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Polymorphism in Selenospinels—A High Pressure Phase of $CdCr_2Se_4$†

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The selenospinel, $CdCr_2Se_4$, has been transformed under high-pressure and temperature to a new structure with monoclinic symmetry related to the defect-NiAs structure and with the lattice parameters: $a = 14.62$ Å, $b = 6.90$ Å, $c = 11.45$ Å, and $\beta = 91.0°$. This is consistent with the spinel-to-monoclinic transformations found for the thiospinels, $FeCr_2S_4$, $CoCr_2S_4$, and $MnCr_2S_4$. The high-pressure phase is retained indefinitely at atmospheric pressure and room temperature but retransforms at 125C. The pressure-temperature boundary between the phases has a slope of $-15.2°$/kbar over the temperature range of 400–750C. Under pressure, the structural change is accompanied by a change from semiconducting to metallic electrical behavior with a drop in resistance from 5×10^2–5.5×10^{-2} ohms. The magnetic moment at 4.2K decreased from $\sim 5.6\mu_B$ for the spinel phase, which orders ferromagnetically, to $\sim 0.035\mu_B$ for the monoclinic phase, which has weak antiferromagnetic ordering.

Introduction

$CdCr_2Se_4$ is one of a family of compounds of the general formula AB_2X_4, where A and B are divalent and trivalent metal atoms, respectively, and X is O, S, Se, or Te. These compounds crystallize with either the cubic spinel structure or a monoclinic distortion of the NiAs structure. In the former, the anions form an essentially cubic close-packed lattice with A atoms in the tetrahedral holes and B atoms in the octahedral holes. In the latter, the anions have hexagonal packing with the A and B atoms in only the octahedral holes, and the vacancies are ordered to give an overall monoclinic structure. (If the vacancies were disordered, the structure would be the NiAs type with hexagonal symmetry.) The oxides form only spinels while the sulfides are found in either the cubic or monoclinic structures. The selenides and tellurides are found primarily in the monoclinic form (*1, 2*) but the compounds $M\,Cr_2Se_4$, where M is Cu, Zn, Cd, or Hg, have the cubic structure because the A cations are strongly stabilized on the tetrahedral sites.

$CdCr_2Se_4$ is of current interest because it is a ferromagnetic semiconductor (*3, 4*) with a non-magnetic ion in the A sites. Small single crystals have been grown by various methods (*5, 6*) and their properties studied (*6, 7*). It has not been possible to grow crystals from a stoichiometric melt since at atmospheric pressure $CdCr_2Se_4$ decomposes to CdSe and Cr_2Se_3 above 700C (Ref. *8*). Recently we attempted to grow larger crystals by prolonged heating of the compound at 700–750C under elevated pressures. We found that, at these temperatures, pressures over 20 kbar transform the spinel phase into a new phase with the monoclinic defect-NiAs structure, which can be retained at atmospheric pressure by quenching to room temperature before dropping the pressure.

The high pressure transition from spinel to defect-NiAs structure is not unusual for the thiospinels and has been demonstrated for $FeCr_2S_4$, $CoCr_2S_4$, $MnCr_2S_4$, and $CuCr_2S_4$ (*9–11*). In the case of the selenospinels, $CuCr_2Se_4$ (*9*) is the only compound for which this transformation has been demonstrated. In this research, we have observed the same type of transformation for $CdCr_2Se_4$ and determined the P–T boundary between the cubic and monoclinic phases. We have also measured electrical and magnetic properties of this new phase.

