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Magnetic behavior of pressure-quenched CdS containing Cl

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Pressure-quenched CdS containing Cl has been shown previously to exhibit both very large diamagnetism and paramagnetism. The diamagnetism observed at 77 K approached Meissner proportion and suggested superconductinglike behavior in this material. The effect is known to depend sensitively on the Cl content of the starting material. This paper describes the results of a survey of the magnetic behavior of pressure-quenched samples prepared from CdS systematically doped with increasing amounts of Cl. The Cl-doped material was prepared in a variety of ways: from mixtures of CdS and $CdCl_2$, by precipitation from aqueous solution, and by acid doping. The differently doped starting materials were analyzed for Cl and other impurities before being pressure quenched. The magnetic susceptibilities were subsequently measured. The results of the survey indicate that the concentration of Cl required to produce specimens with anomalously large magnetism is 0.75 ± 0.10 wt. %. The technique for the preparation of such material is described.

I. INTRODUCTION

Recently, dc flux exclusion approaching Meissner proportions in pressure-quenched CdS materials at 77 K has been reported.[1] Corroboration of these results has been provided by the work of Nam *et al.*, who found strong ac diamagnetism in several samples of CdS materials that had also been rapidly pressure quenched.[2] Cuprous chloride has also displayed similar diamagnetism after being subjected to rapid temperature variations while under pressure.[3]

Several theoretical models have been proposed to explain this anomalous diamagnetic behavior including surface superconductivity,[4] pairing of holes in semiconductors,[2] finite-momentum pair binding in a one-dimensional system,[5] and an excitonic mechanism for superconductivity related to the presence of impurities.[6]

In the magnetically active CdS materials, it was also found that anomalous and very large paramagnetism occurred in some of the pressure-quenched samples.[7] The most recent work describes the simultaneous decrease of both the ac and dc electrical conductivity with the loss of flux exclusion, which supports the claim of some form of collective behavior in such materials.[8,9] Both the anomalous diamagnetism and paramagnetism were found to be metastable.[10] The magnetically active samples had a morphology of lenticular platelets embedded in a polycrystalline matrix[11] and contained a mixture of wurtzite (Greenockite), zinc-blende (Hawleyite), and NaCl crystal structures. The magnetic effects were also found to be dependent on sample material origin and chemistry.[1,7–10]

In all the previous work published by the present authors, these unusual electrical and magnetic properties were observed in samples made from a single lot of commercial high-purity CdS powders obtained from Alpha Inorganic (AI) and only after rapid pressure quenching (greater than 10^5 bar/sec) from above the well-known wurtzite-to-NaCl phase transition at ambient temperatures.[12] These anomalous phenomena were *never* observed in samples made from any source other than the particular lot from AI or in any samples which were slow quenched from above the high-pressure transition.

It is thus clear that the anomalous behavior depends on both the sample chemistry and pressurization parameters. Here we describe our investigation of the chemistry of the as-received materials used in the previous work and identify the critical chemistry involved in the phenomena. This chemistry was determined by the correlation of the electrical and magnetic properties with the sample impurities and dopants of both as-received and -prepared materials. We will also describe material-preparation techniques which provide samples which gave similar anomalous results after pressure quenching. Other physical properties which depend on the sample chemistry, as well as the resulting morphology, are described.

The implications of these material studies will be discussed. A tentative model relating to metastable phase decomposition (NaCl phase) will be suggested to explain the correlation between sample chemistry and morphological behavior after various pressure treatments.

II. CHEMICAL ANALYSIS OF AS-RECEIVED CdS MATERIALS

Since a qualitative analysis of the magnetically active AI and nonactive Eagle Picher (EP) materials by a sparkemission technique did not show any appreciable difference in the metallic impurity spectrum,[10] a more comprehensive chemical analysis was performed by the National Bureau of Standards (NBS) on these materials and on other magnetically nonactive sample materials.

