data on the $c(2\times 2)$ oxygen layer on Ni(100) should be reexamined, to see if improved agreement between theory and experiment can be achieved by placing the oxygen layer quite close to the surface. It is our understanding that for the $p(2\times 2)$, the fit between theory and experiment is excellent with the layer 0.9 Å above the surface, but the fit is less satisfactory for the higher-density $c(2\times 2)$ structure.

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Level-Crossing Transition in the Cluster Compounds Nb_6I_{11} and HNb_6I_{11}

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The cluster compounds Nb_6I_{11} and HNb_6I_{11} exhibit a coupled structural and electronic phase transition. The structural deformation is accompanied by a *crossing* of electronic levels which leads to a reduction of the *spin* degeneracy. We expect such level-crossing transitions to occur in other compounds containing transition-metal clusters.

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There exists a large variety of ordered compounds where the building blocks are metal clusters rather than individual atoms.[1] With the exception of the so-called Chevrel phases, whose extraordinary superconducting properties have recently created wide interest,[2] such cluster compounds are usually considered too complicated for physical investigation. It is our belief that the physical properties of cluster compounds are highly varied, often interesting, *and* amenable to theoretical understanding. This we substantiate by considering the cluster compounds Nb_6I_{11} and HNb_6I_{11} which are built from the same cluster as the Chevrel phases but have cluster separations so large that the *d* electrons do not conduct but are localized onto the individual clusters. As a consequence each cluster may carry a magnetic moment and we have found that Nb_6I_{11} and HNb_6I_{11} exhibit a coupled magnetic and structural phase transition which is not of the usual Jahn-Teller type.[3] At the transition there is a reduction of *spin* degeneracy due to a *crossing* of electronic levels. In this Letter we present experimental and theoretical evidence for the existence of this crossing.

We first describe the structure of the two compounds.[4-6] The unit, Nb_6I_8, forms a distorted cube with I atoms at the corners and Nb atoms at the face centers. The Nb atoms thus form a distorted octahedron. There are six additional I atoms located approximately on the perpendiculars of the cube faces. Each of these additional I atoms are shared between two neighboring Nb_6I_8 clusters and hence provide the intercluster bond-

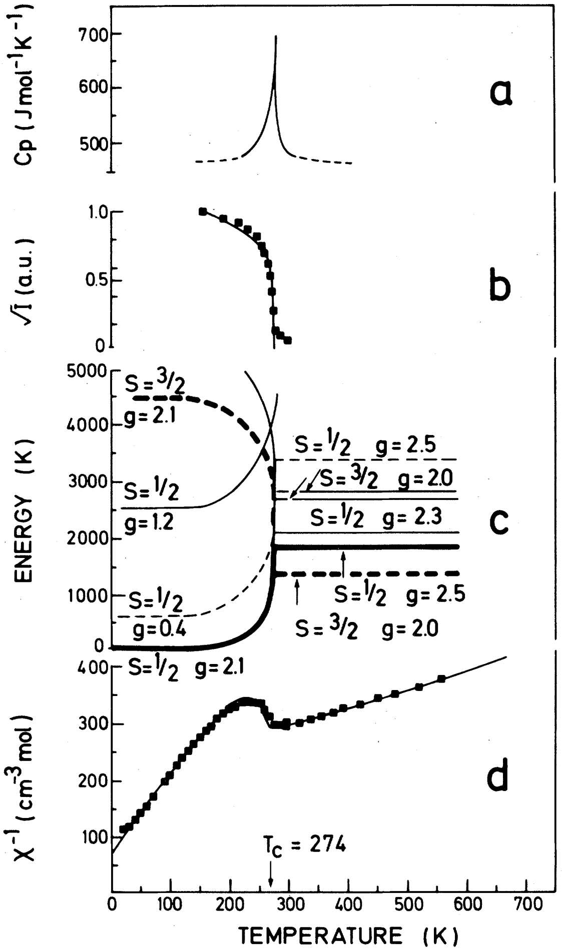

FIG. 1. The (a) heat capacity, (b) square root of the x-ray reflection intensity, (c) calculated energy levels, and (d) inverse magnetic susceptibility vs temperature for Nb_6I_{11}.

ing. The formula unit Nb_6I_{11} therefore corresponds to $[Nb_6I_8]I_{6/2}$. The structure of HNb_6I_{11} is the same, with the exception that the hydrogen atoms, as shown by neutron scattering,[5] are located inside the Nb_6 octahedra. We will first discuss the properties of Nb_6I_{11}. Those of HNb_6I_{11} may then be easily understood.

The first indication of a phase transition in Nb_6I_{11} came from preliminary magnetic susceptibility measurements[4] and x-ray powder investigations. Conclusive evidence was provided by specific-heat measurements,[7] the results of which are shown in Fig. 1(a). At 274 K $\equiv T_c$ there is a large peak with a shape typical for a second- or higher-order transition.

