these atoms and their experimental cohesive energies exhibit essentially a parabolic behavior. The ir-

regular behavior of the cohesive energy of the 3*d* metals is therefore essentially an atomic effect [5].

It would appear that there is *no a priori* reason why the irregularities shown by the surface and cohesive energies of the 3*d* metals should scale in such a manner as to satisfy the relation $E_S \cong 0.2E_{\text{coh}}$. The experimentally observed approximate proportionality must therefore to a large extent be fortuitous.

To substantiate the claims made above we have performed self-consistent local-spin-density calculations of the surface energies of the 3*d* metals, by means of a recently developed Green's-function technique [6] based on the linear muffin-tin orbitals method [7,8] within the tight-binding [9,10], frozen core, and atomic-sphere approximations together with the local-spin-density approximation in the Vosko-Wilk-Nusair parametrization [11]. The technique has been applied in the calculation of work functions and surface energies of forty elemental metals [12], and the non-spin-polarized results were found to be in excellent agreement with the surface energies compiled by de Boer *et al.* [2]. In addition, with a few exceptions the results agreed to within 10% with a recent full-potential, all-electron, slab-supercell calculation of the surface energies of the 4*d* transition series [13].

The surface energies compiled by de Boer *et al.* [2] are derived from the measured surface tensions of liquid metals. They do not correspond to any particular surface facet and may be regarded as estimates of the surface energies of the most densely packed-solid surfaces. To establish the background from which the magnetic effects may be judged we have therefore calculated the surface energies without spin polarization of the fcc 111 facet of the 3*d* metals which we take to be the series of eleven elements from K to Cu. The results are shown in Fig. 1 and they exhibit the expected parabolic variation with valence which our experience with the 4*d* and 5*d* metals indicates is an accurate estimate of the surface energies of the non-magnetic metals.

In the case of the magnetic 3*d* elements we have chosen to present results for the bcc 100, bcc 100, bcc 110, hcp 001, and fcc 111 surfaces of Cr, Mn, Fe, Co, and Ni, respectively. These surfaces have been selected because the surface energies of the magnetic metals are

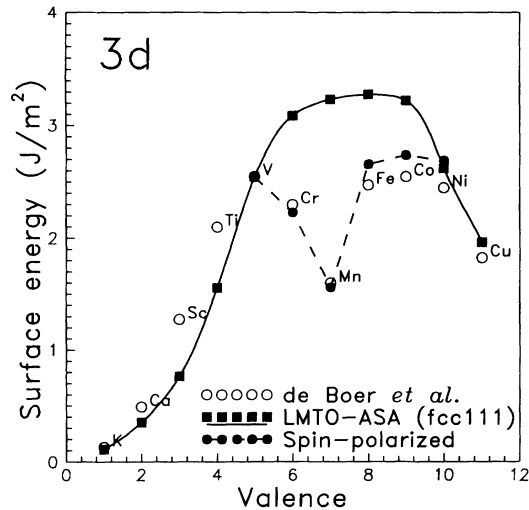


FIG. 1. Comparison between the calculated and the experimentally derived surface energies of the 3d metals. The solid line which is a guide to the eye is drawn through the results of the paramagnetic calculations of the energy of fcc 111 surfaces. The solid circles correspond to spin-polarized calculations of the energy of the bcc 100, bcc 100, bcc 110, hcp 001, and fcc 111 surfaces of Cr, Mn, Fe, Co, and Ni, respectively. The open circles represent the surface energies derived by de Boer *et al.* [2] from the measured surface tensions of liquid metals.

found to be more sensitive to the choice of facet than those of the nonmagnetic metals, and hence would not be well represented by fcc 111 calculations alone. In the underlying bulk calculations the spins were assumed to be aligned ferromagnetically except for Cr which was treated as a commensurate antiferromagnet. A full report of the calculations including surface energies and work functions for other facets will be given elsewhere [14].

The results of the spin-polarized surface calculations for the magnetic 3d metals Cr, Mn, Fe, Co, and Ni are shown in Fig. 1. It is seen that the complete theory, spin polarized and nonpolarized, gives a qualitatively correct description of the variation of the experimentally derived surface energy through the whole 3d series from K to Cu. It is furthermore seen that the onset of magnetism leads to a reduction of up to 50% in the surface energy, and that for the series from V to Cu the theory is in complete quantitative agreement with experiment. Based on this evidence, we conclude that the anomaly in the surface energy of the 3d metals does not have the atomic origin which leads to the anomaly in the cohesive energy but is caused purely by a solid-state magnetic effect.