Initially, a qualitative evaluation by x-ray fluorescence (XRF) was made using both energy- and wavelength-dispersive spectrometers. This technique has detection limits of the order of 1—10 ppm for all elements $Z > 11$. Trace elements Cl, K, Fe, Cu, Zn, and Ge were detected near the limit of detection by XRF in the magnetically active AI material suggesting that impurity levels were of the order of 10 ppm.[1]

Both pressed starting pellets and pressure-quenched samples of the various as-received materials were further analyzed by electron-probe microanalysis with dispersive x-ray spectrometry (EDS). In general, this technique is sensitive to all elements $Z > 11$ with a limit of detection of the order of 0.1 wt. % and a sampling depth of about 1 μm. Five samples were examined on the outer surfaces or on freshly exposed fracture surfaces using the NBS theoretical-matrix frame-P procedure for rough surfaces.[13] Frame P is believed to have an error distribution within 20% relative.

Six pressure-quenched samples (three each from the AI and EP material) were metallographically cross-sectioned and analyzed, corresponding to interior and near-surface regions of the samples. Quantitative analysis of these samples were made using NBS frame-C procedures.[14] Frame-C procedures yield an error distribution such that 95% of all samples fall within 5% relative to the amount present on metallographically polished surfaces.

The metallographically mounted samples were further analyzed by an ion-microprobe analysis (IMA). This analytical technique has very high sensitivity (typically 1 ppm) for all elements of the Periodic Table.

The result of these extensive analyses were that the magnetically active AI starting powder had substantial levels of Cl impurities in addition to the trace metallic impurities reported earlier.[10] The quantitative analyses by EDS and IMA technique revealed that the Cl levels in pressure-treated and magnetically active AI materials was about 1.0 wt. % and that the Cl was distributed nonuniformly within the samples. The nonactive materials, especially the EP material, showed *no* detectable Cl contamination within the combined sensitivities of the EDS and IMA techniques. This analysis shows that Cl levels, if present, were below 0.01 wt. % in the nonmagnetic materials such as the EP materials.

Si was also detected in the pressure quenched samples from both AI and EP materials. The EDS technique indicated that Si was also distributed nonhomogeneously in the samples with an average level of 0.15 wt. % in the AI materials and 0.05 wt. % in the EP materials. Since Si was not detected in the as-received powders from these sources, we concluded that the Cl impurity contamination was critical in producing the magnetic anomalies. Si may have been introduced by either exposure to the pyrophyllite gaskets used in pressurizing the samples or from the silicone grease used to mount the samples for the magnetic measurements after pressurization before chemical analysis. This conclusion was supported by the fact that samples containing Si introduced by either means did not show magnetic anomalies when the Cl content differed significantly from the AI material.

III. PREPARATION OF Cl-DOPED CdS MATERIALS

In view of the above results, a variety of preparation techniques were used in an attempt to make suitable doped materials. Earlier differential scanning calorimetry (DSC) results had suggested that the active AI material had been prepared by a precipitation technique.[15]

A. Mixtures of CdS and $CdCl_2$ powders

Pure CdS powders (EP) were mixed with reagent-grade $CdCl_2$ powders to yield nominal Cl contents of about 1.0, 1.5, and 2.0 wt. % of the mixture. The thermal properties of these materials, both in the as-prepared and in the as-quenched condition were measured by the DSC technique described elsewhere.[15] The only peaks observed were the dehydration peak at 100 °C from the hydrated $CdCl_2$ powder and the eutectic melting peak at 535 °C of the mixture suggesting that the NaCl high-pressure phase was not retained after pressure quenching. None of these materials exhibited anomalous magnetism after pressure quenching.

B. Precipitation reaction

The standard procedure of producing CdS materials by precipitation from a hydrous $CdCl_2$ solution using H_2S gas was used. Small batches (~ 100 ml) of $CdCl_2$ solutions with starting molarities in the range 0.1—1.0M with respect to Cl were prepared. These solutions had the natural pH of solution. Precipitation of CdS materials from these solutions at ambient temperatures occurred when the insoluble CdS precipitated as H_2S gas was slowly bubbled through the solution. The CdS precipitate contained between 0.5 and 4.11 wt. % Cl varying roughly with the molarity of the starting solution. The nominal Cl and S contents were determined by an ion-chromatography method developed by NBS.[16] Ultrasonically washing the precipitate in distilled water revealed that roughly half of the Cl content was easily removed. The remaining Cl is probably incorporated in the CdS lattice.