A single-crystal x-ray study[6] established that the deformation essentially involves a twist of 7° between the two opposite triangular faces of the Nb_6 octahedron. This twist removes the only symmetry element, the center of inversion. Because of the change of the space group, new x-ray reflections appear and the square roots of their intensities, $\sqrt{I}$, corrected for the effect of thermal vibrations, are proportional to the degree of deformation from the higher symmetry. The temperature dependence of the average of $\sqrt{I}$ is shown in Fig. 1(b) and we see that there is a rapid change at $T_c = 274$ K and saturation below $T_s = 156$ K. The solid line in the figure corresponds to the fit: $\sqrt{I} = [(T_c - T)/(T_c - T_s)]^b$, for $T < T_c$ and with $b = 0.2$. This expression will be used in the theoretical two-level model described below.

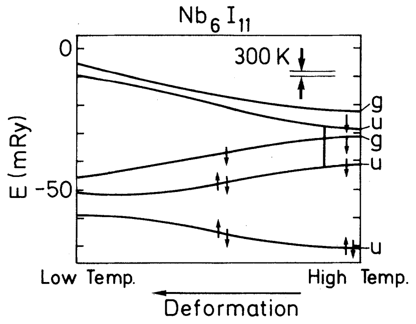

FIG. 2. The energy of the t_{2u} and e_g one-electron levels as a function of distortion for Nb_6I_{11}. The distortion is proportional to $\sqrt{I}$.

The x-ray investigations together with the original magnetic susceptibility measurements[4] indicated that the electronic structure might depend sensitively on the distortion, and a spin-unrestricted molecular-orbital calculation[8] was performed for an isolated $[Nb_6I_8]I_6$ cluster. The highest occupied and the lowest unoccupied one-electron levels are formed from the five nearly degenerate $e_g(x^2-y^2)$ and $t_{2u}(x^2-y^2)$ molecular orbitals of the perfect octahedron.[9] The separation between these one-electron levels is of order 1000 K in the high-temperature phase but increases to about 5000 K in the more distorted low-temperature phase where the mixing between even and odd one-electron states is allowed. The separation thus increases beyond the spin-flip energy, which is 2000 K for a flip from one to three unpaired spins per cluster and, as a consequence, level crossing occurs. This is illustrated in Fig. 2. The resulting many-electron level scheme is presented in Fig. 1(c). The high-temperature ground state has $S = \frac{3}{2}$ and the low-temperature ground state has $S = \frac{1}{2}$. These two levels cross near T_c and hence the spin degeneracy is reduced from 4 to 2 as the temperature is decreased below T_c. The corresponding decrease of entropy contributes to the peak of the specific heat. The g factors (given in the figure) and the Van Vleck contributions to the susceptibility ($\chi_{\mathrm{VV}H}=8.0$ and $\chi_{\mathrm{VV}L}=6.4\times10^{-4}$ cm^3 mol^{-1}) were calculated by including the spin-orbit coupling and Zeeman terms in the Hamiltonian. The accuracy of the energy levels is presumably better than 500 K. However, the g factors are uncertain by about 15%. Ratios between g factors of different levels are more accurate.

New magnetic-susceptibility data is presented as the dots in Fig. 1(d). The inverse susceptibility shows two distinct straight-line Curie-Weiss regions connected by a bump. The two regions are associated with the two different ground states. *Inter*cluster exchange interactions must, however, be included if the measured temperature dependence is to be reproduced in detail. We propose a simple two-level model which keeps only the most essential features of the system: The two levels have, respectively, $S=\frac{3}{2}$ and $S=\frac{1}{2}$ and they are separated by a temperature-dependent gap, $\Delta(T)$, which takes the constant values Δ_H above T_c and $\Delta_L(<0)$ below T_s. In the transition region, $\Delta(T)=\Delta_L\sqrt{I}+\Delta_H(1-\sqrt{I})$, where the temperature dependence of $\sqrt{I}$ is the one given previously. For the Van Vleck terms the theoretical values given above were used.

With this model[10] we obtained, in mean-field theory, the theoretical curve given by the solid line in Fig. 1(d) which is seen to match the measured susceptibility quite well. Although several parameters (g factors, intercluster exchange constants, and gaps) enter the calculation, the values used are relatively well determined because the g factors are given by the slopes of the Curie-Weiss lines while the exchange constants are given by the intercepts. Moreover, the values ($g_{1/2}=2.45\pm0.05$, $g_{3/2}=2.3\pm0.1$, $J_{1/2,1/2}=160\pm20$ K, $J_{1/2,3/2}=150\pm20$ K, $J_{3/2,3/2}=530\pm20$ K, $\Delta_L=-1400\pm100$ K, and $\Delta_H=1000\pm200$ K, where the error indicates the range of allowed values of a parameter when the rest are fixed) of the single-cluster parameters are in reasonable agreement with those obtained from the molecular-orbital calculation, considering the level of accuracy of the latter and the oversimplification of the two-level model. Finally, it should be noted that common models, such as the *rigid* two-level model, cannot explain the behavior of the measured susceptibility.

