the heavier elements of relativistic effects which we have ignored and which are known to be significant in these metals.[1] Furthermore, one would expect band-structure effects to be relatively more important in the case of Cs. Finally, as a general observation we note that the calculated Knight shift is very nearly a linear function of the nuclear charge Z. To the extent that the experimental values follow this trend it appears that the Knight shift in simple metals is essentially a local property characteristic of a single ion screened by an electron gas.

In conclusion, we have demonstrated an effective method of calculating Knight shifts in simple metals using a linear-response formulation of density functional theory. It should be emphasized that the main virtue of this approach is that, by treating core and valence states in the same way, one can avoid the ambiguous choice of parameters that tends to plague the pseudopotential approach. It also indicates the rather delicate interplay of various important effects, such as core polarization and achieving self-consistency for both the charge and spin densities.

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Rare-Earth Magnetic Isolation and Superconductivity of the Chevrel-Phase Compounds

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Results of *ab initio* self-consistent linear muffin-tin orbital energy-band studies for $EuMo_6S_8$, $GdMo_6S_8$, $SnMo_6S_8$, and $SnMo_6Se_8$ including all electrons in all 15 atoms/unit cell are reported. The large charge transfer from both the Eu, Gd, and Sn sites and from the Mo sites to the chalcogens is shown to be the driving mechanism with which to explain their unusual magnetic and superconducting properties.

The unusual magnetic and superconducting properties of the ternary molydenum chalcogenides have attracted a great amount of experimental and theoretical interest.[1] These Chevrel-phase compounds, with general formula $M_xMo_6S_8$ (or Se_8) and x between 1 and 4, occur for a large number of metals M including the rare earths. The numerous experimental observations performed on these materials have far outstripped theoretical understanding and have generated many unsolved questions. One area of particular interest concerns the unusual behavior of rare-earth (RE) magnetic moments on the superconductivity of these compounds[1]: Contrary to observations on all other materials and the theory of Abrikosov and Gor'kov,[2] the superconducting T_c is only weakly depressed (if at all) by the magnetic moment through the pair-breaking effect of the exchange interaction. All the $M_xMo_6S_8$ (or $M_xMo_6Se_8$), with the exception of Ce and Eu, are superconducting—some with relatively high T_c's.[3,4] The results for the system $Sn_{1.2(1-x)}Eu_x$-$Mo_{6.25}S_8$ are particularly illustrative. As x increases to about 0.5, T_c is hardly changed[5] with the depression occurring abruptly only at very high concentrations. The strength of the depairing interaction studied by ^{151}Eu Mössbauer experiments[6-8] shows (1) a divalent Eu isomer shift (and hence a large magnetic moment of $7\mu_B$) typical for Eu^{2+} in an ionic compound without conduction-electron contributions and (2) a spin-lattice relaxation rate which yields the product of the exchange coupling and density of states $|\mathcal{T} N(E_F)|$ to be roughly one order of magnitude smaller[6,8] than that measured in binary superconductors like Eu in $LaAl_2$.

From the theoretical side, few, even simplified non-self-consistent, energy band studies have been performed mostly because the complexity of the Chevrel phase's crystal structure —15 atoms per unit cell—make such calculations difficult. For this reason early pioneering model calculations were carried out non-self-consistently[9-11] to give important qualitative understanding of these materials. This Letter presents results of the first *ab initio* self-consistent linear muffin-tin orbital (LMTO) band studies of $SnMo_6S_8$, $SnMo_6Se_8$, $EuMo_6S_8$, and $GdMo_6S_8$ including all electrons in all 15 atoms in the unit cell. Superconductivity is found to be due to the high Mo d-band density of states (DOS) at E_F resulting from the unusual large charge transfer of Mo electrons to the chalcogens. There is also a large charge transfer from the M site to the cluster and this gives Eu and Gd essentially no occupied conduction bands and Eu a typically divalent isomer shift in agreement with experiment. The Eu and Gd conduction-electron DOS and hence $|\mathcal{T} N(E_F)|$ are reduced by an order of magnitude from its metallic-state value. This results in a very weak coupling of the $4f$ electrons to the conduction electrons and hence only a very weak Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction leaving the dominant magnetic interaction to be the weak dipole-dipole interaction as surmised by Redi and Anderson.[13]

