Zeeman Effect in Solids

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Zeeman Effect in Solids

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The transverse Zeeman effect on the absorption lines of the monoclinic $GdCl_3 \cdot 6H_2O$ was examined at various field strengths. Photographs were made with the crystals at various temperatures. Enlarged reproductions and microphotometer curves are given. The results are discussed and explained on the assumption that if an electron is excited as a first approximation only its spin can orient in a magnetic field.

RECENTLY considerable interest has developed in the nature of energy states in solids and several theoretical papers have appeared which deal either directly or indirectly with the subject. Unfortunately the experimental evidence in this field is very meager so that the theorist has been greatly handicapped by the lack of facts upon which to build and check his theories. For this reason it was thought advisable at this time to report in some detail the progress made in experiments on the Zeeman effect in solids which are being carried out in this laboratory, even though the experiments will not be fully completed for some time.

Hund,[2] from rules of spectra, predicted the basic levels of the gaseous rare earth ions and then calculated their magnetic moments. As data on the gaseous ions were lacking he compared his results with those on solids and obtained excellent agreement with the experimental results. On the other hand, he obtained very poor agreement with ions of the iron group. If one examines the electronic structure of the two types of ions one can see why this might be true. In the case of the iron group the "active" or "magnetic" electrons are outside the kernel where they are subjected to the strong electric fields of the neighboring ions, while in the case of the rare earths the active electrons are in the $4f$ shell which is strongly shielded by the completed $5s$ $5p$ shells from the action of the neighboring ions.

Kamerlingh Onnes[3] and his associates have measured the magnetic susceptibility of the gadolinium ion in both the monoclinic $Gd_2(SO_4)_3 \cdot 8H_2O$ and the hexagonal $Gd(C_2H_5SO_4)_3 \cdot 9H_2O$ over a temperature range of from 1.3°A to room temperature, and Giauque[4] has shown that the $^8S_{7/2}$ level predicted by Hund is in good agreement with the results over the entire range. He has also shown that the action of the crystalline electric fields on this level must be very small as the magnetic behavior is just what one would expect for the case of the free or gaseous ion.[5]

The absorption spectra of the gadolinium ions must therefore consist of lines which arise from transitions between this basic level (all S levels are single in the absence of fields) and various excited levels and the position of these lines will be effectively an energy level diagram of the excited states. These lines occur in multiplets, the positions of which are approximately the same for all gadolinium compounds examined. The numbers and position of the lines, however, within the multiplets, as Spedding and Nutting[6] have shown, change greatly with the various compounds and depend to a large extent on the crystalline symmetry of the compound, the higher the symmetry the fewer the lines and

[1] National Research Fellow in Chemistry.

[2] Hund, *Linienspektrum*, Julius Springer, Berlin.

[3] Woltjer and Kamerlingh Onnes, Leiden Comm. No. 167C.

[4] Giauque, J. Am. Chem. Soc. **49**, 1870 (1929).

[5] This result might particularly be expected for Gd^{+++} ion for as Kramers has pointed out, S levels as a first approximation do not split in crystalline electric fields. H. Kramers, Proc. Amst. Acad. **32**, 1176 (1929).

[6] Spedding and Nutting, Phys. Rev. **38**, 2294 (1931); J. Am. Chem. Soc., January, 1933.

the less the overall spread of the multiplet.[7] Therefore the excited levels are greatly affected by the crystalline fields and these multiplets arise when the original levels become non-degenerate, because of the fields.

In a letter to *The Physical Review*[8] it was stated that the lines around 2700A in the Gd^{+++} ion in solids do not split into two components, as had been reported previously,[9] but that they split into several (usually nine), and that the apparent doublets were due to intense outer components which were unresolved. Since then these lines have been investigated in more detail, as well as lines at 3100A and 3050A, and this paper will give the experimental data observed.