Experimental

The spinel form of $CdCr_2Se_4$, which we used as a starting material in studying the high-pressure phase, was prepared by several methods. Two types of material have been obtained. The first was a loosely sintered ingot prepared by long anneals at 750 or

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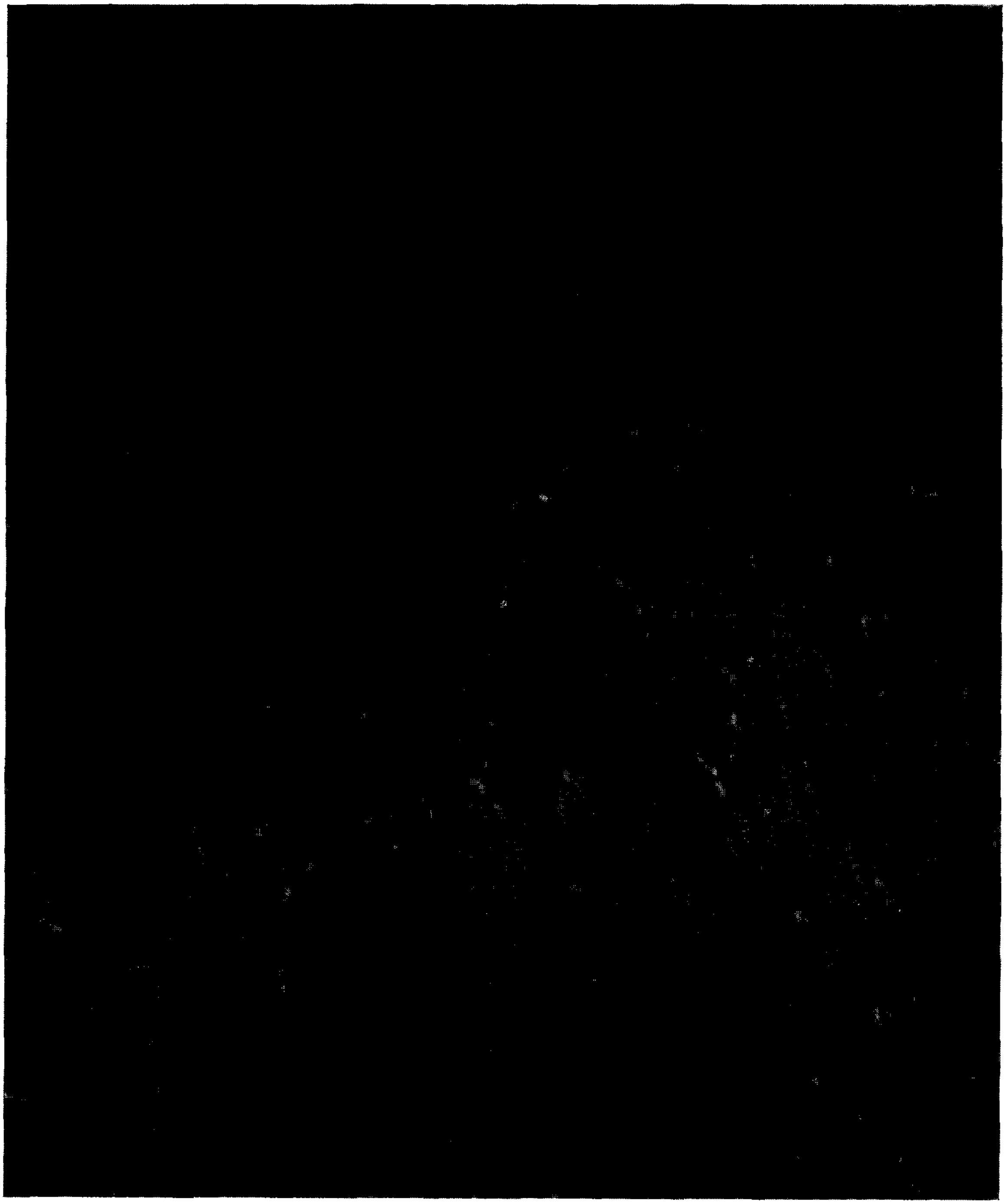

FIG. 1. Photomicrograph of $CdCr_2Se_4$ powder made by the first method, pressed at 10 kbar and 500C. The large gray grain is CdSe, the small white rods are Cr_2Se_3, and black areas are voids. Both impurities were also observed in the X-ray diffraction pattern for this powder.