In all our Chevrel-phase calculations, the crystal-structure data of Marezio *et al.*[14] on $PbMo_6S_8$ was used for the arrangement of the atoms without distortion of the Mo octahedron, with a rhombohedral angle of 90° and the actual lattice parameters of the different compounds. Further, if one considers spherically symmetric potentials around each site, this leaves only four types of atoms in the structure, whereas including the distortion would make most of the 15 atoms per cell inequivalent. In this simplified structure there is one Sn site, six equivalent Mo sites, but two types of S sites. The S atoms along the diagonal (around which the smaller Mo_6S_8 cube is tilted in the unit-cell cube) have different surroundings (and potential) than the other six S atoms. The band calculations were performed with use of the LMTO method[12,15] and the Hedin-Lundqvist treatment of exchange and correlation. The charge densities from the core states as well as from partly occupied f states were recalculated in

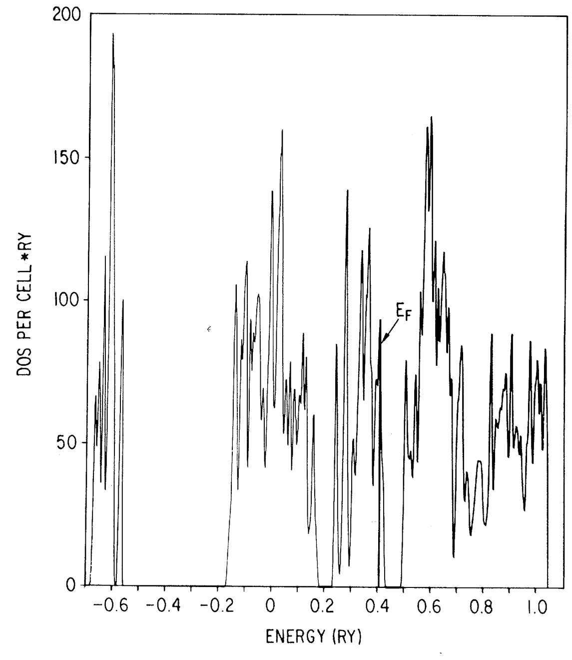

FIG. 1. Total DOS (in states/cell-Ry-spin) for $EuMo_6S_8$ including a ~ 7-mRy Gaussian broadening function. The Fermi energy falls on the peak of 0.405 Ry.

each iteration by using the actual MT potential.

The sharp structure in the total DOS shown in Fig. 1 for $EuMo_6S_8$ arises from the very flat nature of the energy-band structure. [Very similar results were also found for the other compounds.] The DOS shown was calculated from the band structure fixed by Fourier series and found to agree very well with a direct 41-k-point histogram calculation. Because of the limited number of k points used, only the main features should be taken seriously. The flat bands yield low electron velocities at E_F and thus an unusually high contribution to the upper critical field from orbital effects, $H_{c2}^*(0)$; they also explain why a molecular-cluster approach with its resulting discrete eigenvalues is not so poor a first approximation.[10] There is a distinct gap in the DOS just above E_F which falls in the middle of the Mo d bands and a smaller band gap between the Mo d and S p states as was also inferred or seen in the earlier calculations.[9-11] In the "divalent" Sn and Eu compounds, E_F falls just two electrons below the middle of the bonding-antibonding "gap" of the metal d states. (This explains why the ternaries $Mo_2Re_4S_8$, which have two more electrons per cluster, are semiconductors.[1]) The additional electron contributed by Gd, in $GdMo_6S_8$, raises E_F by one electron towards the gap and results in a reduced $N(E_F)$, as shown in Table I.