Monoclinic crystals of $GdCl_3 \cdot 6H_2O$ were chosen to be studied first, as its spectrum had been studied in some detail and many of the lines of its multiplets were well separated from one another so that their Zeeman patterns would not overlap. Also the Paschen-Bach effect would be small.[10]

Experimental Procedure

A large single crystal of $GdCl_3 \cdot 6H_2O$ which crystallizes in flat plates with its flat faces perpendicular to the *b* or symmetry axis was mounted on the end of a long rod. The whole was placed in a large glass Dewar that had a small square quartz Dewar sealed to its bottom by means of quartz glass seals. The quartz Dewar fitted in between the poles of a large electromagnet which were about 1.5 cm apart. The crystal was thus immersed in a cooling liquid and could be raised, lowered, or rotated as desired.

Most of the photographs were made with the light parallel to the *b* axis and the field parallel to the *a* or *c* axis. In one case the crystal was rotated about 15° about the *a* axis. (Figs. 2, 3, 4.)

The source of light was a H_2 discharge of the Bay and Steiner type. A Hilger (185) Littrow type 3 meter spectrograph was used for the earlier work. This later was supplemented by the prism from a smaller Hilger instrument so that the spectrograph was effectively a three prism instrument with a dispersion of about 1.4A per mm at 2700A.

In the study of the lines at 3100A two additional prisms, were added, giving effectively a seven prism instrument with a dispersion of about 9A per mm at 3000A. These prisms were very generously lent us by the Physics Department while their spectrograph was being rebuilt. While the resolving power of the instrument did not increase in proportion nevertheless it was possible to resolve lines which were not resolved before.

The tremendous dispersion and loss of light in the optical path made very long exposures necessary. Thus the exposures varied from 30 to 100 hours, depending on the size of the crystal and the region of the spectrum investigated. Only a few plates at this dispersion were made in the 2700A region as the general absorption in the crystal made necessary exposures of excessive length.

While increased temperature tends to broaden the lines, it was found that the components could be resolved at liquid nitrogen temperatures and as liquid hydrogen runs of such long duration were impracticable most of the photographs were taken at 78°A.

The room containing the spectrograph was of course thermostated to 0.1°C.

Results. Zero Fields

The positions of the absorption lines from various crystals are in general quite reproducible; however, this is no longer the case if the crystals are strained as is frequently the case when they are grown rapidly in contact with some object such as the side of the beaker. Then some lines are broadened, others seem to be resolved into two or three components and still others are not noticeably affected. (See Fig. 1 spectra made with Hilger 185, 3 prisms instrument.) The broadening is particularly noticeable if the light travels parallel to the flat faces where its path length along the strained region is long.

[7] Bethe, Ann. d. Physik **3**, 133 (1929), has predicted such behavior from theoretical grounds.

[8] Spedding, Phys. Rev. **38**, 2080 (1931).

[9] Freed and Spedding, Phys. Rev. **38**, 670 (1931).

[10] As pointed out, crystals of higher symmetry have their lines very close together so that at fields where the components can be resolved the patterns will overlap and strong Paschen-Back effects will be present. However, we hope to be able to study a hexagonal crystal in the near future.

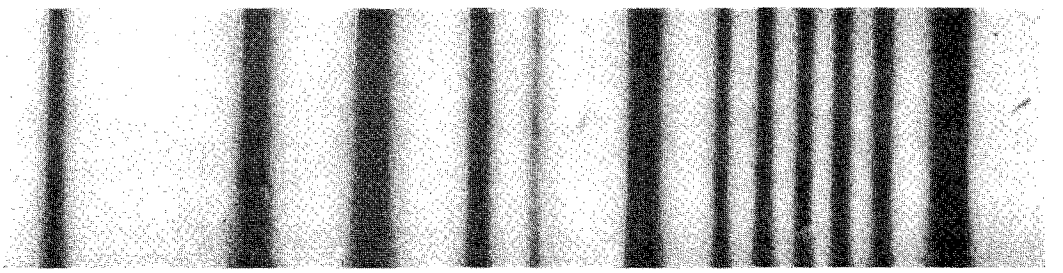

FIG. 1. $GdCl_3 \cdot 6H_2O$. Strained crystal, zero field.

