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THERMAL AND STRUCTURAL ANALYSIS OF THE EFFECTS OF CHLORINE IMPURITIES ON PRESSURIZED CADMIUM SULFIDE

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Anomalous large diamagnetism ($\chi \sim 0.25/4\pi$ cgs units) and large positive magnetism ($\chi_V \sim +10^{-4}$ cgs units) have recently been reported in pressure quenched CdS polycrystalline samples by Homan and MacCrone. These effects were shown to be sample material source dependent, and as a first step toward characterizing these samples, we compared the thermal and structural properties of various CdS samples before and after pressurization. Samples

(CONT'D ON REVERSE)

20. Abstract (Cont'd)

containing up to 6 wt % Cl were prepared by precipitation from a chloride containing aqueous bath. We find that (i) Cl impurities are probably present in the form of a complex which can decompose on heating to CdS + $CdCl_2$, (ii) melting of a portion of the samples containing high levels of Cl occurs at 535°C and is attributed to the eutectic temperature of the CdS + $CdCl_2$ mixture, and (iii) heating beyond 535°C produces complete volatization of the $CdCl_2$ component. The results on samples prepared by mixing of CdS and $CdCl_2 \cdot H_2O$ were examined and found to have similar thermal behavior. The cadmium sulfide used in the previous magnetization study was examined and, based on the similarities in the thermal and structural properties, we conclude that the samples which exhibit the anomalous magnetic effects were also prepared by precipitation. In agreement with earlier studies, metastable phases are observed after various pressurizations to above 4.0 GPa.

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INTRODUCTION

Cadmium sulfide (CdS) exhibits a well known semiconducting to conducting transition near 3.0 GPa at room temperatures.[1] Anomalous magnetic effects including both large diamagnetism[2-4] and large positive magnetization[2,3,5] are observed in some CdS samples after "pressure quenching" from above this transition. Other CdS sample material, differing only slightly in the impurity spectrum of the heavy elements, show the normal diamagnetism of CdS after similar pressure treatments.

The CdS materials used in the Homan and MacCrone study[5] exhibit electrical resistivity as a function of pressure which differs from that of high purity CdS. These results agree with the earlier work of Miller et al[6] who found that the presence of chlorine (Cl) in precipitated samples strongly affects the electrical transport of pressurized CdS. Structural studies have been published on similar impure CdS materials,[6,7] but more detailed information is required to help establish the origin of these interesting magnetic effects.

Cadmium sulfide normally has the wurtzite (hexagonal) and/or the zinc-blende (cubic) structure at atmospheric pressure. A transformation to a high pressure phase having the NaCl structure occurs near 3.0 giga pascals (GPa).[8] The earlier structural studies[6,7] have shown that the high pressure sodium chloride (NaCl) phase can be retained in CdS samples which have been prepared from aqueous baths containing chlorine.

References are listed at the end of this report.

This study will present thermal and structural results in pressure treated CdS samples which have high Cl levels due to the sample material preparation technique and in the materials used in the earlier magnetic studies. A separate communication will present magnetic moment studies in pressure treated samples of CdS starting materials containing chlorine.

EXPERIMENTAL

The CdS samples in this study are precipitated powders with high chlorine content, prepared for us by the National Bureau of Standards. Also included are powders from Alpha Inorganics and granules from the Eagle-Picher Company. A variety of analyses have detected little difference between the three sources in the impurity levels of the heavier elements;[2-4] the most significant difference is in the chlorine content:[9] Eagle-Picher < 0.01 wt % Cl; Alpha-Inorganics ~ 1 wt % Cl; NBS ~ 6 wt % Cl.

Our samples were processed in the same manner as that which produced the magnetic anomalies.[2-5] CdS pellets were pressurized in a gasketed Bridgeman anvil device which was arranged to permit release of the applied load in the region of the Wurtzite → NaCl transformation at ~3.0 GPa, at rates up to $\sim 10^6$ bar/sec. After the pressure treatment, the pellets were removed and analyzed by differential scanning calorimetry (DSC) in pure argon using a Dupont 990 Thermal Analyzer. Debye-Scherrer x-ray diffraction patterns were recorded for portions of each sample before and after the DSC runs. The starting materials were also analyzed by DSC and x-ray diffractometry.