800C of stoichiometric mixtures of the elements or of CdSe and freshly prepared Cr_2Se_3. These ingots were evaluated both by taking long-exposure X-ray-diffraction powder patterns and by hot pressing in gold capsules at 10 kbar and 500C to produce a dense compact for metallographic examination. Even samples that showed no CdSe or Cr_2Se_3 lines in the X-ray patterns frequently contained ~1% of CdSe or Cr_2Se_3 (identified by electron microprobe analysis) visible in the compacts as isolated islands (Fig. 1). Chemical analysis showed that ingots in which the starting compounds were not observed had the stoichiometric composition to within 1% (for example, $CdCr_{1.99}Se_{4.03}$). No metallographic or chemical analysis has previously been reported for $CdCr_2Se_4$.

The other type of starting material was obtained by growth from a $CdCl_2$ melt resulting from the reaction,

$$4\,CdSe + 2\,CrCl_3 \rightarrow CdCr_2Se_4 + 3\,CdCl_2$$

It consisted of crystals varying in size from less than 0.1 mm to over 2 mm in diameter. The crystals were separated into size ranges of >2, 1–2, 0.5–1, and <0.5 mm using standard sieves. At liquid N_2 temperatures, crystals of $CdCr_2Se_4$ could be separated from particles of CdSe and $CdCl_2$ by means of a magnet since the spinel is strongly ferromagnetic at this temperature. However, they could not be separated from Cr_2Se_3 since this compound is antiferromagnetic.

The crystals smaller than 1.0 mm were generally well developed octahedra with some undeveloped faces and pits. A few were intergrown with other crystals. Crystals with diameters >1.0 mm were almost entirely intergrown clusters having large voids and pockets. Metallographic examination on polished sections showed that the single crystals 0.5–1 mm in diameter were free of inclusions. Larger crystals, even those selected to have the minimum of intergrowth and growth twinning, always contained CdSe and sometimes Cr_2Se_3 inclusions (identified by electron micropropbe analysis). Chemical analysis of the various fractions of one batch of crystals showed that the crystals 0.5–1.0 mm diameter were stoichiometric ($Cd_{1.00}Cr_{1.998}Se_{4.041}$) while large crystals (1–2 and >2 mm) contained about 5 moles/100 moles excess CdSe. The sieve fraction <0.5 mm consisted of tiny octahedra of $CdCr_2Se_4$ mixed with flakes of free Cr_2Se_3, confirmed by X-ray and chemical analysis. The cubic lattice parameter for the stoichiometric crystals was found to be 10.746 ± 0.002 Å, compared with 10.775 Å (*4*) and 10.721 Å (*8*) given in the literature for samples with no reported analysis. It is possible that the spinel phase has an appreciable range of homogeneity and that the variation in the lattice parameters is due to differences in sample composition.

To prepare samples of the high-pressure phase and to study the pressure-temperature phase diagram for $CdCr_2Se_4$, single-phase spinel samples were sealed in gold capsules with 0.002-in. walls and annealed at pressures from 10–50 kbar and temperatures from 350–800C for from 20 hr to more than 3 days. A 1-in. piston-cylinder high-pressure unit was used for pressures up to 25 kbar. A 2000-ton-per-ram tetrahedral-hinge unit was used for the higher pressures. Pressures are based on a room temperature calibration using the transition of Bi, Tl, and Ba at 25.4, 37, and 59 kbar, respectively. Temperatures were measured by chromel-alumel thermocouples placed as close to the sample as practical. The emf was not corrected for the effect of pressure, and the temperature is therefore accurate to ±15C. The temperature was controlled to within ±10C of the desired temperature for the duration of the runs. At the end of each run, the temperature was dropped rapidly to quench in the phase formed at the annealing conditions, after which the pressure was generally dropped slowly to minimize cracking of the sample. The gold was peeled off after the sample was removed from the sample holder, and a powder pattern of the product was made using a 114.6 mm Debye-Scherrer camera with CuK_α radiation. After polishing, the product was also examined metallographically. The polished sections were also used for the electron microprobe analyses.