A simple picture of the *d*-electron contribution to the surface energy of the transition metals was suggested by Friedel [15]. Assuming a constant state density with bandwidth W for bulk *d* electrons, and a similar state density for the surface but with a reduced width ($W - \delta W$), the *d*-electron contribution to the surface energy for a paramagnetic metal becomes

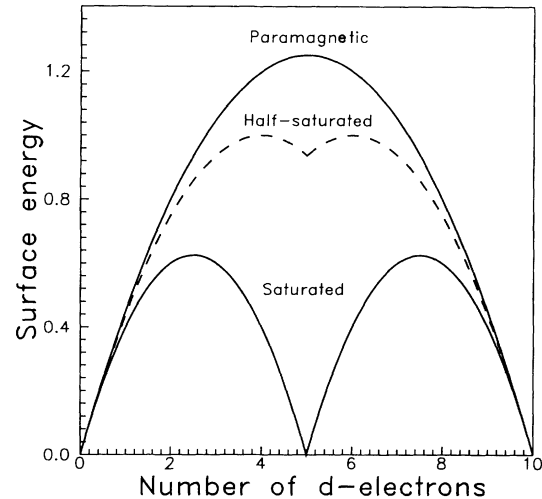


FIG. 2. Models of the surface energy of the 3d transition metals based on a constant *d* state density. The three curves correspond to the paramagnetic, the half-saturated, and the saturated cases described in the text.

$$E_S = \frac{1}{2} n \left(1 - \frac{1}{10} n\right) \delta W, \quad (1)$$

where n is the number of *d* electrons. It is this parabolic expression which immediately explains the variation of the experimentally derived surface energy of the 4*d* and 5*d* metals as well as the variation of the calculated paramagnetic fcc 111 surface energy of the 3*d* metals shown in Fig. 1.

The effect of magnetism may be explained if we assume that the metal ground state is a saturated itinerant magnet. In a purely *d*-electron description this means that for $n < 5$ the occupied part of the spin-down band is completely separated from the empty spin-up band, and that for $n > 5$ the unoccupied part of the spin-up band is separated from the fully occupied spin-down band. In this situation the Friedel model of the surface energy only involves a change in the energy of the partly occupied spin band because the other band is either empty or full. For $n < 5$ the surface energy of the saturated magnet becomes

$$E_S^{\text{sat}} = \frac{1}{2} n \left(1 - \frac{1}{5} n\right) \delta W \quad (2)$$

and for $n > 5$ the same expression is valid if n is replaced by $n - 5$.

The Friedel model for the nonmagnetic and the saturated magnetic cases is illustrated in Fig. 2 by the top parabola and the lowest double parabola, respectively. The spin-polarized bulk calculations reveal that Ni and Co are close to being saturated magnets, and this observation is confirmed by the fact that their surface spin moments essentially retain the bulk values [16-19]. As a consequence the *d*-electron contribution to the surface energies follows the double parabola (2) rather than (1). Hence, the difference between the lowest and highest

curves in Fig. 2 at $n \approx 8$ immediately explains the observed anomaly in Co. In the case of Ni ($n \approx 9$) the difference between the two models and hence the magnetic effect on the surface energy is small. This is confirmed by the complete calculation for the fcc 111 surface presented in Fig. 1 and by calculations for other fcc surfaces [14].

For a nonsaturated magnet with magnetization m the situation is more complex. Assuming, however, that the surface magnetic moment is the same as in the bulk, we obtain the surface energy as

$$E_S^m = \frac{1}{2} \left[n - \frac{n^2 + m^2}{10} \right] \delta W. \quad (3)$$

For the "half-saturated" case, i.e., $m = n/2$ for $n < 5$ or $m = (10 - n)/2$ for $n > 5$, one obtains the dashed curve in Fig. 2. Now, the surface magnetization will in general be enhanced relative to the bulk value and the energy of the surface atoms may be lowered even further resulting in surface energies below the dashed line. On the other hand, the lowest double parabola in Fig. 2 corresponding to the saturated magnetic case is expected to be the lower limit of the surface energy for an itinerant ferromagnet. The reason is that the surface magnetic moment will always be closer to the saturated value than the bulk moment. Hence, the true result must lie somewhere between the two double parabolas in Fig. 2.

It is now easy to understand the main results of the complete calculations for the magnetic $3d$ metals presented above. Thus, by the mere introduction of a uniform magnetization into the system, the surface layer included, the surface energy may be reduced over its nonmagnetic value. In addition, by increasing its magnetization over the bulk value, the surface layer may gain further energy and thereby enhance the surface energy anomalies. The second alternative is realized in Cr, Mn, and Fe while the first is found in Co and Ni.

In this work we have reproduced by direct calculations the experimentally derived surface-energy data for the $3d$ transition metals. Not unexpectedly, the anomalous behavior of the elements Cr-Co is shown to originate from their magnetic properties. The possibility of magnetism, realized in the bulk, gives the system access to an extra degree of freedom which in the surface region can be utilized to further minimize the energy difference between a bulk and a surface atom. As a result, the surface energies may be strongly affected and appear anomalously low when compared to related paramagnetic systems. We have introduced a simple model, which is confirmed by our complete calculations and which offers a semi-quantitative explanation of the irregular surface energy of the $3d$ metals. Finally, we conclude that the anomalies in the surface and cohesive energies of the $3d$ metals are

of different origin, and that the experimentally observed approximate proportionality between these two quantities must to a large extent be fortuitous.

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