RESULTS

DSC and X-Ray Diffraction on As-Received CdS

The DSC traces shown in Figure 1 are representative of more than 30 traces on as-received and pressurized CdS. The as-received Alpha Inorganics powders (curve A) produce a sharp endotherm at 535°C (typically, 2 cal/gm). This is reversible as shown in the (dotted) cooling curve, provided the temperature is not increased further; heating to ~600°C completely removes this peak in subsequent DSC runs in the sample. (Occasionally, a small endotherm is also seen at 550°C in some samples.) The same endotherm at 535°C occurs with the NBS powders but the magnitude is much larger (~ 10 cal/gm) and thus varies directly with the Cl impurity level. Inspection after heating showed that much of the NBS sample had melted. This is consistent with the endotherm at 535°C which is observed with the Alpha Inorganics and NBS powders. Pure CdS does not melt at atmospheric pressure but instead sublimes at 980°C.

Weight loss measurements show that components of the melt sublime or decompose and evolve volatile products on heating beyond 535°C. This weight loss is typically 2% for the Alpha-Inorganics powders and 16% for the NBS powders. Thermogravimetric analysis indicated that the bulk of this weight loss occurs between 535 and 625°C. Using an electron microprobe, we found that all of the chlorine is driven off on heating beyond 535°C (i.e. 600°C).

The x-ray diffraction results provide further information on the nature of the chlorine impurity. The as-received CdS from the three sources give only Wurtzite lines in diffractometer scans. The only observable difference is the broader and weaker lines of the Cds which contains Cl impurities. (The broadest and weakest lines occur with the NBS powders.) Heating the as-received chlorine containing CdS to ~600°C produces no changes aside from line sharpening; however, heating up to the melting point (535°C) but not beyond, produces cadmium chloride lines in the x-ray patterns; the compound detected after removal from the DSC is $CdCl_2 \cdot H_2O$. The hydrate is observed presumably because the $CdCl_2$ is very hygroscopic. (The dehydration peak is found to occur at ~120°C on a subsequent DCS trace.)

The observation of $CdCl_2$ after heating indicates that it is a thermal decomposition product because the high solubility of $CdCl_2$ in water precludes its co-precipitating simply as $CdCl_2$ with CdS in the aqueous bath during the preparation of the powders. To further substantiate this, we heated NBS powders to 450°C and then washed them in water and found all traces of $CdCl_2$ had been removed; for example, no evidence of the melting peak at 535°C could be found with these annealed and washed powders. By contrast, washing unannealed NBS powders has no significant effect on the chlorine level. Thus, heating decomposes the original Cl compound into a CdS + $CdCl_2$ mixture which can then be washed to remove the $CdCl_2$.

We also observed that mixing pure $CdCl_2$ and pure CdS in the approximate proportions present in our samples produces the same melting peak at 535°C that we observe in our samples. This supports the x-ray results and indicates that 535°C is the eutectic temperatue of the CdS + $CdCl_2$ mixture.

Regarding the weight loss on heating beyond 535°C, we performed several measurements on NBS powders in an Aero-Vac mass spectrometer-type gas analyzer and could detect no gas evolution on heating to 600°C. The volatile component is thus in the form of a chlorine compound which condenses on the cooler sur-

surfaces. Samples heated to 600°C showed no evidence of $CdCl_2$ in the x-ray patterns, which is in accord with the microprobe measurements.

The results on the Eagle-Picher granules are consistent with the above: the as-received granules have a very low chlorine content, (< .01%) and exhibit no measurable thermal effects (curve B) and negligible weight loss (< .05%) on heating to 630°C.

DSC and X-Ray Diffraction Results on Pressurized CdS

After pressurization to 4.0 GPa, new DSC peaks are observed at ~200°C and/or 400°C in CdS samples from all three sources. The nature of the peaks, however, is very sensitive to the Cl impurity levels in the as-received CdS. As shown in curve C, Alpha Inorganics samples which have been "pressure-quenched" from ~4.0 GPa give a broad shallow exotherm centered at ~ 200°C (~0.3 cal/gm) and a relatively large exotherm at ~400°C (~1.3 cal/gm). With the NBS powders, the 200°C exotherm is much larger (~11 cal/gm) while only a suggestion of an exotherm is observed at ~400°C. Similar "pressure-quenching" of Eagle-Picher samples yields only a broad shallow exotherm at 300-400°C.

The x-ray data again give the origin of the various DSC peaks. The x-ray lines from the pressurized samples are more diffuse than those of the as-received samples but are still clear enough to establish the predominant phases. It should be noted, however, that small quantities (5-10%) of additional phases may remain undetected even after five to six hour exposures because of the general diffuseness of the lines.