Both pellets and pressure-quenched samples made from these materials were studied by DSC and their behavior was similar to the behavior of the AI material reported earlier.[15]

Some variability in Cl conent within each precipitate aliquot occurred suggesting that critical chemical parameters, such as the decrease in molarity as the reaction proceeds, were affecting the Cl content of these batch-produced materials.

An analysis of the various ionic species present in the aqueous solutions of $CdCl_2$ was made using equilibrium constants (K_i) in the following set of competing reactions:

$$Cd^{2+}+Cl^{-}\overset{K_1}{\rightleftarrows}CdCl^{+}, \quad K_1=21.0 \tag{1}$$

$$Cd^{2+}+2Cl^{-}\overset{K_2}{\rightleftarrows}CdCl_2,\quad K_2=166.0 \tag{2}$$

$$Cd^{2+}+3Cl^{-}\overset{K_3}{\rightleftarrows}CdCl_3^{-},\quad K_3=204.0 \tag{3}$$

$$Cd^{2+}+4Cl^{-}\overset{K_4}{\rightleftarrows}CdCl_4^{2-},\quad K_4=7.15 \tag{4}$$

which can be expressed in the generalized form

$$Cd^{2+}+nCl^{-}\overset{K_n}{\rightleftarrows}CdCl_n^{(-n+2)},\quad K_n,\ n=1,2,3,4\ . \tag{5}$$

The fraction α_n of a particular equilibrium species present in solution can be given as

$$\alpha_n=\frac{[CdCl_n]}{C}=K_n[Cl^{-}]^n\alpha_0\ ,$$

where

$$\alpha_0=\frac{[Cd^{+2}]}{C}\ ,$$

and C is the total concentration of cadmium-containing species. Given the initial Cd^{+2} and Cd^{-} concentration, the equations can be solved for α_n. The results for various $CdCl_2$ molarities are shown in Fig. 1. The wide variation in the different ion species especially in the region of molarity below 0.5M where the magnetically active AI materials were produced is quite apparent. It is not clear which ion or combination of these ions produces the necessary complex in the precipitate which yield anomalous magnetism after pressure quenching.

A preliminary examination of the precipitated materials by transmission-electron-microscopy (TEM) and small-angle x-ray-scattering techniques showed the presence of small spherical crystallites (diam. ~50 Å) in the precipitated powders in good agreement with the results of Sato, Itoh, and Yamashita.[17]

Examination of these materials by DSC show only the eutectic melting peak associated with a mixture of $CdCl_2$ and CdS, indicating that the initial complex compound decomposed to a simple mixture upon heating; no dehydration peak was observed, which indicates that the as-precipitated powders are not a simple mixture of CdS and $CdCl_2$. These results were also obtained on the magnetically active AI starting powders.[15] Pressure-quenched samples of the precipitated powders containing Cl > 0.7 wt. % exhibited the exothermic peak associated with the transformation of the metastable NaCl high-pressure phase. Pressure-quenched samples made from powders containing less than 0.7 wt. % Cl showed a retained NaCl phase in addition to the wurtzite and zinc-blende phases by both x-ray examination and optical evidence of small platelets. The magnetic behavior of pressure-quenched samples of these materials are shown in Fig. 2 and will be discussed subsequently.

IV. ACID-DOPING TECHNIQUE

Samples of pure CdS were stirred and heated with various HCl and NaCl solutions to determine whether Cl^{-} could be incorporated directly into the CdS lattice. This technique produced CdS materials containing Cl levels of about 0.1 wt. %. Again about 50% of the Cl content could be removed by ultrasonically washing the powders in distilled water. It was not possible to obtain Cl contents above 0.2 wt. % by this technique.

DSC analysis of the acid-leached samples revealed no eutectic melting peak at 535 °C in the precipitate powders and a broad weak exotherm centered around 350 °C in pressure-quenched samples. This indicates retention of only a small quantity of the zinc-blende phase, characteristic of very pure CdS.[15] Metallographic examination of the samples revealed a small fraction of platelets after quenching, which suggests a retained NaCl phase in these samples which was below the sensitivity of the DSC technique.

The magnetic behavior of pressure-quenched samples made from these materials are shown in Fig. 2 and are discussed subsequently.