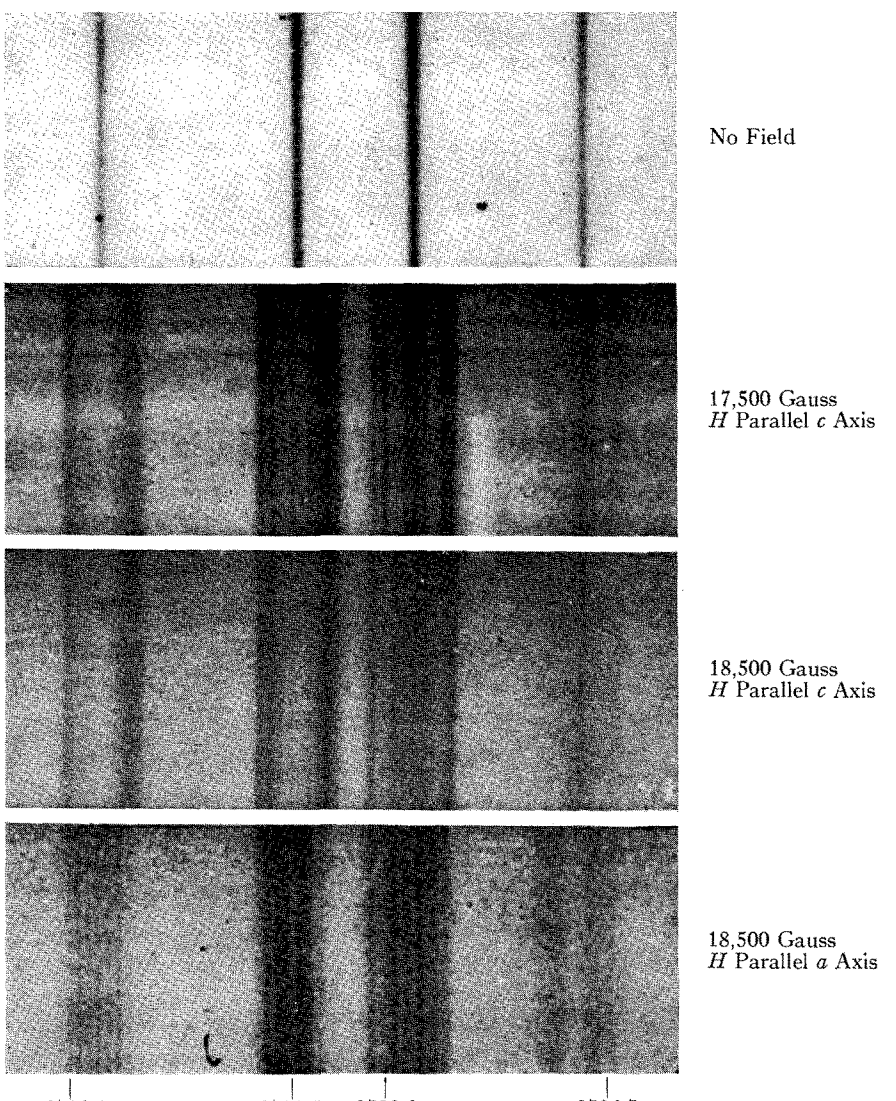

FIG. 2. Transverse Zeeman effect in $GdCl_3 \cdot 6H_2O$. Light ray parallel *b* axis, temperature, 78°A.

Repeated cooling tends to strain the crystals and they tend to break up into fragments. For these reasons crystals can be used for only one or two runs.

Just as is to be expected no difference in the position of the lines could be detected when the light traversed the crystal in different directions. The intensities and polarizations of the lines, however, were quite different.