After pressurization to 4.0 GPa, the Alpha Inorganics powders retain a mixture of ZnS and NaCl phase as metastable phases; judging from the relative line intensities, ZnS is predominant. The largest effect is found with the

NBS powders: pressurization to 4.0 GPa results in retention of the high-pressure NaCl phase; no other phases are detected. Similar pressurization of the Eagle-Picher granules leads to retention of ZnS and Wurtzite structures with no indication of the NaCl phase; as with the Alpha-Inorganics powders, the predominant phase is ZnS.

We heated these samples in the DSC up through each of the DSC peaks and immediately cooled to room temperature to determine the structural changes associated with each exotherm: the 200°C exotherm in the NBS and Alpha-Inorganics powders reflects the NaCl → Wurtzite transformation; the 400°C peak is due to the ZnS → Wurtzite transformation. The relative magnitudes of these two DSC peaks seem to correspond roughly to the relative retained percentages of the ZnS and NaCl phases. The presence of Wurtzite and the broad ZnS → Wurtzite exotherm in the Eagle-Picher samples probably reflect a lower stability of the retained ZnS phase because of their higher purity.

Results of additional tests are as follows: (i) "Pressure quenched" Alpha-Inorganics samples which had previously been heated to 600°C to drive off the chlorine compound give only ZnS and Wurtzite lines; the NaCl phase is no longer retained. Thus, driving off the volatile impurity produces the same behavior as that of the pure Eagle-Picher CdS, indicating that this is an effective purification procedure; (ii) Alpha Inorganics samples pressurized up to (but not beyond) the NaCl transformation retain the original Wurtzite structures; (iii) No dependence on "pressure-quench" rate is detected in either the x-ray patterns or the DSC traces.

It should be noted that we often observe superstructure lines in the x-ray patterns of as-received and/or pressure-quenched CdS samples from the three sources. The corresponding d-spacings are approximately three times larger than those of the most intense lines of the various CdS phases. Similar observations were reported by Corll.[7] At present, the origin of these lines is unexplained and their presence does not appear to correlate with any measured physical property of the sample.

SUMMARY AND DISCUSSION

Several of our results are similar to those previously reported. In particular, the retention of ZnS and NaCl phases after pressurization of impure CdS is well documented.[6,7] The present study extends these earlier results in providing more specific information on the interaction of the chlorides with CdS in the as-received and pressure-treated conditions.

Our results are consistent with the suggestion of Miller et al[6] that a complex compound involving cadmium, chlorine and sulfur is present in the precipitated CdS. The appearance of $CdCl_2$ on heating, for example, can be explained as due to the decomposition of this complex compound. The severe line weakening and broadening of the high Cl samples suggests that this complex has a highly disordered structure.

The melting of the chlorine containing CdS at 535°C results from the mixture of CdS + $CdCl_2$; this is apparently the eutectic temperature. The weight loss after melting and the absence of chlorine in the sample after heating to 620°C indicates that most of the $CdCl_2$ has evaporated from the melt. Miller et al[6] observed that heating to 700°C under an 0.1 GPa pressure produced $CdCl_2$

crystallites in the CdS powders that contained chlorine. Thus, pressurization of 0.1 GPa is sufficient to prevent the evaporation which we observe at atmospheric pressure.

The transformation of the metastable NaCl phase, which is retained after pressurization to ~4.0 GPa, occurs between ~ 150-300°C according to the DSC and x-ray results (heating rates: 20°C/min). The zincblende → wurtzite transformation occurs in the 350-450°C region. The stability of these phases in the impure CdS can be attributed to the presence of the complex compound.

The detailed study of the nature of the chlorine impurity and its effect on the properties of CdS was motivated in part by the reported magnetic anomalies in CdS powders containing chlorine. Information on the preparation technique could not be obtained for the Alpha Inorganics powders which exhibit the interesting magnetic anomalies. However, it is quite clear from the similarities in the structural and thermal properties of the Alpha Inorganics and NBS powders that the former were also prepared by precipitation in an aqueous bath containing chlorine.

The presence of a complex and the retention of the high-pressure phase in CdS after pressurization correlates with the existence of magnetic anomalies in "pressure-quenched" Alpha Inorganics CdS. However, this cannot yet be considered a significant factor since, for example, the magnetic effects are sensitive to "pressure-quench" rate while the structural effects are not; also, the magnetic effects vary over relatively short times while the structural features do not. A more extensive study of the relationships between the magnetic effects and the structural properties reported here is in progress.