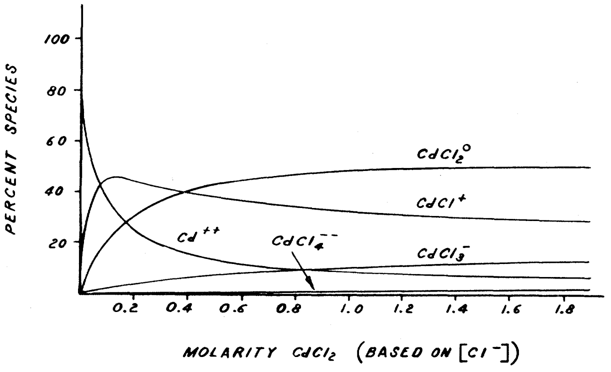

FIG. 1. Variation of ionic species present in aqueous solution of $CdCl_2$ as a function of the molarity of solution based on [Cl^{-}] chloride-ion concentration in mole/l.

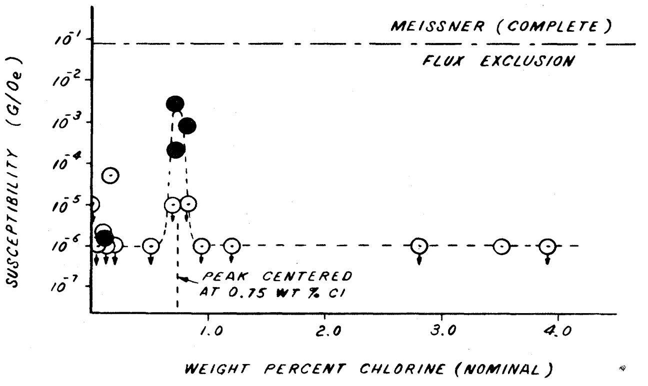

FIG. 2. Mean value of the absolute magnetic volume susceptibility from each sample lot is plotted as a function of the nominal Cl content of the lot. Solid symbols represent the mean value determined from 10 or more observations on a particular sample lot as tabulated in Table I. Of the 115 observations represented in this figure, all but nine measurements which were measured at liquid-He temperatures in either the SQUID or ac magnetometers; the rest were measured at liquid-N_2 temperatures.

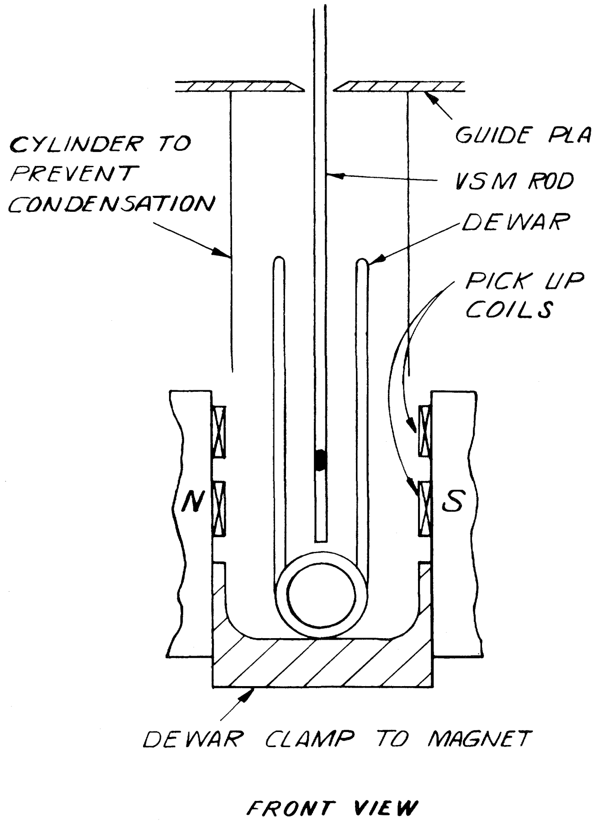

FIG. 3. Schematic of the sample chamber of the VSM. A Helitran cryogenic cooling system was used to provide the liquid-N_2 measurement temperatures.