A series of experiments were also made using diamond-anvil high pressure X-ray cameras (*12*) to determine the room temperature transition pressure. One type of camera is pressurized by means of N_2 gas and therefore can be loaded reproducibly. The load can be converted to approximate internal pressures using a calibration obtained from the known compressibility of NaCl. Pressures in this unit then can be known to ±5 kbar. A second unit is loaded by means of a screw with long lever arms; therefore, it is difficult to load reproducibly and pressure can be known only if internal standards are used. The complex diffraction patterns of the high pressure phase of $CdCr_2Se_4$ made use of this technique impractical. The NaCl lines are either masked or too faint at the high pressures to be much more reliable than the estimates of pressure based on experience with the unit. These estimated pressures are probably good to ±10 kbar. With either unit it was possible to obtain data for the compressibility of the spinel phase of $CdCr_2Se_4$.

Electrical measurements using the van der Pauw technique (*13*) were made on some samples of both the spinel and high-pressure structures. In addition, the magnetic moment for both phases was determined at 4.2K by a vibrating coil magnetometer (*14*), and more detailed magnetic studies as a function of field or temperature were made using a vibrating sample magnetometer (*15*).

Results

The phase diagram obtained from the annealing experiments is shown in Fig. 2. In general, the transformation to the high-pressure phase was complete in the normal 20–24 hr annealing time. However, at 22 kbar and 700C, the product contained both phases. This is probably due to pressure and temperature gradients within the sample bulk. With the annealing conditions of 600C and 30 kbar, one sample gave spinel as the product while a second gave the high-pressure phase. This result can be explained by deviations of the sample conditions from the nominal annealing conditions. The point at 40 kbar and 400C is definitely in the spinel area since samples annealed for over 3 days did not show any of the high-pressure phase's X-ray diffraction lines, and metallographic examination also showed the sample to be single phase. At 20 kbar and 700C, the retransformation from high-pressure phase to spinel was observed after annealing for 24 hr under these conditions. This confirms that the phase boundary represents equilibrium conditions. At room temperature the high-pressure phase is metastable and does not transform back to the spinel structure over a period of several months. However, at 125C partial transformation to spinel takes place within 34 hr at atmospheric pressure.

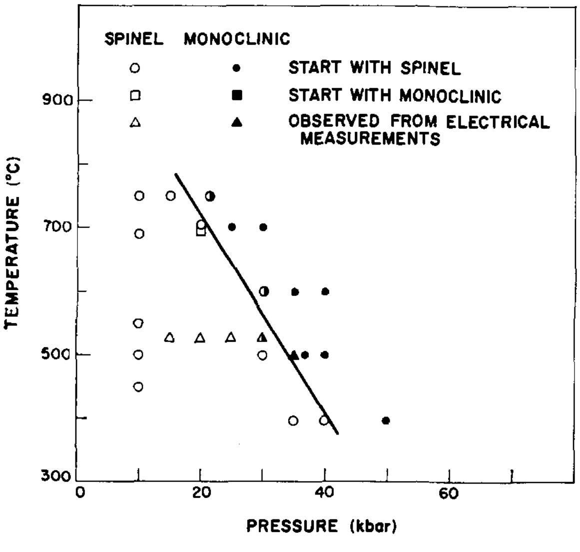

FIG. 2. Pressure temperature phase diagram of $CdCr_2Se_4$. Data shows annealing conditions prior to temperature quench at the designated pressure. Open points gave product with spinel structure, solid points product with monoclinic structure. Triangles are from electrical resistance data under pressure.

