However, a susceptibility correction for assumed paramagnetic impurities would only tend to increase the discrepancy rather than to reduce it. Instead, it is believed that the ≃19 ppm displacement of the chemical shift from the expected value is caused by the effect of hydrogen bonding between N and F in NH_4BF_4. Although Rb^+ and NH_4^+ have the same Pauling radius, an x-ray study of $RbBF_4$ and NH_4BF_4 did show small structural differences which were interpreted as being due to hydrogen bonding in NH_4BF_4.[5] The chemical shift study reported here supports this conclusion.

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Comment on the electronic structure of small beryllium and magnesium clusters and their anions

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Be_2 and Be_3 are weakly bound species[1-3] with binding energies less than 0.1 and 0.3 eV, respectively. On the other hand, studies of Schaefer and co-workers[1] have indicated that tetrahedral Be_4 is stable to dissociation to four Be atoms by about 1.7 eV. The chemical bonding in Be_4 results from the strong hybridization of the atomic $2p$ orbitals with the $2s$ orbitals. One might expect therefore that the tetrahedral clusters of the other group IIA and IIB metals will display similar chemical bonding.

Theoretical calculations[4] predict that the $(1s^2 2s^2 2p)^2P$ anion of Be lies only 0.15 eV above the ^1S ground state of the neutral atom. Experimental studies[5] have shown that the corresponding ^2P anions of atomic Mg, Cd, Zn, and Hg lie between 0.15 and 0.50 eV above the ground states of the neutral atoms. This suggests that small clusters of these metals will possess stable anions. Indeed, we have presented theoretical results predicting electron detachment energies of 0.3, 1.0, and 1.0 eV for Be_2^-, Be_3^-, and Be_4^-, respectively.

In the present communication we report the results of LCAO–MO–SCF calculations[6] which show that the bonding in tetrahedral Mg_4 and Mg_4^- is very different than in Be_4 and Be_4^-. The spin-restricted and spin-unrestricted Hartree–Fock methods were employed for the neutral and anionic species, respectively. A $6s/4p$ contracted Gaussian basis was employed for Mg and a $5s/2p$ basis for Be. As a justification for the use of the Hartree–Fock approximation we note that: (1) Dykstra *et al.*[1] obtained SCF and correlated dissociation energies of 1.47 and 1.54 eV, respectively for Be_4, and (2) our SCF and correlated electron detachment[2] energies for Be_2^- were 0.20 and 0.31 eV, respectively.

The results of the calculations are summarized in Fig. 1, which shows the ground state potential energy curves of Mg_4, Be_4, and their anions. The present calculation indicates that Be_4 is bound by 1.9 eV, in good agreement with the previous values. Mg_4, on the other hand, shows little tendency towards chemical bonding, the SCF dissociation energy is only 0.03 eV. The inclusion of electron correlation is expected to increase this latter value to a few tenths of an eV. The minimum of the Be_4 potential energy curve occurs near a Be–Be bond length of approximately 2.10 Å. Allowing only for the differences between the Be and Mg covalent radii, a minimum would be expected near 3.0 Å for the Mg_4 potential curve were the bonding in Mg_4 similar to that in Be_4. Instead, the Mg_4 potential curve is strongly repulsive near this bond length; the very shallow minimum occurs near a bond length of 4.1 Å.

The equilibrium bond length of Be_4^- (2.08 Å) is nearly the same as for the neutral molecule. The electron detachment energy at this bond length is 1.0 eV. Hence, we have the somewhat surprising situation that the additional electron is strongly bound but does not cause appreciable shortening of the Be–Be bonds. This is perhaps due to the fact that much of the charge density of the "extra" electron is localized in the center of the tetrahedron rather than between the beryllium atoms.[2] Mg_4^- has an equilibrium bond length of 3.50 Å and an electron detachment energy (0.49 eV), about half that of Be_4^-.

The electron affinities of Mg_2 and Mg_3 are also much smaller than those of the corresponding berrylium species.[7] The smaller affinities of the magnesium clusters appear to be due in part to the greater repul-

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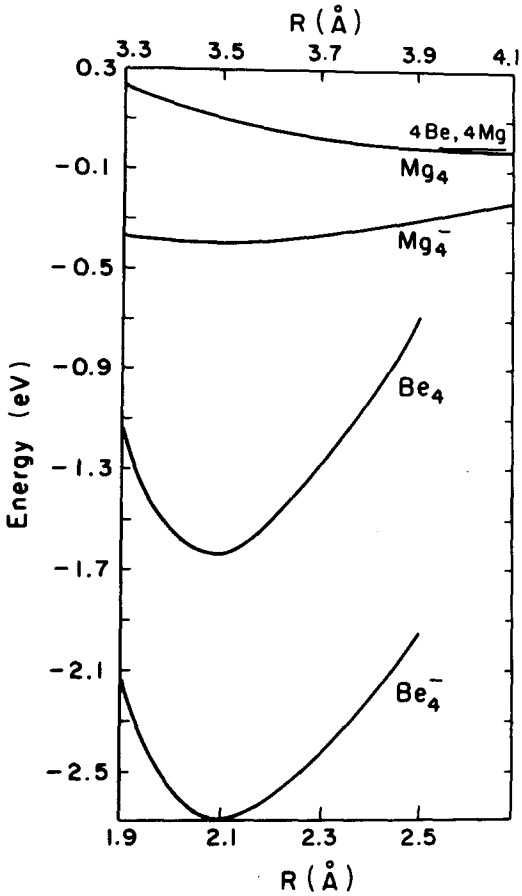

FIG. 1. Potential energy curves of tetrahedral Be_4, Mg_4, and their anions. The zero of energy is chosen to correspond to four separated beryllium and magnesium atoms. The lower and upper horizontal axes give the bond length variation for Be_4 and Mg_4, respectively.

sive nature of their potential surfaces. This causes their negative ions to have their minima at much larger bond lengths than would be expected just on the basis of the differences in covalent radii between Mg and Be. Calculations on Mg_2 at a bondlength of 3.2 Å, obtained by increasing the bond length of Be_2^- by twice the difference between the Be and Mg covalent radii, did not give rise to a stable anion.

We believe that the major factor responsible for the above-noted differences between the magnesium and beryllium clusters is that the Mg 3*p* orbital is substantially more diffuse than is the Be 2*p* orbital and, due to its orthogonality to the 2*p* orbital, more spatially extended relative to the Mg 3*s* orbital than is the Be 2*p* relative to the Be 2*s*.[8] As a result[9] in Mg_4 the 3*p* orbitals do not hybridize[10] as effectively with the 3*s* as do the 2*p* with the 2*s* in Be_4. This causes a pronounced difference in the bonding in Be_4 and Mg_4 and in their anions. We have also found that relaxation makes a smaller contribution to the EA's of the magnesium than to the berrylium clusters. This may also be due to differences in hybridization.

The findings of the present study lead us to question the applicability of berrylium clusters to model (even qualitatively) Zn, Cd, or Hg clusters.[11] We expect that the bonding in the tetramers and other small aggregates of these species will be very weak and more similar to that of the magnesium than to the berrylium clusters. In concluding, we observe that Be metal has a much higher sublimation energy/atom (3.38 eV) than does Mg (1.54 eV) or the other group II metals. It is tempting to speculate that this difference is largely due to the greater *p* character in the bonding in the berrylium case.

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[10] For example, the HOMO of Be_4 has an appreciable contribution from atomic *p* orbitals, while the HOMO of Mg_4 does not.
[11] Due to the low-lying atomic *d* orbitals of calcium, the bonding in the Ca_n clusters may be quite different from that in both the IIB clusters and Be_n.