Effect of Magnetic Fields

For a description of the effect of magnetic fields on the lines it was thought best to reproduce microphotometer curves of typical lines and multiplets. (See Figs. 2–8.) While the large grain of the Speedway plates tends to show up under the high magnification used and to mask the lines so that components which are visible to the eye do not show, nevertheless enough components do show to give a very good idea of the patterns. Across the face of each print a scale has been drawn the divisions of which are 2ω where ω equals the normal Larmor splitting for that field strength.

The reproductions and curves are self-explanatory so in order to conserve space the reader can obtain the details from the curves and, attention will be called only to a few striking points.

Lines 2786 to 2793A

All lines split into nine components with a separation of approximately 2ω between them. The intensities of the component vary greatly depending on the direction of the field. In some cases the outer components are the more intense, in others, the inner. The separations are not exactly equal, the components toward higher frequencies being usually a little closer together than those towards the red. This inequality becomes much greater at fields where the Paschen-Back effect is definitely present. The intensities of the lines are also not symmetrical about the center.

For some lines in certain directions of the field the components became blurred. However, polarized spectra tended to show these were actually sharp but were blurred because of overlapping of the lines.[11]

Lines at 2766A, 2764A, 2745A and 2743A

These lines behaved very similarly to the above. The rest of the lines in these multiplets were very close together so that their Zeeman components overlapped. They are not reported here, however, where the patterns could be observed, and where the Paschen-Back effect was not pronounced the 2ω separations could be clearly seen. (See Figs. 9 and 10.)

Lines at 3110A, 3112A, 3115A and 3117A

These lines behaved very much like the above except that in the directions photographed fewer components were observed. More components existed, however, as photographs made with lower dispersion in other directions of the field, showed envelopes of the components where these outer ones must have been present.

Also the components of these lines tended to be more diffuse in some directions of the field showing a dependence of the patterns on field direction.

Lines at 3057A, 3061A, 3065A

These lines behaved similarly to those at 3100A. In general the more diffuse the lines the greater the dissymmetries in their intensities and positions. All the lines became diffuse with fields above 20,000 gauss where the Paschen-Back effect becomes pronounced.

There were some indications that the separation of the components did not decrease linearly with the field but this could not be determined with certainty because of the blurring together of the components on account of their width.

Some longitudinal photographs were attempted but because of the long optical path through the pole pieces and the scattering of light at glass faces of the Dewar no spectra were obtained at liquid N_2 temperatures. One photograph was obtained at room temperature where the b axis

[11] While the intensity was too low to use the small nicols we had available, some photographs were obtained where the light was elliptically polarized by passing it through the Cornu prisms used as four 30° instead of two 60° prisms. The two rays were separated by this means by about 15 mm on the plate, the ordinary ray being very intense and the extraordinary ray faint.

