Table III. The Specific Susceptibility, χ_g (cgs units/gram)

Temp, °K	Ag_2Ca	Ag_2CaH
296	2.3×10^{-7}	-1.5×10^{-7}
77	3.0×10^{-7}	-1.0×10^{-7}

inclusion. The extrapolated values of the susceptibility to infinite field strength were then taken as representing the intrinsic alloy and hydride susceptibilities.[7] These values are shown in Table III. χ_g is the specific susceptibility in cgs units/gram.

The estimated accuracy of these values is $\pm 0.5 \times 10^{-7}$ cgs/gram so that the experimental error blurs any apparent significance in the increase in χ_g between 296 and 77°K for each sample. However, the difference between the positive or paramagnetic susceptibility of the Ag_2Ca alloy and the negative or diamagnetic susceptibility of the Ag_2CaH ternary hydride is considered a valid experimental result.

The reasons for the shift from a net paramagnetism in the alloy to a net diamagnetism in the hydride are not clear. It is conceivable there might be some parallels with the palladium hydride binary system in which the normal paramagnetism of the palladium metal is suppressed as hydrogen is added to the metal.[8] This effect has been attributed by some to the filling of holes in the palladium d band by electrons from the hydrogen atoms. It has also been speculated that the addition of hydrogen causes the palladium lattice to expand with an accompanying decrease in the susceptibility.[8] A simple qualitative explanation of the Ag_2CaH behavior might therefore be advanced based on the idea that electrons from the hydrogen fill up the conduction band in the alloy responsible for the predominant spin paramagnetism and thereby reduce the available number of empty electron states or holes in the band.

Qualitative resistance measurements on the hydride phase indicated that there was no detectable difference in measuring the resistance of a 2-mm thick pellet and shorting of the leads. Although it is recognized that a crude single temperature measurement on a compressed powder sample does not differentiate between metallic and semiconductor properties, it is of interest to note that the resistances of alkaline earth iridium and ruthenium hydrides indicated they were nonconductors[2a] and that the alkaline earth rhodium[2a] and palladium[2b] hydrides had conductivities at least an order of magnitude less than that observed for the calcium silver hydride.

It should be pointed out that although various ratios of calcium hydride and silver were reacted, the only ternary hydride phase discovered was that related stoichiometrically to the alloy phase. This observation is of interest in that the stoichiometry of new ternary hydride systems is often unpredictable. Some hydrides such as $NaBH_4$, $LiAlH_4$, Li_2BeH_4, and $KMgH_3$ are stoichiometrically related to the complex halides.[9] Some hydrides such as iron titanium hydride[10,11] are alloy hydrides. Since they result from solubility of hydrogen in metals and alloys,[12] the stoichiometry of the metal atoms of the hydride is that of the alloy phase. The stoichiometries of some ternary hydrides are not predictable on the basis of either analogy. Examples are Sr_2IrH_5,[2a] Ca_2RhH_5,[2a] Sr_2PdH_4,[2b] and Ca_3PdH_4.[2b] Some pattern for the model a ternary hydride system might be expected to follow is emerging, but reliable predictability of stoichiometry awaits the characterization of other new hydrides.

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Registry No. $CaAg_2H$, 56689-00-0; $CaAg_2$, 56629-70-0; CaH_2, 7789-78-8; Ag, 7440-22-4.

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High-Pressure Synthesis and Properties of NiPS[1]

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NiPS was synthesized at 60 kbars pressure and 1300°C using a high-pressure belt apparatus. The X-ray diffraction patterns obtained from pure NiPS can be indexed assuming a cubic pyrite type structure. The cubic cell dimension was 5.549 (2) Å and a density of 4.75 (2) g/cm^3 was determined by a hydrostatic technique. Magnetic susceptibility and resistivity measurements indicate that the nickel cations can be assigned a low-spin d^7 electronic configuration. No spontaneous magnetism was observed over the temperature range from 100 to 540°K.

Introduction

The electrons of the transition metal chalcogenides have been characterized as ranging from those that are localized and highly correlated in MnS_2[2] with strong magnetic ordering and semiconducting behavior to others such as $NiSe_2$[2] in which the d electrons are completely delocalized and uncorrelated. Compounds such as $NiSe_2$ show metallic behavior and Pauli paramagnetism.

