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LETTER TO THE EDITOR

A Test of the Application of Extended Hückel Calculations to the $ThCr_2Si_2$ and $CaAl_2Si_2$ Structure Types: the Case of $SrMn_2P_2$ and $BaMn_2P_2$

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AMn_2P_2 (A = Sr, Ba) is an example of a composition that can assume a different structure type, depending on the identity of the cation. $BaMn_2P_2$ crystallizes in the $ThCr_2Si_2$ structure type, whereas $SrMn_2P_2$ crystallizes in the $CaAl_2Si_2$ structure type. These compounds have been characterized by temperature-dependent magnetic susceptibility, neutron diffraction, and resistivity. The results indicate that extended Hückel calculations cannot adequately account for the electronic or magnetic properties of these compounds.

Recently, extended Hückel calculations have been used to examine the local and extended views of bonding in different structure types of the AB_2X_2 composition (1–8). In particular, the $ThCr_2Si_2$ and $CaAl_2Si_2$ structure types have been the subject of a number of publications (1, 3, 4, 6–8). The $ThCr_2Si_2$ structure type is of interest because of the large number of compounds that possess this structure type and the unique properties that these compounds exhibit. To a lesser extent, there are also a number of compounds that crystallize in the $CaAl_2Si_2$ structure. A distinguishing feature of the two structure types is the electronic flexibility of the $ThCr_2Si_2$ structure type compared with that of the $CaAl_2Si_2$ structure type. In the former case, the B-site can be occupied by a variety of transition elements with various d-electron counts, while the $CaAl_2Si_2$ type is found only when the B-site element has d^0, d^5, or d^{10} configurations (9). In order to understand these electronic requirements, Zheng and Hoffmann have considered these two structure types in great detail, using extended Hückel calculations. This computational method ignores correlation and exchange effects; thus, local moment formation and magnetic exchange cannot be taken into account. Furthermore, the calculations focused only on the bonding within the $B_2X_2^{2-}$ layers, with no role for the A cations beyond that of an electron source.

In particular, Zheng and Hoffmann have performed calculations on the AMn_2P_2 compounds (6). This composition crystallizes either in the $CaAl_2Si_2$ structure type (A = Sr, Ca) (10) or the $ThCr_2Si_2$ structure type (A = Ba) (11). Figure 1 shows a view of the two different structure types. The calculations show that the $CaAl_2Si_2$ structure is favored over the $ThCr_2Si_2$ structure for d^0 and d^{10} configurations, which is generally consistent with observation. The d^5 configuration is an unfavorable case for the Hückel method, as neglect of correlation and exchange is more difficult to justify. It was argued, but without a detailed calculation, that inclusion of exchange would give rise to a high spin d^5 state for Mn and that this would stabilize the $CaAl_2Si_2$ structure (6). Taking these predictions literally, one would expect that the $BaMn_2P_2$ phase would be metallic and Pauli paramagnetic, i.e., "low spin or spin-paired," in the language of Ref. (6), while $SrMn_2P_2$ would be insulating or semiconducting and would exhibit local moment magnetism of some kind. To date, only the synthesis and structure of these compounds have been reported (10, 11). We have synthesized $SrMn_2P_2$ and $BaMn_2P_2$ and measured the magnetic and electronic properties in order to investigate further the electronic requirements for the d^5 case and to compare our experimental data with the theory.

AMn_2P_2 is prepared by reacting stoichiometric mixtures of the elements, pressed into a pellet, in an alumina boat sealed in a quartz ampoule under about 0.5 atm of purified argon. The elements, P (J. Matthey, 99.999%), Ba (APL Engineering, 99.9%), and Sr (Strem, 99.95%) were used as received and the Mn flake (J. Matthey, 99.9%) was etched with 15% HNO_3/methanol. All materials were handled in a dry box under argon. The samples were