The considerable structure in the total DOS, particularly around E_F, arises from the Mo $4d$ electrons. Usually for Mo compounds, the d bands are occupied up to the "gap" region where the DOS is low, but in the Chevrel compounds a large charge transfer from Mo to S (about one electron per Mo atom) was found to occur and E_F falls in a high-DOS region below the "gap". A partial DOS calculation (cf. Table I) shows that there is a high $4d$ DOS at E_F which is favorable for superconductivity. Indeed, the DOS per transition-metal atom at E_F in the divalent systems is about 75% of that for the best superconducting $A15$ compounds.[15] Fradin *et al.*[16] showed that the electron-phonon coupling parameter λ is proportional to $N(E_F)$ in a number of Chevrel compounds; the results of Table I follow the observed trend in T_c for the superconductors. Estimates of λ and η (the electronic part of λ) made using the band results in the rigid-ion approximation[17] and strong-coupling theory[18] are shown in Table I. As expected from the above, the dominant contribution to η comes from the Mo d band (60% from p-d and 30% from d-f scattering) with only

TABLE I. Partial and total density-of-state values at the Fermi energy (with 8-mRy resolution) for the different compounds in states per cell per Rydberg along with calculated η and experimental T_c values.

	Density of States (per Ry-cell)						
	s	p	d	f	total	η (eV/Å^2)	T_c(expt)
$SnMo_6S_8$							
Sn	1.0	1.3	0.4	0.2			
Mo_6	0.9	5.8	114.2	4.9			
S_6	0.6	14.5	13.3	6.1			
S_2	0.07	2.4	3.1	1.9	171	3.7	14.2
$SnMo_6Se_8$							
Sn	0.7	1.8	0.5	0.2			
Mo_6	0.7	5.3	102.4	4.7			
Se_6	0.6	14.3	10.7	5.6			
Se_2	0.05	3.1	2.5	2.0	155	3.4	6.8
$GdMo_6S_8$							
Gd	0.11	0.2	1.3	-			
Mo_6	0.7	4.2	83.1	3.7			
S_6	0.4	10.2	9.9	4.6			
S_2	0.03	1.3	2.8	1.3	124	2.7	1.4
$EuMo_6S_8$							
Eu	0.08	0.3	0.6	-			
Mo_6	0.9	4.0	93.4	3.8			
S_6	0.7	10.6	10.1	5.1			
S_2	0.3	3.5	2.5	2.0	141	2.7	···

small contributions from the M and chalcogen sites. [The f DOS given in Table I, calculated as a tail contribution, gives reasonably good results for non-f-electron elements. For Gd and Eu which have their f charge treated as a core state, the tail analysis does not give good values for the f DOS and hence those values are not given.] The trend in η also follows the observed trend in T_c as expected if the phonon spectra in the different compounds are similar. Our calculated η values are twice that of Andersen, Klose, and Nohl.[10] Estimates of λ, with use of the site-decomposed $\langle\omega^2\rangle$ phonon data of Bader and Sinha[19] for the Sn compounds, give the correct relative trend for the T_c's but the wrong magnitude (too small by a factor of 2–3). About 90% of the total contribution to λ comes from the Mo sites. Although clearly questionable, if one assumes the approximate validity of the theory[17,18] for such complex systems as the Chevrel ternaries, agreement with experimental T_c's would be obtained if one further assumes the existence of low-frequency modes, such as the breathing and rocking modes proposed earlier.[10,19] The much reduced T_c values for the trivalent rare earths compared with those for the Sn (and Pb) and the divalent Yb compounds [$T_c(\mathrm{YbMo_6S_8}) = 9.1$ K] is seen as a natural consequence of the reduced $N(E_\mathrm{F})$, both total and Mo 4d, seen for Gd in Table I.