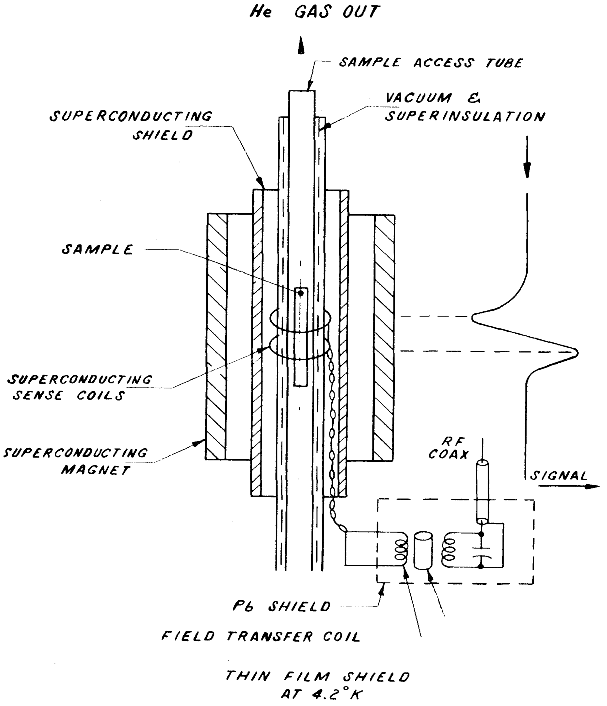

FIG. 4. Schematic of SQUID magnetometer used at liquid-He temperatures. Typical signal generated as the sample is drawn through the sense coils is shown at right.

V. MAGNETIC MEASUREMENTS

The dc magnetization as a function of magnetic field was determined by either a vibrating-sample magnetometer (VSM) or a superconducting quantum interference device (SQUID) magnetometer. The ac susceptibility was determined using the Hartshorn bridge described earlier.[11]

The VSM measurements reported here were made in a variety of sample chamber configurations. The configuration shown in Fig. 3 was used for more than half the samples tested. A modification of this basic design was used to measure the simultaneous changes in electrical conduction and magnetic moment of 17 samples reported elsewhere.[8,9] In all sample configurations, the magnetic moment was measured using field sweeps below 100 Oe/min and no systematic errors were observed.

The first nine samples measured in the VSM were mounted in a Teflon sample holder which placed the samples in a random orientation with respect to field. This random orientation was fixed for each measurement, however. Sample CdS No. 51, which was measured in the Teflon sample holder, was examined for field-orientation effects. At high field (greater than 1000 Oe) this sample exhibited large paramagnetism. By rotating the VSM vibrator about the axis of the sample rod we observed a large but reproducible variation in magnetic moment at constant field. A cursory examination of our sample geometry suggested that the maximum moment occurred when the field was oriented in the plane of the sample. All subsequent sample holders were designed to align the field with plane of the disc samples. Therefore, all subsequent samples were measured in this manner.

The SQUID magnetometer shown schematically in Fig. 4 allowed the magnitude and sign of the magnetic moment to be determined in fields up to 60 kOe at liquid-He temperatures. Both the SQUID and VSM systems were periodically calibrated using Ni and $CuSo_4 \cdot 5H_2O$ as standards. The ac bridge was calibrated using the superconducting transition in a Pb sample. The diamagnetic susceptibilities were determined from either the slope of the measured M-vs-H curves from the VSM or by direct comparison with known standards in the SQUID and ac magnetometers.

For those samples exhibiting paramagnetism in the VSM, the generally small region of low field where the samples were diamagnetic was neglected and the susceptibility was determined by forcing the intercept of the slope to pass through the origin of the M-vs-H plot. In a few cases where this analytic technique could lead to serious error in determining χ, i.e., when the diamagnetism persisted to above 100 Oe before becoming paramagnetic, the actual slope of the M-vs-H plot was calculated. Six such samples were of the latter type and are included in Table I with both their diamagnetic and paramagnetic susceptibilities. The remaining paramagnetic samples had diamagnetic regions of such small extent that it was not possible

TABLE I. Diamagnetic and paramagnetic susceptibilities of pressure-quenched Cds, containing Cl samples.