The phase boundary between the spinel and high-pressure phase has a negative slope of −15.2 kbar. Extrapolation of the boundary indicates that at one atmosphere the spinel phase would transform to the monoclinic phase at about 1000C. This cannot be observed, however, because of the decomposition of $CdCr_2Se_4$ above 750C at this pressure. In the case of $FeCr_2S_4$ (*9*) the transition from spinel to defect-NiAs structure has been observed at ~970C at atmospheric pressure. This point lies on the straight-line extrapolation of the high-pressure data for this system, so that such an extrapolation appears reasonable also for $CdCr_2Se_4$. Based on a straight-line extrapolation, the transformation should take place at ~70 kbar at room temperature. However, using the gas loaded X-ray camera (pressures known to ±5 kbar) only the spinel phase was observed at pressures up to 80 kbar; between this pressure and ~100 kbar the diffraction lines of both phases were seen. In the screw loaded unit at estimated pressures of greater than 100 kbar only the high pressure phase was found. These data indicate that the transition from spinel to high pressure phase occurs between 80 and 100 kbar, and therefore there is appreciable curvature to the phase boundary at the lower temperatures. It was possible to estimate the volume compressibility of the spinel phase from the lattice-parameter decrease calculated from the diffraction patterns made at various pressures. The compressibility $-\Delta V/V_0$ is relatively small $\sim 5 \times 10^{-4}$ and remains fairly constant with increasing pressure from 1 atm to 98 kbar.

The densities of both the spinel and monoclinic phases were measured by toluene displacement. The value of 5.55 g/ml for the spinel phase is in excellent agreement with the value of 5.65 g/ml calculated from the lattice parameter of 10.746 Å. The density of 5.80 g/ml for the high pressure phase was measured on several different samples and gave a reproducibility of ±0.1 g/ml.

The X-ray diffraction patterns on the retained phase were shown to have monoclinic symmetry. It was difficult to get adequate indexing and lattice parameters due to line broadening and the lack of resolution or absence of most of the weak reflections. The films could not be improved by annealing the samples since annealing caused retransformation to spinel structure. Attempts were made to fit the patterns to the same structures as for the high-pressure phases of $FeCr_2S_4$ and $MnCr_2S_4$ (*16*), which are derived from the structure of $CrCr_2S_4$ (*17*) or, as it is commonly designated, Cr_3S_4. Although a reasonable fit was obtained, the resulting lattice parameters were small enough to give a theoretical density nearly 20% higher than the measured density. A better fit, particularly for the low-angle lines ($2\theta < 25°$), was obtained for a unit cell which was similar to that reported for $CrCr_2S_4$ (*17*), but with approximately doubled a and b parameters. The structural implication of this parameter doubling cannot be explained without single-crystal studies. The best values of the monoclinic cell parameters of $CdCr_2Se_4$ are: $a = 14.62$ Å, $b = 6.90$ Å, and $c = 11.45$ Å, with $\beta = \sim 91.0$. A density of 6.1 g/ml is calculated from these values and is in fair agreement with the value of 5.8 g/ml measured on this phase.

The electrical properties of samples of both phases were measured on crack-free, cylindrical ingots or sections of ingots. The results of these measurements for both phases of the same batch are given in Table I. There was a variation of about a factor of 10 for the resistivity among various samples of the monoclinic phases ($3.2–22 \times 10^{-2}$ Ω-cm), while the Seebeck coefficient varied by a factor of 2 between various samples of both phases. The increase in resistivity with temperature for the monoclinic phase is characteristic of metallic behavior. However, the magnitude of these parameters and those for the mobility and carrier concentration are not those of either good semiconductors or good metals.

Under pressure, the spinel phase shows semiconducting electrical behavior above room temperature while the monoclinic phase shows metallic electrical behavior. For example, a series of runs at various fixed pressures was made to follow the electrical resistance of the spinel phase as a function of temperature. At 15, 20, and 25 kbar, the resistance decreased smoothly ~3 orders of magnitude between 25 and 525C and returned to the initial value on cooling to room temperature (Fig. 3). At 30 kbar, the resistance was appreciably lower on returning to room temperature. After repeating this cycle with a 9-hr hold at 525C, the R.T. resistance was 1/10 the initial value at this pressure indicating partial transformation. At 35 kbar, the resistance decreased steadily on cooling from 500C, showing the same type of conduction as for the monoclinic phase at one atmosphere (Fig. 3). These data show that complete transformation to the high pressure phase occurred at 35 kbar and 500C, and this agrees well with the other data of the *P–T* phase diagram.