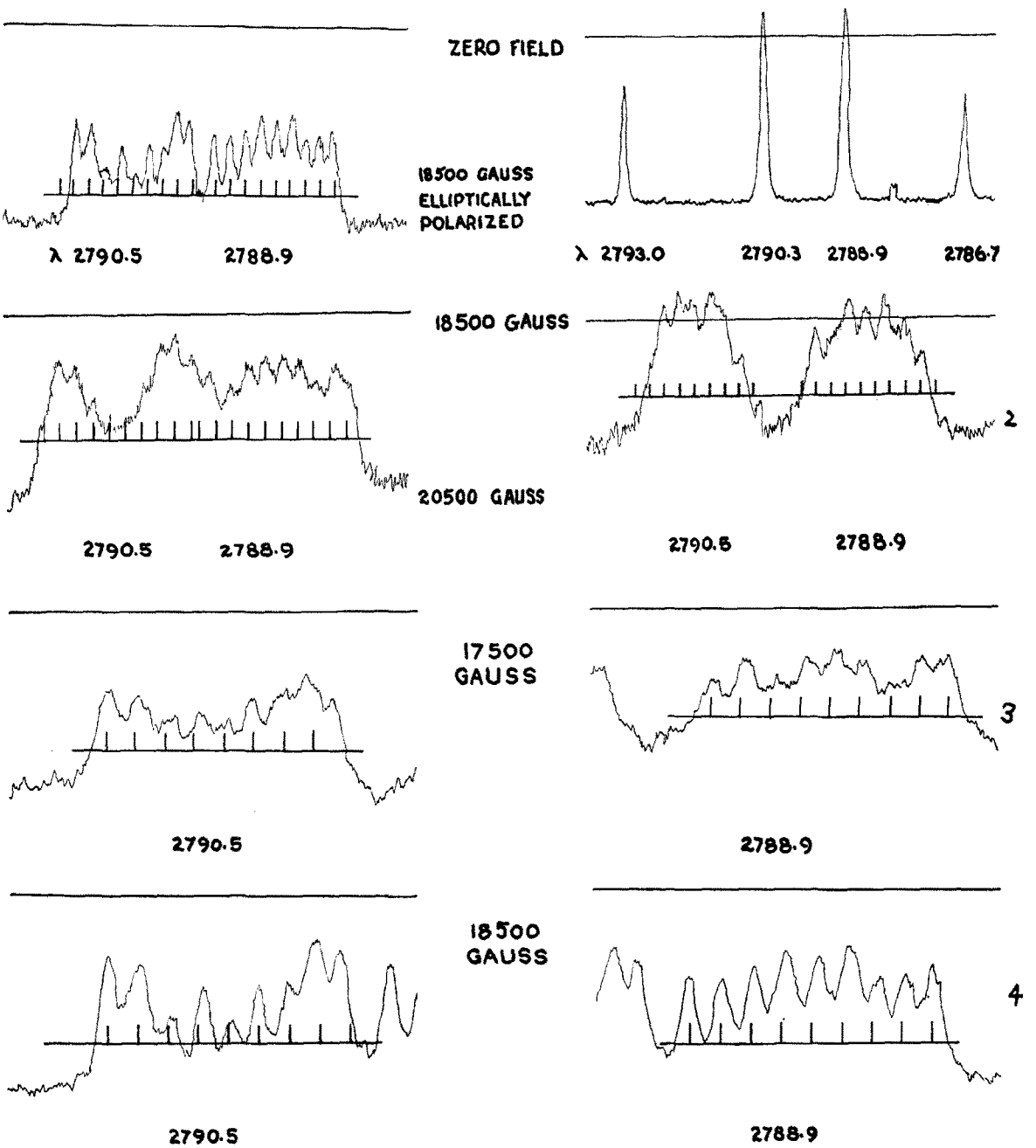

FIG. 3. Transverse Zeeman effect in $GdCl_3 \cdot 6H_2O$. Light ray parallel b axis, temperature, 78°A. (Magnification × 23.)