Sample lot no.	Material source	Cl (wt. %)	Method of preparation	$\lvert\chi\rvert_{\text{mean}}$	$\chi\text{Dia}^{\max}$	$\chi\text{Para}^{\max}$	Number of observations
1	Eagle Picher (EP)	0	n.a.	$<1.0\times10^{-5}$			3
2	Alpha Inorganic (AI)[a]	0	n.a.	$<1.0\times10^{-5}$			2
3	NBS 21A	0.04	acid doped	$<1.0\times10^{-6}$			3
4	NBS 23	0.10	acid doped	$<2.0\times10^{-6}$	-2.0×10^{-6}		1
5	NBS 21	0.13	acid doped	$<1.0\times10^{-6}$			2
6	NBS 22	0.14	acid doped	1.4×10^{-6}	-5.0×10^{-6}		10
7	NBS 26	0.16	acid doped	5.3×10^{-5}	-1.6×10^{-4}		4
8	NBS 25	0.20	acid doped	$<1.0\times10^{-6}$			1
9	NBS 28	0.20	acid doped	1.0×10^{-6}	-1.0×10^{-6}		2
10	NBS 31B	0.50	precipitation	$<1.0\times10^{-6}$			1
11	NBS 5	0.68	precipitation	$<1.0\times10^{-5}$			1
12	NBS 8	0.72	precipitation	2.2×10^{-4}	-1.6×10^{-3}		14
13	AI[b]	0.72	n.a.	2.4×10^{-3}	-4.0×10^{-2}	$+1.4\times10^{-3}$	51
14	NBS 1	0.83	precipitation	7.9×10^{-4}	-7.9×10^{-3}		11
15	NBS 2	0.83	precipitation	$<1.0\times10^{-5}$			2
16	NBS 17	0.93	precipitation	$<1.0\times10^{-5}$			1
17	NBS 31C	1.2	precipitation	$<1.0\times10^{-5}$			1
18	NBS 12	2.8	precipitation	$<1.0\times10^{-5}$			3
19	NBS 20F.5-2	3.5	precipitation	$<1.0\times10^{-5}$			1
20	NBS 11	3.9	precipitation	$<1.0\times10^{-5}$			1

[a] AI stock number 20130, lot number 062778.

[b] AI stock number 20130, lot number 033072.

to determine their diamagnetic susceptibilities.

The average absolute volume susceptibilities of pressure-quenched samples from each sample lot were determined and tabulated in Table I together with source identification, Cl content, preparation technique, the maximum diamagnetic and paramagnetic susceptibilities observed, and the number of observed points.

Not included in this tabulation are the results for an additional 20 samples, which were either starting pellet samples, samples which had been slowly depressurized (less than 10^3 bar/sec) from above the NaCl transition pressure, or samples which had been rapidly quenched from below this transition. These samples were made from various Cl-containing materials described above and none exhibited any detectable anomalous susceptibility in the SQUID or VSM systems.

Only pressure-quenched samples from the AI source containing 0.72 wt. % Cl exhibited both diamagnetism and paramagnetism. The IMA showed that the paramagnetic and ferromagnetic impurity elements in this material were below 20 ppm by weight and cannot account for the large paramagnetic susceptibilities observed here. In addition, the detailed behavior of the paramagnetism observed[7,10] precludes the possibility of sample contamination as being the cause of this anomalous behavior. Of the 51 measurements made on this material we observed anomalous paramagnetism 16 times.

The mean value of $\lvert\chi_v\rvert$ for each sample material lot is plotted as a function of Cl content in Fig. 2. The curve shown is a reasonable fit to these values neglecting the single point at 0.16 wt. % Cl whose value was 5.3×10^{-5} G/Oe. The data shown in Fig. 2 was obtained from 115 observations on 109 different samples. The nominal Cl content is the average Cl determined from several analyses of each sample material lot. The Cl uncertainty was approximately 10% relative in the acid-doped material and approximately 20% relative in the precipitated material.

The mean diamagnetic susceptibility of all observations on sample materials, excluding the magnetically active NBS 1 (sample 14), NBS 8 (sample 12), and AI Lot-033072 (sample 13) materials, was calculated. A mean diamagnetic volume susceptibility of the order of 1×10^{-5} G/Oe was determined using 39 data points which is in good agreement with the volume susceptibility calculated from handbook values of the diamagnetic susceptibility and the mass (~15 mg) of the samples.