The magnetic properties of the monoclinic phase are very different from those of the spinel phase as can be seen in Table II. Thus, the high-pressure phase has a very small magnetic moment at 4.2K and orders antiferromagnetically. The effect of temperature on the magnetic susceptibility for a sample of this phase is shown in Fig. 4, which clearly demonstrates the Néel point of 55K. On other monoclinic samples the Néel point was partially or completely obscured by the presence of small quantities of the spinel phase with its very large ferromagnetic moment. The susceptibility of the sample that was free from traces of the spinel phase was found to vary linearly with field from 0 to 17 kOe at 4.2, 77, and 295K as shown in the lower curve of Fig. 5. This is characteristic of antiferromagnetic and paramagnetic behavior and is consistent with the

TABLE I

ELECTRICAL PROPERTIES OF $CdCr_2Se_4$

	Spinel			Monoclinic	
	300K	77K	Units	300K	77K
Resistivity (ρ)	1.8	1.6	Ω-cm	6.8×10^{-2}	4.6×10^{-2}
Hall constant (R_H)	2.75	1.33	cm^3/Coul	2.2×10^{-2}	2.6×10^{-2}
Hall mobility (μ)	1.6	0.82	cm^2/Volt-sec	0.32	0.56
Carrier conc. (p)	2.3×10^{18}	4.7×10^{18}	cm^3	2.9×10^{20}	2.5×10^{20}
Seebeck coeff. (α)	44		μV/C	61	

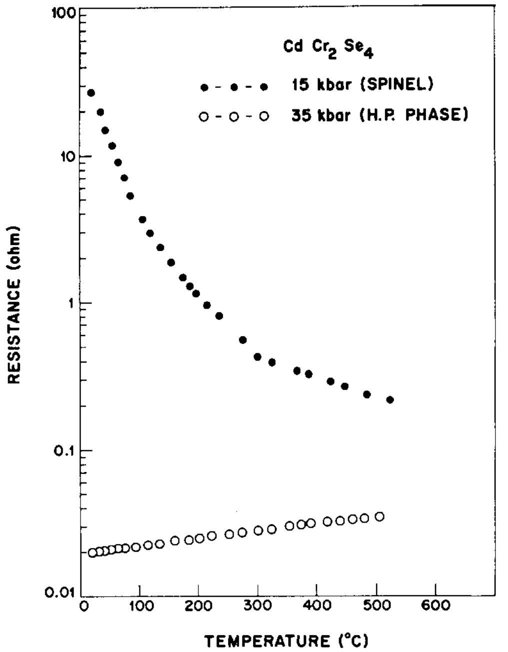

FIG. 3. Electrical resistance vs. temperature for a sample of $CdCr_2Se_4$ at 15 kbar and 35 kbar. ●—heating to 525C at 15 kbar; o—cooling from 507C at 35 kbar after holding for 24 hr under these conditions.

results as a function of temperature. The ferromagnetic ordering temperature (135K at 9.8 kOe) which we observed for the spinel phase is within the range of 130–142K values reported in previous work (*18*), while the magnetic moment is slightly lower than expected.

A sample of the monoclinic phase with 5–10% of spinel phase (estimated from the X-ray diffraction pattern) was prepared by annealing the pure monoclinic sample at 125C for 35 hr. This sample had a magnetic susceptibility that changed with temperature characteristic of both phases with the appropriate Curie and Néel temperatures. The relative susceptibility with field at 77K is the upper curve of Fig. 5. It shows magnetic saturation at low-field caused by the ferromagnetic spinel portion of the sample followed by a linear portion at higher fields similar to the curve for the pure monoclinic phase. In samples with larger amounts of the spinel phase the magnetic behavior of the monoclinic phase was completely obscured. Some samples had been shown to contain traces of Cr_2Se_3. We found this compound to order antiferromagnetically at ~25K. A sample containing 5 wt% Cr_2Se_3 mixed with the pure monoclinic phase showed two Néel temperatures, one at ~25K and one at ~55K. This indicates that the antiferromagnetic ordering observed in the monoclinic phase was not due to this impurity.