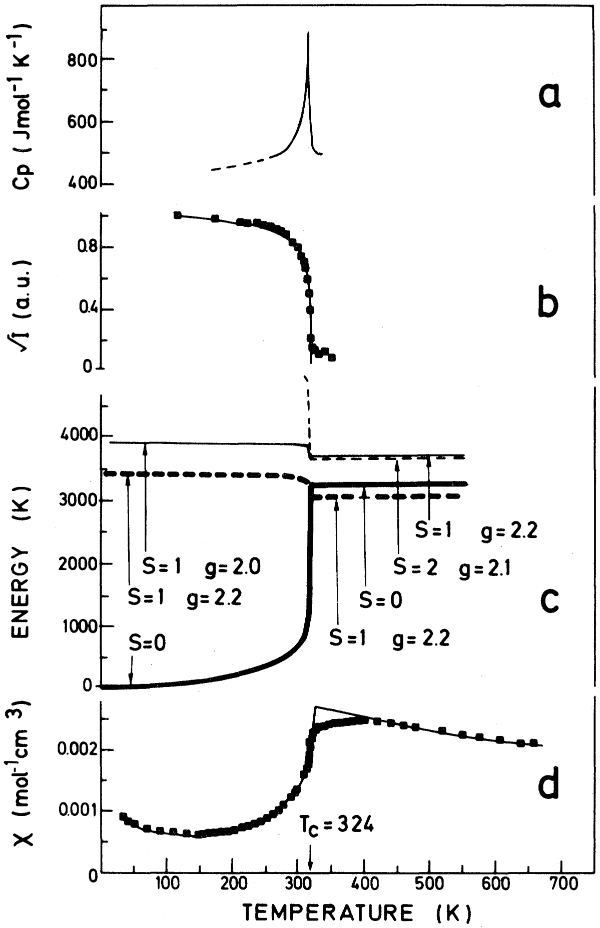

FIG. 3. The (a) heat capacity, (b) square root of the x-ray reflection intensity, (c) calculated energy levels, and (d) magnetic susceptibility vs temperature for HNb_6I_{11}.

The level-crossing mechanism also operates in HNb_6I_{11} although the results for some measurements, particularly the magnetic susceptibility, are rather different. The heat-capacity measurement shown in Fig. 3(a) gave $T_c=324$ K. According to the x-ray measurements HNb_6I_{11} exhibits a phase transition of the same crystallographic type as Nb_6I_{11} and the intensities of the new reflections shown in Fig. 3(b) have a temperature dependence corresponding to $T_s=120$ K and $b=0.1$.

The five e_g and t_{2u} one-electron levels calculated for HNb_6I_{11} are almost identical to those calculated for Nb_6I_{11}. The additional level induced by the hydrogen occurs above the Fermi level so that twenty rather than nineteen electrons occupy the Nb d-band levels. As a consequence there are, respectively, two ($S=1$) and no

($S=0$) unpaired spins in the high- and low-temperature ground states. The corresponding reduction of spin degeneracy from 3 to 1 is larger than in Nb_6I_{11} and this difference between the two materials is reflected in the sizes of their specific-heat peaks. All the low-lying many-electron levels are shown in Fig. 3(c). Moreover, $\chi_{VV_H}=5.6$ and $\chi_{VV_L}=5.0\times10^{-4}$ cm^3 mol^{-1}.

In Fig. 3(d) the dots indicate the measured susceptibility and the full line the results of the two-level model. Except for the rounding off near 324 K the agreement between theory and experiment is satisfactory. In particular the Van Vleck term, which dominates the susceptibility in the low-temperature region, is seen to be given well by the molecular-orbital calculation. The parameters used in the two-level model were $g_1=3.8\pm0.3$, $J_{11}=1900\pm100$ K, $\Delta_L=-1350\pm200$ K, and $\Delta_H=500\pm200$ K, where the large values for g and J are a result of neglecting the strongly magnetic $S=2$ state in the two-level model. Inclusion of this state would reduce the g factor to approximately 2.3 and would also reduce J.

The x-ray and magnetic measurements for Nb_6I_{11} and HNb_6I_{11} are well explained by the idea of a coupled structural and electronical phase transition[11] where degeneracy is reduced through the crossing of electronic levels.[12]

This type of transition is made possible by the competing effects of flipping a spin within a cluster and of changing the molecular-orbital levels through deformation of the cluster. Compared to the single-ion situation these effects are analogous to the Hund's-rule and crystal-field effects. For a transition-metal cluster spin-flip energies are comparatively small because, *per atom*, there is only a fraction of a spin. Moreover, there are more molecular-orbital levels for a cluster than for a single ion in a crystal field. Therefore we expect that level-crossing transitions are less rare in transition-metal cluster compounds than in single-ion systems.

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