VI. PLATELET VOLUME MEASUREMENTS

Quantitative metallography often serves as a sensitive guide to the physical processes that material specimens have undergone and is an especially useful adjunct technique in studying the morphology of samples of different chemical compositions which may have a profound effect on the physical behavior observed.

Fast- and slow-quenched EP samples appeared to be nearly 100% wurtzite phase after quenching. The small amount of zinc-blende phase reported earlier in the x-ray and DSC analysis[15] could not be distinguished by this technique. In both cases, the crystallites were pancake shaped with the axis of rotational symmetry along the load axis. The diameter of the crystallites after fast quenching was about 70 μm and the thickness was about 20 μm. After slow quenching these values became 120 and 30 μm, respectively. It is important to note that over 4 orders of magnitude, change in the depressurization rate

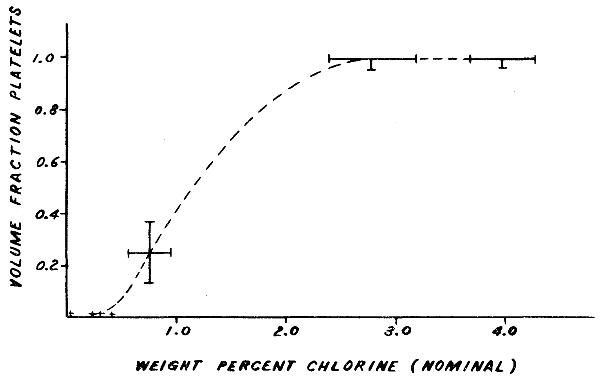

FIG. 5. Volume fraction of NaCl phase (platelets) retained after pressure quenching is plotted as a function of the nominal Cl content.

produced little effect on the grain size observed.

In the AI samples, both the retained NaCl phase (platelets) and wurtzite (and zinc-blende) matrix-phase grain size appeared bimodal, and had similar distributions. Both phases were composed of a mixture of equiaxed crystallites 10—50 μm in diameter and platelets 100—300 μm in diameter and 15—30 μm in thickness oriented roughly perpendicular to the load axis. Fast-quenched and slow-quenched samples were very similar in appearance.

The above results suggested an influence of the specimen composition on the postquench morphology. Microstructural investigation over a wide variation of Cl contents confirmed this suspicion. The volume fraction of NaCl phase (platelet) retained and the microstructural features observed seems to vary continuously with the Cl level of the starting material as shown in Fig. 5.

The internal structure of the NaCl phase (platelets) were studied using optical microscopy and surface-electron-microscopy (SEM) techniques. No discernable microstructure was observed in the platelets to within the resolution of these techniques. The platelets showed little optical rotation in polarized light and were harder than the polycrystalline matrix material. Transverse cracks were generally observed in the platelets which often terminated at the interface between the platelets and matrix material. The latter result is interpreted as evidence of the brittle nature of the platelets and results from the large volume change which occurs in the NaCl-to-wurtzite transition upon depressurization.

Although crystal structure determination of the platelets was not made directly on those samples having less than 20 vol % of platelets, it can be deduced that the platelets are of the retained NaCl high-pressure crystal structure. This deduction is based on the following facts: (i) The platelets of NaCl structure observed in samples highly doped with Cl, where the platelet volume fraction is greater than 90 vol %, were similar in character to the platelets observed in the lower-Cl-content material, and (ii) the qualitative estimate of the amount of quenched-in NaCl phase determined from both the DSC and x-ray measurements were in good agreement with the volume fraction of platelets determined in similar samples. Both sets of measurements correlated with the nominal Cl content.

VII. DISCUSSION OF EXPERIMENTAL RESULTS

Several interesting results are apparent from an examination of these data.

(i) The largest diamagnetism exceeded the largest paramagnetism observed by about an order of magnitude for the AI material containing 0.72 wt. % Cl.

(ii) The large scatter of susceptibilities observed for CdS materials having $0.7 < \mathrm{Cl} < 0.83$ wt. %. If one conservatively defines anomalous magnetic behavior when $\chi_{\mathrm{sample}} > 10\chi_{\mathrm{literature}}$, then the reproducibility of obtaining anomalous behavior was about 57% for this group. A somewhat lower "success" rate was obtained in sample material prepared by techniques described in this paper (about 35%) than in the as-received AI material.