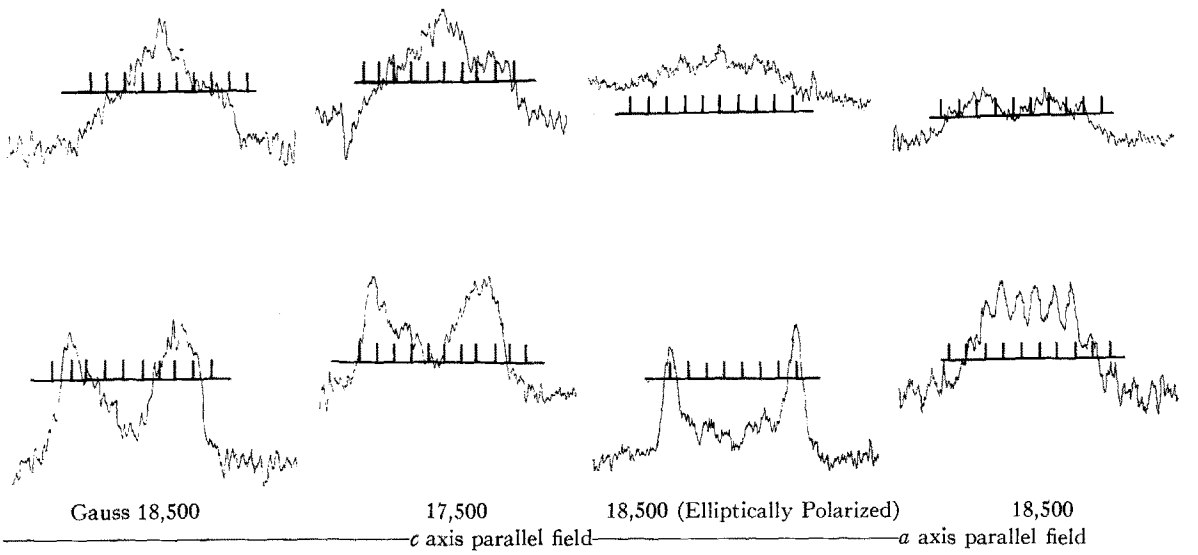

FIG. 4. Transverse Zeeman effect in $GdCl_3 \cdot 6H_2O$. Light ray parallel b axis, temperature, 78°A. Upper curves, λ2786.7. Lower curves. λ2793.0. (Magnification × 23.)

was parallel to the field and the envelopes of the components were very similar to those observed in the transverse effect.

DISCUSSION OF RESULTS

While the evidence is not yet complete enough to state with any certainty the nature of the magnetic behavior in solids, many facts have been presented which any theory advanced must take into account.

The theory put forward by the writer in a letter to *The Physical Review*, while not proved, will account for all the observed facts.[12]

It is known from magnetic susceptibilities that the basic level, a $4f^7$, $^8S_{7/2}$, is split into eight components with 2ω separation between them and as the absorption lines are split into components with this separation the excited levels must also be split by this amount.

The fact that the magnetic susceptibilities of the rare earths show that the $4f$ electrons are coupled by Russell-Saunders coupling seems to eliminate terms arising from a $4f^7$ configuration as the three factors of such terms are usually different for each term and are rarely equal to two. Also, when the fields are not strong enough to destroy the R.S. coupling the selection rule for $\Delta n = 0$, $\Delta 1 = 0$ should be effective and the transitions forbidden.

Therefore the excited states must arise from a $4f^6 5x$ configuration and one might expect that the completed $5s$ $5p$ shells which partially shield the $4f$ electrons from the neighboring ions would also partially shield them from the $5x$ electron. The $4f^6$ electrons would then couple together with R.S. coupling to give a resultant such as $^7F_6$, $^7F_5$, etc. The $5x$ electron would be outside the kernel where it would be subjected to the strong electric fields of the neighboring ions.

As the external magnetic field is usually weak with respect to these fields it would not be able to orient the orbit of this electron. While the electron in travelling about the gadolinium ion will have a magnetic moment, because of the strong electric fields present, its direction will be constantly varying so that the total moment of the atom due to this electron will be zero. This moment, however, will be exerted on resultant moment of the inner electrons and as they are free to orient will carry them with it so that their moment will also precess out. The spin of the external electron, however, will not be firmly coupled with the orbital moment as it will resemble very much the circular type orbits of the alkali atoms and it would orient rather freely in a magnetic field. Thus all the excited

[12] This theory also explains the abnormal behavior of the magnetic susceptibility of samarium ion. Spedding, J. Am. Chem. Soc. **54**, 2593 (1932).