Intermediate between these extremes and having characteristics of both localized and delocalized systems are the cobalt dichalocogenides where electrons exist in a periodic field. Consequently, electrons occupy a series of energy bands separated by gaps of forbidden energy. It is the widths of these bands that determine the degree of correlation and transfer energy. With a narrow bandwidth there is a greater degree of electron correlation, thereby increasing the possibility of magnetic ordering.

Interest in the cubic pyrite CoS_2 (Figure 1), as a narrow

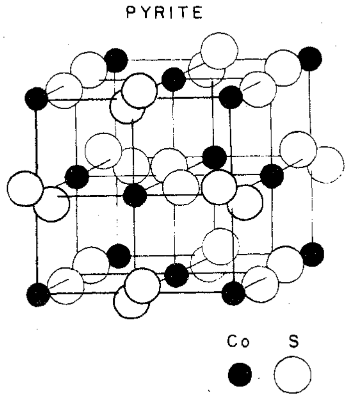

Figure 1. Cubic pyrite structure.

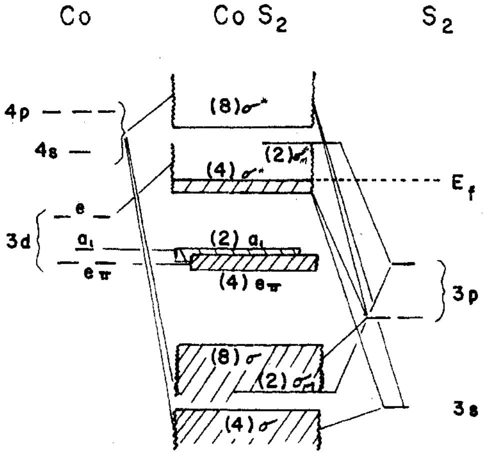

Figure 2. Energy bands for the pyrite type structure.

d-band ferromagnet, has resulted in a number of studies[2-6] describing the effects of cation and anion substitution on the ferromagnetic behavior. Goodenough[7,8] has proposed a one-electron band model which relates the metallic and ferromagnetic behavior of these compounds to the formation of a partially occupied and isolated σ*-antibonding band (Figure 2). For the compound CoS_2, the σ*-antibonding band is one-fourth filled, and at low temperatures ($T < 122°K$), the delocalized electrons, in this band, become spontaneously magnetized. Substitution of selenium for sulfur leaves the electron concentration within the band unchanged but changes the magnetic state from ferromagnetic to antiferromagnetic.[9] Substitution of arsenic[10] or phosphorus[11] for sulfur leaves the interactions ferromagnetic while reducing the electron concentration in the band. For CoAsS and CoPS, the σ*-antibonding band is empty and there is no spontaneous magnetism.[12]

The substitution of Ni for Co, in CoAsS,[13] resulted in a change from semiconducting, diamagnetic behavior to metallic, paramagnetic behavior. Although the end member, NiAsS, attains a one-fourth filled σ*-antibonding band as in CoS_2, the magnetic behavior of NiAsS is not ferromagnetic. NiAsS exhibits weakly temperature-dependent paramagnetism, indicative of a broadened σ*-antibonding band.

The electronic configuration of NiPS is similar to those of both CoS_2 and NiAsS. All three compounds have a one-fourth filled σ* band. The more covalent character of nickel relative to cobalt would be expected to broaden the σ*-antibonding band, thereby reducing the possibility of spontaneous magnetization. However, since phosphorus is smaller and less polarizable than arsenic, the broadness of the σ*-antibonding band should be reduced in NiPS relative to NiAsS. As a result of a reduced σ* bandwidth, a possibility exists for magnetic ordering to be observed in NiPS.

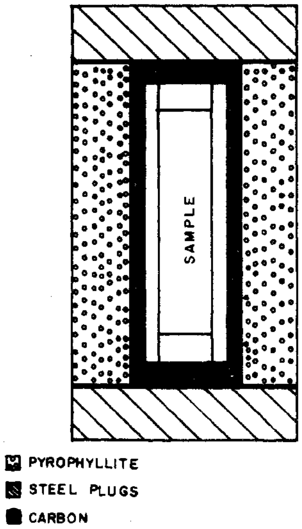

Figure 3. High-pressure sample cell.

