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	

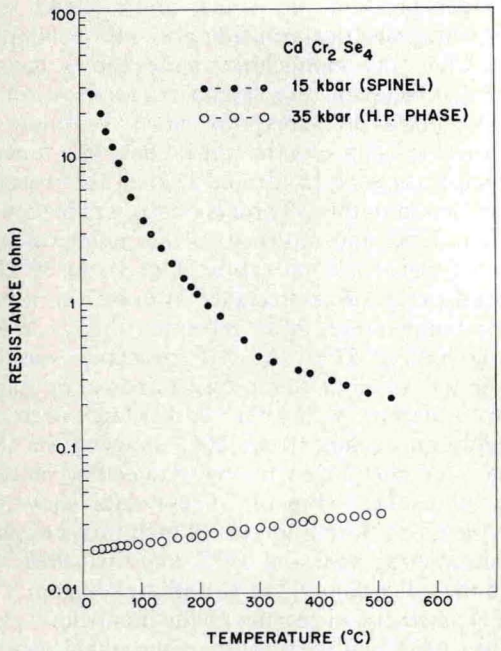


FIG. 3. Electrical resistance vs. temperature for a sample of $CdCr_2Se_4$ at 15 kbar and 35 kbar. ●—heating to 525C at 15 kbar; o—cooling from 507C at 35 kbar after holding for 24 hr under these conditions.

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)