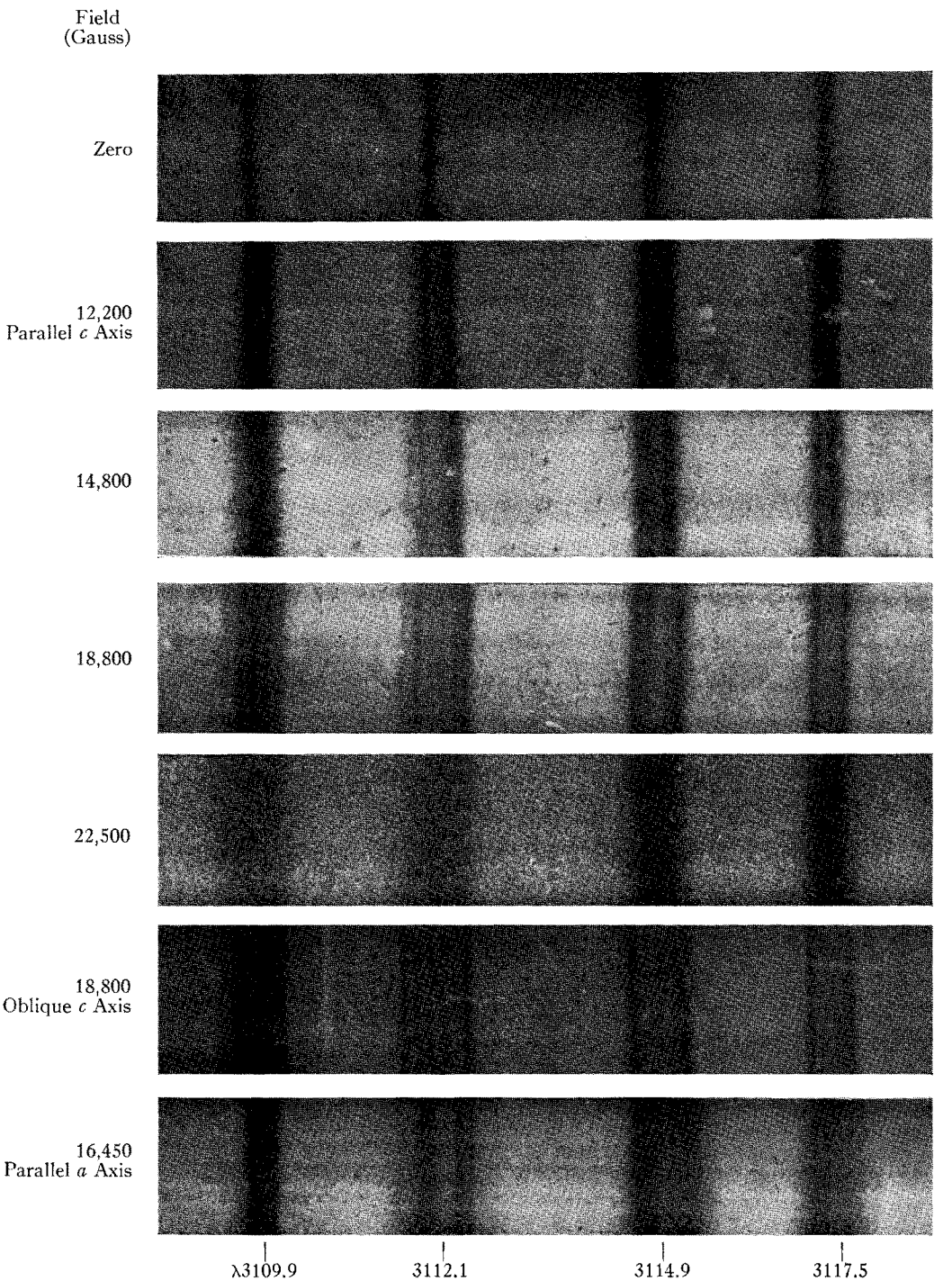

FIG. 5. Transverse Zeeman effect in $GdCl_3 \cdot 6H_2O$. Light parallel b axis.

