width calculations. Discussions with J. Keller, K. Baberschke, P. Schlottmann, K. D. Schotte, and E. Tsang have been helpful. We would like to acknowledge the hospitality and support of the Bereich Kern- und Strahlenphysik, Hahn-Meitner-Institut, Berlin. This work was strongly supported by the Deutsche Forschungsgemeinschaft (Sondersforschungsbereich 161).

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Spin Fluctuations at the Surface of Vanadium

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The finite-temperature magnetic properties of the (100) surface of vanadium have been studied by means of spin-fluctuation theory. It is found that the surface contribution to the magnetic susceptibility exhibits strong temperature dependence having its origin in the appearance of large localized moments at the surface. These moments show antiferromagnetic interactions. These findings are in agreement with recent experiments.

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The magnetic properties of transition-metal surfaces have attracted a great deal of interest both from the theoretical and experimental points of view. It is generally believed that the modification of the electronic spectrum near the surface produces significant changes in the surface magnetic properties of itinerant-electron systems.[1-3]

Recently, magnetic susceptibility measurements have been made on small particles of vanadium.[4] The magnetic susceptibility of these particles was found to consist of two parts, one of the Pauli type as usually observed in the bulk metal and the other following an almost perfect Curie law typical of local moment systems. The temperature-dependent part of the susceptibility varies with the size of the particles as the inverse of the average diameter, suggesting that the magnetic moments responsible for it are localized in the surface region of the particle. If that point of view is taken, the size of the local moments can be estimated as $\sim 2\mu_B$ per surface atom. Extrapolation of the high-temperature results show that the local moments interact antiferromagnetically with an apparent Néel temperature of 2 °K.[4]

Motivated by these experimental findings, we have investigated the surface magnetic properties of vanadium. We start with a tight-binding Hamiltonian H_0 including the five d subbands and nearest- and next-nearest-neighbors interactions.

The parameters in the Hamiltonian are chosen to fit the bulk d bands of vanadium calculated by Yasui *et al.*[6] The surface diagonal elements have been scaled in the usual way in order to satisfy charge neutrality.[7] In Fig. 1 we show the bulk and the (100) surface density of states calculated by the continuous-fraction–expansion method.[8] The point to note is that in the surface density of states a large peak is present near the Fermi level associated with a surface resonance.[9] This particular feature is known to be characteristic of the (100) surfaces of elements with the bcc structure and is rather insensitive to the details of the surface potential.[10] The peak is less pronounced on other faces. We therefore expect the (100) face to show the strongest enhancement effects. Below, we make a detailed study of its magnetic properties.

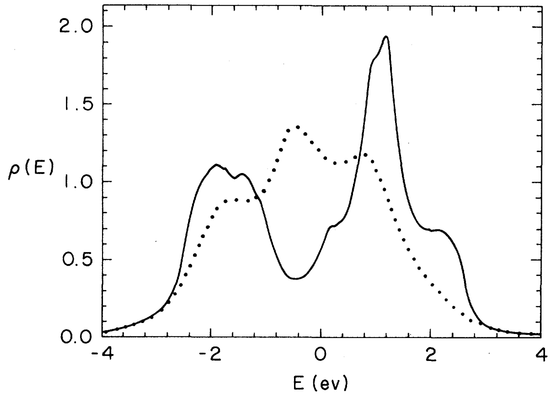

FIG. 1. Densities of states for vanadium (100) surface. Solid line; bulk density of states; dotted line, surface density of states.

We introduce the local exchange interaction[11] into the Hamiltonian:

$$H = H_0 - \tfrac{1}{4}\textstyle\sum_i U_i \vec{S}_i \cdot \vec{S}_i, \tag{1}$$

where $\vec{S}_i$ is the total spin at site i and U_i is the exchange constant which can be different in the surface region. By a generalization[12] of the standard continuous-fraction–expansion method[8] to the evaluation of off-diagonal elements of the Green's functions we have calculated the magnetic susceptibility in the Hartree-Fock approximation and studied the stability of the paramagnetic surface. For an exchange interaction independent of position a bulk instability first appears at $U = 1/N(E_F) \sim 1$ eV. It has been estimated that for bulk vanadium $U = 0.8$ eV[13] and hence this metal remains paramagnetic. However, an instability localized near the surface occurs at $U \sim 0.54$ eV.[14] The magnetization profile at the onset is extremely localized in the surface region, with 98% of the magnetic moment residing on the first layer. A larger exchange at the surface layer would result in an even stronger enhancement but, in the absence of reliable estimates of the variation of U, we shall simply take it to be uniform at its bulk value for the remainder of the discussion.