Discussion

The high-pressure transformation of $CdCr_2Se_4$ from the spinel to the monoclinic structure is the same as the transformations previously reported for MCr_2S_4 compounds where M is Mn, Fe, Co, and Cu (*9–11*). The P–T phase diagram for $CdCr_2Se_4$ is similar to the one found for $FeCr_2S_4$ (*9*) except for the slope of the phase boundary, which is much steeper for $FeCr_2S_4$. This transition at pressure is consistent with the increase in coordination number of the A, B, and X atoms, respectively, from 4, 6, 6 in the spinel to 6, 6, 6 in the defect-NiAs structure. Both $CuCr_2Se_4$ and $CuCr_2Te_4$ have a similar transformation, but under the conditions of preparation (*9*) they appear to have the disordered hexagonal structure rather than the ordered monoclinic structure. Since $CuCr_2S_4$, when treated at 65 kbar and 1000C, also gave primarily the hexagonal structure, Cu atoms appear to prefer a disordered array rather than to order on specific planes in the structure.

$ZnCr_2S_4$ was found not to transform but to retain the spinel structure even after annealing at 1500C and 65 kbar (*10*). Since Zn^{++} has nearly the same ionic radius as Fe^{++}, which does transform, and as Ni^{++} (Ref. *19*), which is monoclinic at ambient conditions, the Zn^{++} ions apparently have an extremely strong preference for tetrahedral symmetry. It is therefore unlikely that $ZnCr_2Se_4$

TABLE II

MAGNETIC PROPERTIES OF $CdCr_2Se_4$

	Spinel	Monoclinic
Magnetic moment (4.2K)	$5.55\mu_B$	$0.035\mu_B$
Magnetic ordering temp.	135K (Curie point)	55K (Néel point)

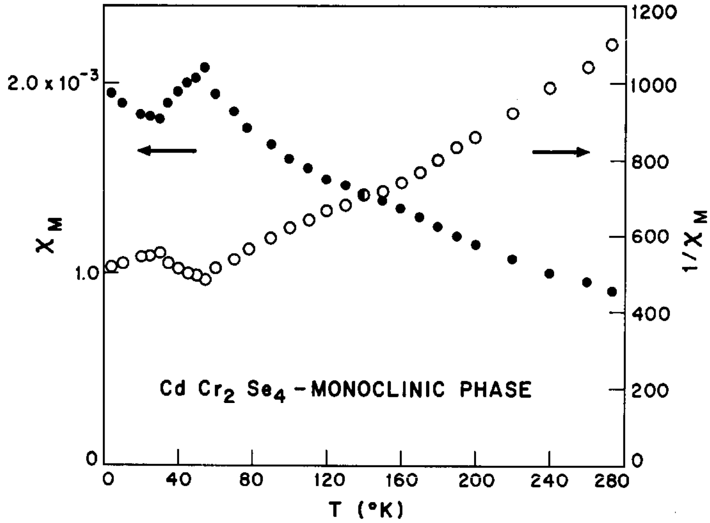

FIG. 4. Magnetic susceptibility and reciprocal susceptibility vs. temperature for high pressure monoclinic phase of $CdCr_2Se_4$. ●—χ_M; ○—$1/\chi_M$.

would be forced into a high pressure structure of the NiAs type.

The lattice parameters suggested for the high pressure monoclinic phase of $CdCr_2Se_4$ indicate a much larger unit cell than that reported for the $Cr_3Se_4(CrCr_2Se_4)$, $FeCr_2Se_4$ and $NiCr_2Se_4$. However, the divalent Cd^{++} ion is appreciably larger than the other divalent ions (*19*), and the atomic weight of Cd is also greater. The fit obtained with parameters of the same magnitude as those reported for the Fe/$NiCr_2Se_4$ was quite good for lines occurring at $2\theta > 25°$; however, the calculated density was then much greater than the very reproducible measured density. The discrepancy in density cannot be explained by voids, since the samples are not porous, nor by impurity since the magnetic measurements are sensitive to contaminations of small amounts of spinel. Additionally, the few lines observed at $2\theta < 25°$ could only be indexed if the larger parameters were used.