(iii) Another rather subtle result is that, with the exception of a single sample of CdS containing 0.16 wt. % Cl, which was prepared by the acid-doping technique, all magnetically active samples were prepared by precipitation from an aqueous bath and had a nominal Cl content between 0.7 and 0.83 wt. %. (The role of Si in conjunction with Cl, if any, is not known at present.)

(iv) We have not observed lossless electrical conduction in any of our samples.

VIII. DISCUSSION

These results show that the conditions under which the anomalous electrical and magnetic behavior may occur are the rapid pressure quenching (greater than 10^5 bar/sec) from above the wurtzite-to-NaCl phase-transition pressure in CdS samples doped with Cl to levels in the range of 0.75 ± 0.1 wt. %.

The results also show that there is considerable scatter in the measured susceptibilities in this range. The many possible parameters that could generate this scatter are either uncontrollable or uncontrolled under present experimental conditions. The former category includes the possibility of critical ranges in the minor constituents of our material (~ 10 ppm) and quenching defects. The latter category includes the ambient conditions of the material-preparation process, chemical variability of the Cl impurity in samples prepared from the same lot, elapsed time between the pressure treatment and magnetic measurement, sample surface contamination with Si from the pyrophyllite gaskets (although the results of Nam *et al.*[2] would seem to obviate this possibility), etc.

The metastability of the measured susceptibilities[10,11] and their variability described above suggests that this anomalous behavior may be caused by some critical structural or chemical phenomena.

To examine the nature of such a critical phenomena, let us speculate on the interelationship of the quenching process and sample chemistry. The quenched-in platelets (presumably the retained NaCl phase) appear featureless under SEM examination to a resolution of about 10^4 Å.

The existence of these platelets are not the necessary and sufficient conditions for the anomalous behavior since they exist in samples which never showed the anomalous behavior and remain in samples in which the anomalous behavior has decayed to below the detection limits of the magnetometers. Also, we can accomplish nearly complete recovery of the NaCl phase in samples with a Cl content larger than 2.8 wt. % without pressure quenching. None of the latter samples together with fast-quenched samples from the same group ever showed detectable anomalous magnetic behavior.

We consider therefore a metastable decomposition of the high-pressure NaCl phase. This decomposition is strongly dependent on quenching statistics within a narrow range of sample chemistry. The metastability, as determined from electrical and magnetic measurements, has been shown to depend on annealing conditions.[11] We are unable to determine any structural change in the character of the platelets (NaCl phase) to the limit of the resolution of the SEM; thus such a decomposition may involve the motion of a mobile specie, e.g., Cl in interstitial sites.

Gibbs[18] separated into two categories the infinitesimal changes to which a metastable phase (e.g., NaCl phase) must be resistant. One is a change that is infinitesimal in degree but large in extent, as exemplified by a small compositional fluctuation spread over a large volume. Cahn[19] has shown that the early stages of such a decomposition (spinodal decomposition) in a solid proceed in a continuous and coherent manner such that detection is usually accomplished by observing the resultant periodic elastic strain effects on physical properties. To experimentally study such a process, one would require techniques sensitive to unusual electronic distribution and behavior, since we recognize that the anomalous effects reported here must ultimately be related to such electronic behavior, whatever the underlying physical structure.

Of course other models for such phenomena exist.[2–6] Only further experimental tests will determine which, if any, of these models apply or if a new collective phenomenon is occurring in these samples.

IX. CONCLUSION

The anomalous electrical and magnetic properties occur in CdS samples which have been heavily doped with Cl to levels of 0.75±0.1 wt. % after pressure quenching from above the high-pressure phase transition at rates in excess of 10^5 bar/sec.

The material which may exhibit these anomalous phenomena can be prepared by precipitation from a Cl-containing bath if the resultant Cl concentration is within the range above.

The active material is not a simple mixture of CdS and $CdCl_2$, but rather a material containing (a) CdS_xCl_{1-x} complex(es). The particular complex(es) has (have) not been identified nor has (have) the structure(s) of the complex(es) been determined in the anomalous samples at present.

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