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EXPLANATION OF FIGURE 1

The differential heat flow Q (in arbitrary units) between sample and standard is plotted against temperature. Curve A is the result for the as-received Alpha Inorganics CdS powders; the dotted trace is the cooling curve, illustrating the reversibility of the reaction at 535°C. Curve B is the result for the as-received Eagle-Picher CdS granules; a broad shallow exotherm occurs between ~ 300 to 450°C after pressurizing these granules to 40 kbars. Curve C shows the new exotherms at ~ 150 to 250°C and at ~ 400 °C that occur after pressurizing the Alpha Inorganics powders to 40 kbars.

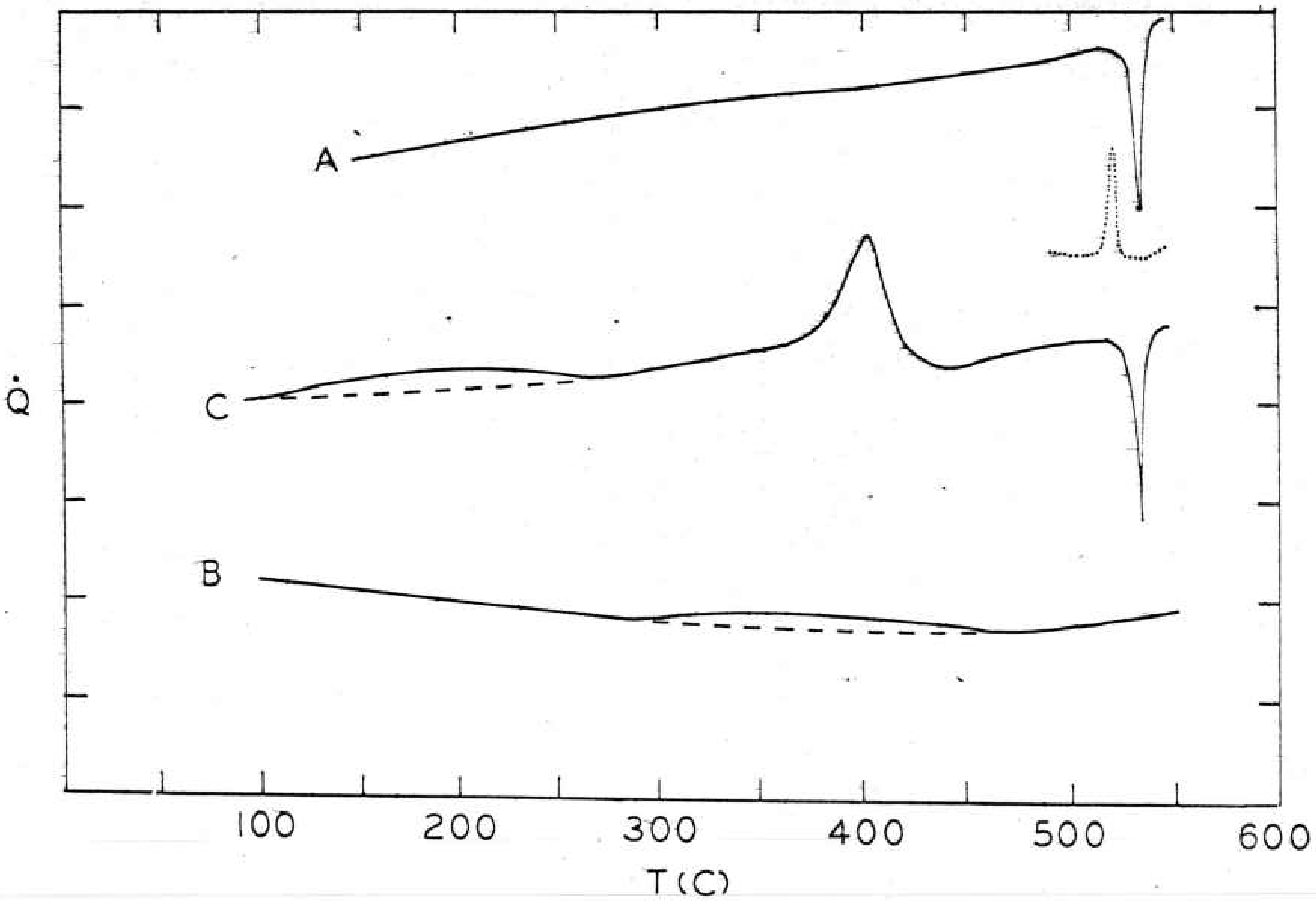

Figure 1. Differential Heat Flow $\dot{Q}$ versus Temperature
(See explanation on previous page.)

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