The resistivity of the spinel phase of $CdCr_2Se_4$, when it shows *p*-type conduction, varies by about six orders of magnitude depending on the doping atom and level (*20*). Since our samples are *p*-type, variations in resistivity of a factor of three for the spinel samples and a factor of ten for the monoclinic samples are not surprising. The resistivities of the monoclinic samples are about an order of

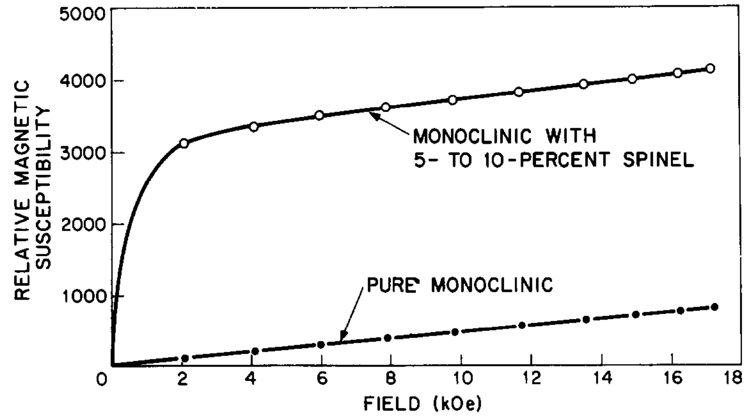

FIG. 5. Magnetic susceptibility as a function of magnetic field for two samples of the high-pressure phase of $CdCr_2Se_4$. ●—pure monoclinic; ○—monoclinic with 5–10% spinel.

magnitude higher than those for the monoclinic thiospinels and have a much lower temperature coefficient than that for the thiocompounds. The Seebeck coefficients for both phases of $CdCr_2Se_4$ are of the same magnitude as for $NiCr_2Se_4$ and Cr_3Se_4 (*16*). The overall electrical properties do not show whether the monoclinic phase of $CdCr_2Se_4$ is a semimetal or a heavily-doped degenerate semiconductor.

The observation of antiferromagnetic ordering in the monoclinic phase of $CdCr_2Se_4$ shows that this compound behaves in the same manner as do the monoclinic sulfides MCr_2S_4, where M is Mn, Fe, Co, or Ni, although the antiferromagnetic ordering temperature (55K) is much lower than those for the sulfur compounds (*21*). In the case of $CdCr_2Se_4$, we were able to get a sample completely free of the spinel phase so that the Néel point is well defined, and we do not have to make a correction for the contribution of the spinel phase with its very large ferromagnetic moment as has been done for the sulfides (*18*). A ferromagnetic ordering transition and partial or complete obscuring of the antiferromagnetic ordering was found in specimens that showed no spinel phase by X-ray diffraction. Thus, the presence of the spinel phase in amounts $<5\%$ can be detected by magnetic measurements when they cannot be observed by X-ray diffraction techniques. The presence of the spinel phase was not the result of slow retransformation from the monoclinic phase, since the specimen that was free of the spinel phase had been kept at room temperature for nearly a year while the samples with it were only ~2 months old.

The low magnetic moment for $CdCr_2Se_4$ and the antiferromagnetic ordering could be explained in two ways. The defect-NiAs structure is the result of ordering of divalent ions (Cd^{++}) and vacancies on planes between the planes of trivalent ions (Cr^{+++}) (*1, 2*). Therefore, the alternate planes of Cr ions could have their magnetic vectors opposed as suggested by Bertaut *et al.* (*22*) for Cr_3S_4 and Cr_3Se_4. On the other hand, alternate Cr^{+++} ions within each plane $(10\bar{1})$ could have their spins aligned in opposition so that the overall structure had antiferromagnetic behavior. However, this latter alternative is improbable since there is no reason to expect that the 90° cation–anion–cation interactions within the basal planes are not ferromagnetic, as in the spinel phase.

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