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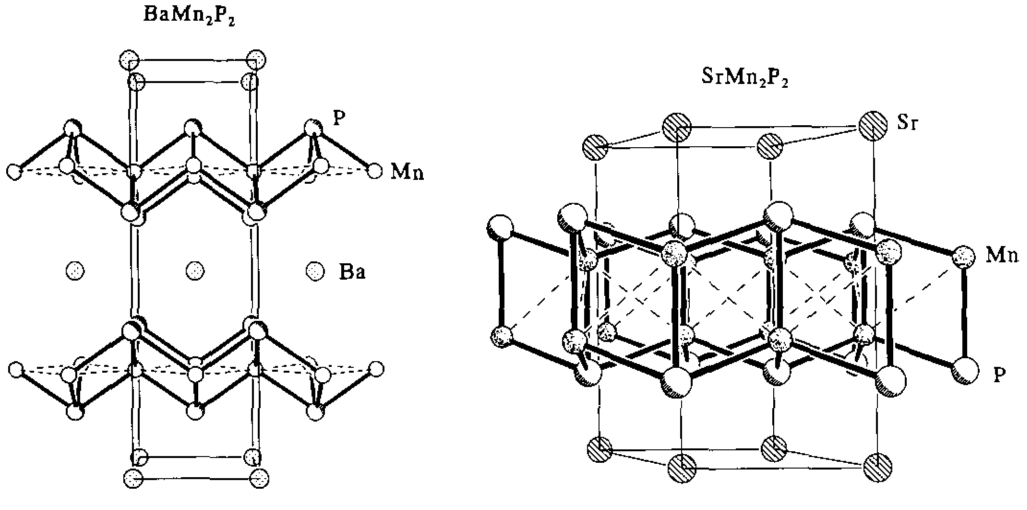

a

b

FIG. 1.

heated to 900°C or 20 hr, then reground and heated once or twice more to 1100°C. The products were black microcrystalline solids that were characterized by powder X-ray diffraction. Figure 2 shows the X-ray diffraction patterns. Indices for the peaks are as given; there are no unidentified peaks.

Temperature-dependent resistivity data indicate that both compounds are semiconductors. Magnetic susceptibility measurements from 10 to 750 K for $BaMn_2P_2$ and $SrMn_2P_2$ are shown in Fig. 3. A Quantum Design SQUID magnetometer with the high temperature option was employed for making the magnetic measurements. The susceptibility for $BaMn_2P_2$ steadily increases as a function of temperature, indicating a strongly antiferromagnetically coupled system with a very high T_N. In contrast, the susceptibility of $SrMn_2P_2$ exhibits a broad transition at about 150 K, indicative of low dimensional coupling (12). Analysis of the contribution of the magnetic susceptibility to the heat capacity, $\delta\chi T/\delta T$ (13), indicates a $T_N \approx 52$ K for this compound. In both cases, the susceptibilities suggest the presence of magnetic spin interactions; however, the magnetic moments could not be simply obtained from the data. In order to verify the analysis of the magnetic data and to unambiguously determine the magnetic moments, neutron diffraction studies were performed.

Details of the neutron diffraction are the subject of another publication (14); only the conclusions will be briefly outlined here. The room temperature neutron diffraction pattern of $BaMn_2P_2$ shows additional diffraction lines indicative of antiferromagnetic coupling and of type G magnetic structure (15). The moment for Mn is 4.2(1) μ_B, in reasonable agreement with the expected value of 5.0 μ_B for high spin Mn(II). The interpretation of the neutron data for $SrMn_2P_2$ is more complicated. $SrMn_2P_2$