Below the onset of the Hartree-Fock instability, as in bulk vanadium, the susceptibility in the high-temperature paramagnetic phase has only a very weak temperature dependence, characteristic of enhanced Pauli paramagnetism and Hartree-Fock theory gives a satisfactory description of the magnetic properties. However, the surface layer of (100) vanadium is far above the onset of the local instability. Under such conditions several authors[11] have shown that fluctuations around localized moments are important and lead to a drastically different temperature dependence of the susceptibility.

To study the spin-fluctuation effects, we employ the Hubbard-Stratonovich transformation[15] to transform the problem of interacting electrons into one of noninteracting electrons moving in a randomly varying magnetic field with a Gaussian distribution. The partition function in the grand-canonical ensemble is given in terms of a functional integral as[16]

$$Z \equiv e^{-\beta\Omega} = \int \textstyle\prod_i D\vec{\xi}_i(\tau) \exp\left[-(\pi/\beta)\int_0^\beta d\tau \sum_i \vec{\xi}_i^{\,2}(\tau)\right] Z_0[\lambda\vec{\xi}_i(\tau)], \tag{2}$$

where $\lambda = (\pi U k T)^{1/2}$ and Z_0 stands for the partition function of noninteracting electrons in the magnetic field $\vec{h}_i(\tau) = \lambda\vec{\xi}_i(\tau)$. It has been shown[16] that expansion of the integrand in (2) up to second order in the fields reproduces the Hartree-Fock result which is a good description for bulk vanadium. Accordingly, we have kept terms of all orders in the fields localized at the surface, but expanded up to the second order in the fields localized on the rest of the layers. We found that the susceptibility can be divided into bulk and surface components.[17] The bulk part is the usual exchange-enhanced Pauli susceptibility of vanadium. Within the static approximation[18] the surface contribution to the susceptibility is given by

$$\chi_s = (2\mu_B^{\,2}/U)\textstyle\sum_{ij}\left(\tfrac{2}{3}\pi\langle \vec{\xi}_i \circ \vec{\xi}_j\rangle - \delta_{ij}\right), \tag{3}$$

where the sum is restricted to the surface sites. The average in (3) is over a distribution of fields given by the probability distribution function $P[\vec{\xi}] \sim \exp(-F[\vec{\xi}])$, with

$$F[\vec{\xi}] = \pi \sum_i \xi_i^2 + \beta \int_{-\infty}^{\infty} (dE/\pi) f(E) \operatorname{Im} \operatorname{Tr} \ln[1 - \underline{V}_s \underline{G}_s^0(E)]. \tag{4}$$

The potential has matrix elements $V_{ii',mm'}^{ss'} = -\lambda \vec{\xi}_i \sigma_{ss} \delta_{mm'} \delta_{ii'}$, where $\vec{\sigma}$ are the Pauli matrices and m, m' the subband indices. $\underline{G}_s^0(E) = [E - \underline{H}_s^0 - \underline{\Sigma}_s(E)]^{-1}$ where $\underline{H}_s^0$ is that part of $\underline{\boldsymbol{H}}_0$ that acts only on the surface and $\underline{\Sigma}_s(E)$ is the self-energy arising from hopping into and from the bulk.

Restricting the functional integral to those configurations in which the surface fields fluctuate randomly in direction but not in size, we find an upper bound for the free energy,

$$\Omega \leqslant N_s \pi k T \bar{\xi}^2 + \langle \Omega_0 [\lambda \bar{\xi} \hat{n}_i] \rangle_{\hat{n}_i}, \tag{5}$$

where we have written $\vec{\xi}_i = \bar{\xi} \hat{n}_i$ and the average in (7) is over the random orientations of the unit vectors $\{\hat{n}_i\}$. The magnitude of the fluctuating moments, $\bar{\xi}$, is obtained by minimizing the right-hand side of (5). The determination of $\bar{\xi}$ requires the evaluation of the spin-fluctuation contribution to the electron self-energy, $\Sigma^{sf}(E)$. This is done within the spirit of the coherent-potential approximation (CPA).[19] In terms of the self-energy we obtain

$$2\Delta = -U \int_{-\infty}^{\infty} (dE/\pi) f(E) \operatorname{Im} \sum_m \sum_{s=\pm 1} s \frac{\bar{G}_m(E)}{1 + [s\Delta + \Sigma_m^{sf}(E)] \bar{G}_m(E)}, \tag{6}$$

where $\Delta = \bar{\xi} (\pi U k T)^{1/2}$ and $\bar{G}_m(E)$ is the local averaged Green's function for subband m. This has to be combined with the CPA equations[20] for $\Sigma_m^{sf}(E)$ and $\bar{G}_m(E)$. The numerical solution of these equations is complicated by the presence of five bands. However, we found that, with no loss of accuracy, we can assign the same self-energy for all subbands.