The successful synthesis of single-phase NiPS has not been reported. The application of high-pressure synthetic techniques to prepare this material was also of interest.

Experimental Section

Preparation. Ambient-Pressure Synthesis. Polycrystalline powders were prepared initially by direct combination of the elements. Spectroscopic grade nickel, phosphorus, and sulfur were obtained from Atomergic Chemical Co., Division of Gallard-Schlesinger Chemical Corp., New York, N.Y. The high-purity nickel (99.9999%) was reduced (600°C for 3 hr) in a 15% hydrogen–85% argon atmosphere. Elemental red phosphorus (99.999%) and sulfur (99.999%) were used as supplied. White phosphorus was not used because of its pyrophoric character. Stoichiometric amounts of nickel, phosphorus, and sulfur (1:1:1) were allowed to react in evacuated, sealed silica tubes three times at 600°C with two intermediate grindings under a dry nitrogen atmosphere. The resulting multiphased material was pulverized to produce a homogeneous mixture of the phases before being subjected to the high-pressure treatment.

High-Pressure Synthesis. Reactions were carried out in a belt apparatus of the type described by Hall.[14] Figure 3 shows a schematic of the sample cell. A graphite sleeve functions as the internal heater while pyrophyllite (lava stone) serves as the pressure-transmitting medium.

A major problem associated with the high-pressure synthesis of sulfides is sample contamination. Boron nitride was used initially for the reaction container; however, it was difficult to isolate the sample from the boron nitride crucible. Pyrex does not react with the sample and hence was chosen for use as the sample container.

Prereacted, polycrystalline samples were packed in Pyrex capsules and treated at pressures of 60 kbars and temperatures ranging from 1200 to 1400°C. Reaction times ranged from 30 min to 2 hr. The sample temperature was then reduced, over a period of 4 hr, to 600°C followed by a more rapid cooling (<15 min) to room temperature. After the samples had cooled, the pressure was reduced from 60 kbars to ambient pressure.

X-Ray Analysis and Characterization. Powder diffraction patterns were obtained with a Norelco diffractometer using monochromated high-intensity Cu Kα radiation (λ 1.5405 Å). Fast scans of 1° (2θ)/min were recorded to examine materials for the possible presence of extra phases. Slow scans of 1° (2θ)/4 min were obtained for all single-phase samples in the range $12° \leq 2\theta \leq 130°$. Lattice parameters were determined by least-squares analysis, using high-angle reflections ($2\theta > 70°$) corrected relative to an internal MgO standard.

Density Determinations. Sample densities were determined using a hydrostatic technique[15] employing a Mettler H54 analytical balance. The density medium perfluoro(1-methyldecalin) was chosen because of its relatively low vapor pressure and its ability to wet the samples. A high-purity silicon crystal ($\rho = 2.328$ g/cm^3) was used for calibrating the density fluid. In order to obtain reproducible results, care was taken to outgas the samples thoroughly prior to density measurements.

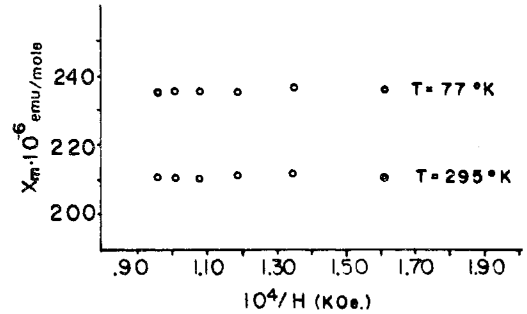

Figure 4. Susceptibility (χ_m) vs. field ($10^4/H$) for NiPS.

Electrical and Magnetic Measurements. Resistivity measurements were made on pressed, polycrystalline bars. The pressed material was lapped to a uniform thickness, after which indium leads were attached to the sample by means of an ultrasonic soldering technique.[16] The resistivity of the material was determined using the Van der Pauw method.[17] Temperatures were measured with a gallium arsenide diode.