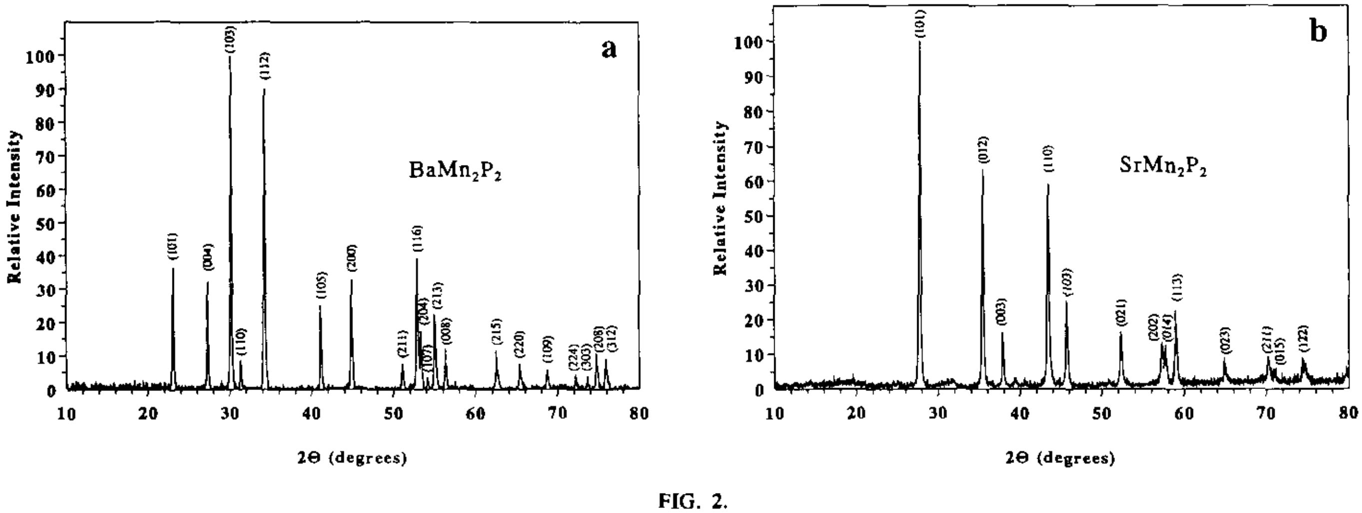

FIG. 2.

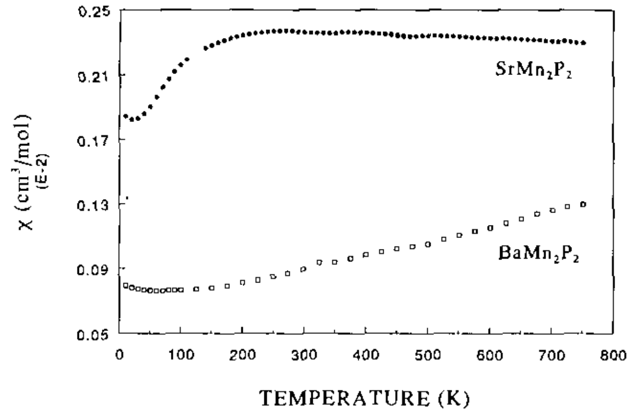

FIG. 3.

is antiferromagnetic below $T_N = 53$ (1) K, as determined from the temperature dependence of the magnetic reflections. There are two distinct sets of magnetic reflections distinguished by different ordering temperatures and indexing schemes. One set is commensurate and the other incommensurate with the chemical cell. While the magnetic structure is complex and a detailed model is lacking, it is clear that Mn is in a high spin rather than low spin configuration.

These results imply that the extended Hückel calculations have neglected important details necessary to account for the electronic structure of these particular d^5 compounds, namely, correlation and exchange. A localized electron, quasi-ionic model would be more appropriate. Detailed lattice energy calculations based on such an approach do not, to our knowledge, exist for these two compounds. It is likely, nonetheless, that the coordination preference of the countercation makes a large contribution to the lattice energy. Indeed, the choice of structure type for the series AMn_2P_2 (A = Ca, Sr, Ba) can be rationalized on this basis. The $CaAl_2Si_2$ structure, in which the cation is in a sixfold octahedral site, is found for the smaller Ca and Sr ions, while the Ba compound crystallizes in the $ThCr_2Si_2$ structure where the cation coordination is eightfold cubic. Thus, the structure type for the d^5 system may be defined by the coordination preference of the cation.

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