The condition for the appearence of a nontrivial solution to Eq. (6) is the local Stoner criterion $U\chi_{\mathrm{loc}}^0 > 1$ where $2\chi_{\mathrm{loc}}^0$ is the local spin susceptibility. We find that this occurs for $U \gtrsim 0.53$ eV. For larger values of U a solution with nonvanishing Δ appears, signifying the onset of local moments. In Fig. 2 we plot the results for $P[\bar{\xi}]$ as a function of the size of the effective moment for different values of U at room temperature. Our treatment includes the orientational but not the size fluctuations of the local moments. This amounts to picking up the contribution from the maxima in $P[\bar{\xi}]$ only. From Fig. 2, we can see that at a value of $U = 0.8$ eV appropriate for vanadium, the half width of $P(\bar{\xi}) - \Delta\bar{\xi}/\bar{\xi} \sim 0.3$ is indeed quite small, thus justifying our neglect of size variations.

The resulting susceptibility determined from (3) and (6) is shown in Fig. 3 as a function of the temperature. It is very accurately linear with a slope corresponding to $2.4\mu_{\mathrm{B}}$ per surface atom.

The single-site theory described so far neglects the correlations between moments localized around different sites. A crude estimate of these effects can be obtained within effective-medium

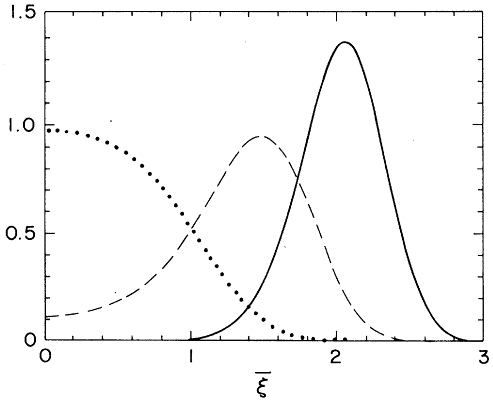

FIG. 2. Probability distribution of the size of the fluctuating moment for different values of U: 0.5 eV (dotted line), 0.6 eV (broken line), and 0.8 eV (solid line). The temperature has been set at 300°K.

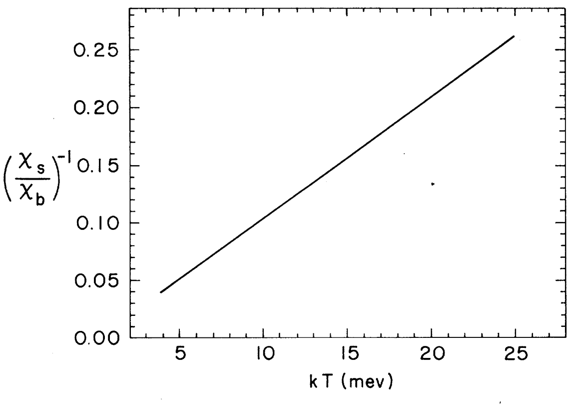

FIG. 3. Inverse surface susceptibility per surface atom relative to its bulk counterpart as a function of temperature.

theory by placing two moments in the effective medium and using perturbation theory to calculate their indirect interaction. The result is the well-known Ruderman-Kittel-Kasuya-Yosida formula,[21] but now with modified propagators that include the effects of spin-fluctuation scattering. We obtain for the interaction between moments at nearest-neighbor sites i and j, $\Delta E_{ij} \sim -\frac{1}{2} J \vec{\xi}_i \cdot \vec{\xi}_j$. The resulting value of J turns out to be negative corresponding to antiferromagnetic coupling between moments. Taking the estimate $kT_N \sim z|J|$, where z is the number of nearest neighbors, we arrive at an ordering temperature $T_N \sim 3.8$ °K.

In summary, we have shown that the magnetic properties at the (100) surface of vanadium are drastically different from those in the bulk, the main difference being the appearance of large localized magnetic moments. The surface contribution is found to obey a nearly perfect Curie law and the surface moments have antiferromagnetic interactions. These results are in qualitative agreement with the experimental findings of Ref. 4. Moreover, the theoretical values for the magnetic moment and Néel temperature are close to the experimental values. Detailed quantitative comparison, however, has to await the type of experiments[22] performed on single-crystalline surfaces.

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Open Orbits in Potassium

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Structure in the induced torque rotation pattern of potassium, observed for magnetic fields above 5 T and at a sample temperature of 1.4 K, gives evidence of open orbits in potassium. The presence of open orbits is expected from the charge-density–wave model of potassium but the directions of induced-torque peaks are not explained satisfactorily by the model.

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Research on potassium has been of interest because of the conflicting evidence that the electronic ground state of potassium is a charge-density-wave (CDW) state as proposed by Overhauser.[1] In this state, the electronic charge is modulated with a wave vector $\vec{Q}$ whose magnitude is deter-