Magnetic susceptibility data were obtained, using a Faraday balance[18] equipped with a Cahn RG Electrobalance, over the temperature range 4.2–550°K. Measurements were performed at field strengths between 6.25 and 10.30 kOe. The balance was calibrated using platinum wire ($\chi_g = 0.991 \times 10^{-6}$ emu/g at 297°K). No corrections were made for core diamagnetism because of the large uncertainty in the magnitude of the corrections relative to the magnitude of the susceptibility of the material studied.

Results and Discussion

Reaction of stoichiometric quantities of nickel, phosphorus, and sulfur at 600°C in sealed silica tubes yields a multiphase product. However, when the multiphase product is treated at high pressure (60 kbars), single-phase NiPS is formed. X-Ray diffraction analysis of NiPS shows only those reflections allowed by the cubic pyrite structure (space group *Pa*3; *hkl*, no conditions; *hk*0, $h = 2n$). The similarity of the scattering factors of phosphorus and sulfur makes it difficult to determine if any ordering of the anions has occurred. Such ordering has been observed for NiAsS[13] in the cubic ullmanite structure (space group $P2_13$).

The lattice parameter for NiPS (a_0 = 5.549 (2) Å) gives a calculated density of 4.73 g/cm^3 as compared to an experimental density of 4.75 (2) g/cm^3. Resistivity measurements at both 296 and 77°K resulted in values of 4.9 (1) $\times$ 10^{-2} and 4.6 (1) $\times$ 10^{-2} Ω cm, respectively, which are indicative of metallic behavior.

Honda-Owens[19] measurements at 77 and 296°K (see Figure 4) gave no indication of the presence of any ferromagnetic phases. A plot of χ_m^{-1} vs. T (°K) is shown in Figure 5. An upper temperature limit of 500°K was chosen in order to be well below the thermal decomposition temperature (600°K) determined by thermogravimetric analysis (Figure 6). The data, from 120 to 500°K, obey the Curie–Weiss law, giving a calculated effective moment of 1.96 (1) μ_B and a Curie Weiss constant of -19.8 (2) $\times$ 10^2°K. The low-temperature behavior of the molar susceptibility may be due to the onset of magnetic order.

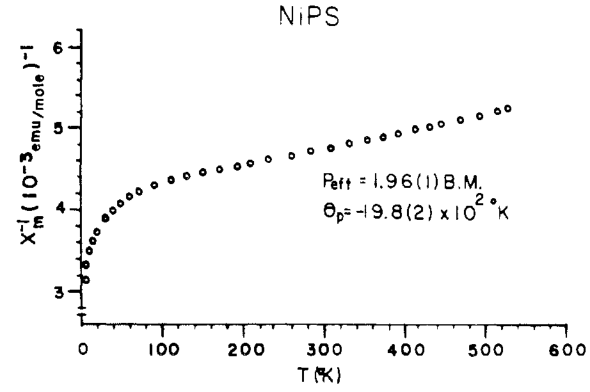

Figure 5. Inverse susceptibility (χ_m^{-1}) vs. temperature (°K) for NiPS.

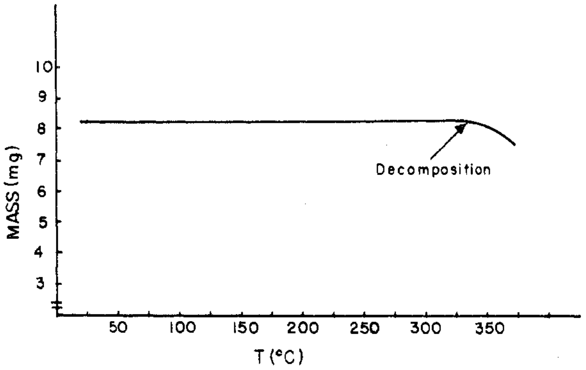

Figure 6. Thermogravimetric analysis for NiPS.

Both the magnetic and electrical properties of cubic NiPS are consistent with the pyrite band model, with nickel cations having a low-spin d^7 electronic configuration. Six of the seven d electrons are spin paired in the nonbonding t_{2g} orbitals, whereas the seventh d electron occupies one of four possible states of the σ^* conduction band. Although NiPS is isoelectronic with CoS$_2$, the more covalent character of nickel relative to cobalt would be expected to broaden the σ^*-antibonding band.

Registry No. NiPS, 56689-01-1.

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