The observed isolation of the rare-earth magnetic moments is clearly understood from the partial DOS in Table I. The extremely low DOS conduction-electron contributions in Eu and Gd arise mostly from the tails of wave functions penetrating their atomic spheres from neighboring sites; the conduction-band states (6s-p, 5d) lie well above E_F in both divalent Eu and trivalent Gd atoms. The resulting DOS contribution at E_F is between one and two orders of magnitude smaller than in their metallic counterparts and leads to the observed decrease in the measured[6,7] $|\mathcal{T}N(E_\mathrm{F})|$. The calculated direct exchange contribution to the total exchange interaction, $\mathcal{T}$, between the Eu 4f and the 6s-p, 5d conduction-electron wave functions at E_F gives a value in close agreement with earlier reported results for the metallic state. The very low conduction-electron DOS for Eu also agrees with the observed Mössbauer Eu^{2+} isomer shift.[6]

One remaining puzzle, in view of the weak magnetic interaction, is the lack of superconductivity in $\mathrm{Eu}_x\mathrm{Mo_6S_8}$. As seen in Table I, its DOS at E_F is large, as is its η value. At the present time, we do not know whether this apparently anomalous behavior indicates the possible importance of magnetic correlations or other many-body effects including valence fluctuations. One possibly important feature still missing within the band model used here is the effect of spin polarization. In view of the larger $N(E_\mathrm{F})$ at the S_2 sites, as well as at the Mo sites, in Eu relative to the Gd compound (cf. Table I) spin-polarized band calculations within local-spin-density-functional theory may well reveal a resultingly greater RKKY interaction path for $\mathrm{EuMo_6S_8}$ and hence a correspondingly greater spin polarization at the Mo sites.[6] Work on this problem has been initiated.

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Two Critical Points for an Electron-Hole System

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Two successive phase separations can exist for an electron-hole system in a semiconductor having isoelectronic impurities within a certain density range: One is between bound excitons and a hole plasma with electrons pinned on the impurities, and the other one is between this hole plasma and the usual electron-hole plasma.

For some time, it has been speculated that the electron-hole (e-h) system in pure Ge could exhibit two critical points, one between a high-density and a low-density e-h plasma and one between the low-density e-h plasma and the exciton gas, the second one being induced by the Mott transition. But no experiment could be made supporting the existence of two such bumps in the e-h phase diagram.[1,2]

The purpose of this Letter is to show for the first time that two critical points can indeed exist for an e-h system if isoelectronic impurities are present in the material: When the density of impurities n_i lies in a certain range, the e-h system can undergo two successive phase separations, while for very low or very large n_i, there exists only one critical point. When the double phase separation exists, the first transition is between the usual electron-hole plasma (EHP) and a hole plasma (HP) with electrons pinned on the impurities, if the isoelectronic impurities are acceptorlike, while the second one is between this hole plasma and excitons.

Several experiments[3-5] have been done on GaP:N but up to now, no satisfactory explanation has been given of the exact role played by the impurities, when the density of electrons and holes is large. The physical picture of this problem, proposed in this Letter, should induce some more experimental work in order to prove the reality of these two critical points. In particular, arguments[3,4] have been given against the existence of a hole plasma in GaP:N on the basis that an electron is too light to be bound alone to the impurity; we will show that the answer is not as simple. First, electrons pinned on impurities polarize the HP and produce an ionic energy which increases with n_i and can stabilize the electrons enough to make the HP finally more stable than the EHP; second, the HP might not be the stablest state at $T=0$ but still appears at finite temperature.

In contrast to what happens for doped semiconductors, isoelectronic impurities will keep an equal amount of electrons and holes in the plasma as for a pure semiconductor. When a host atom is replaced by a lighter (heavier) one, there exists a short-range interaction between the impurity and the electron hole. For simplicity, we will consider only acceptorlike impurities. A bound exciton (BX) can be seen as an electron localized on the impurity and a hole bound by the long-range e-h Coulomb interaction.[6,7] When the impurity density n_i increases such that the distance between bound excitons goes below the Bohr radius, the exciton can no longer exist. One possibility is that the hole *and* the electron leave the impurity and form an EHP; another is that the e-h bond breaks but the electron stays localized on the impurity, the state being in that case the inverse of a metal: a hole plasma (HP) with negative ions.

Let us look at the energies of all these possible states of an e-h system.

(1) The free-exciton (FX) binding energy is $\epsilon_{FX} = -me^4/4h^2\epsilon^2$ if e and h have the same mass m. In the presence of an impurity potential, having a depth $U_0<0$ and a width d_0, one can find bound