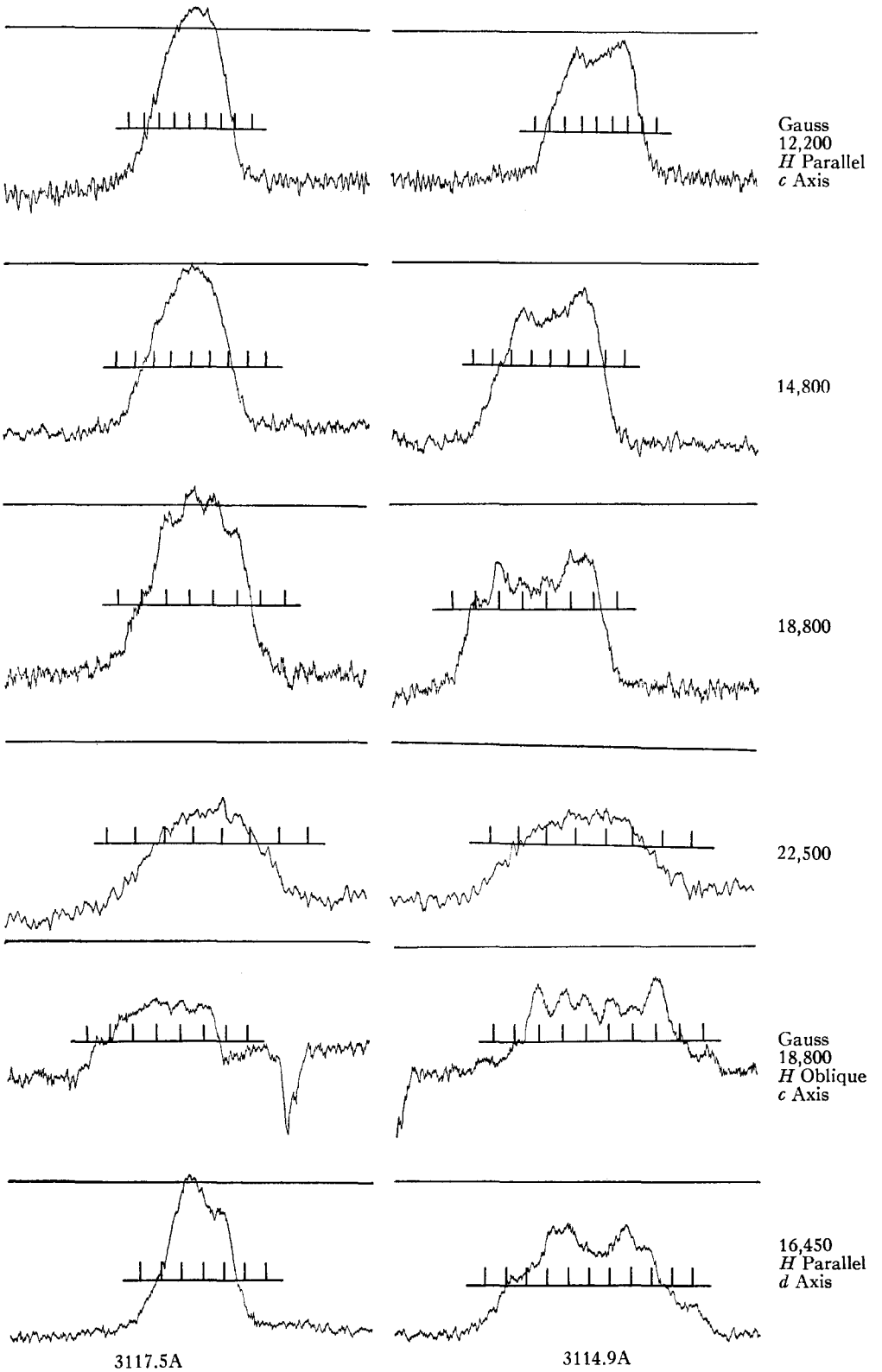

FIG. 6. Transverse Zeeman effect in $GdCl_3 \cdot 6H_2O$. Light ray parallel to b axis. (Magnification $\times$ 21.)

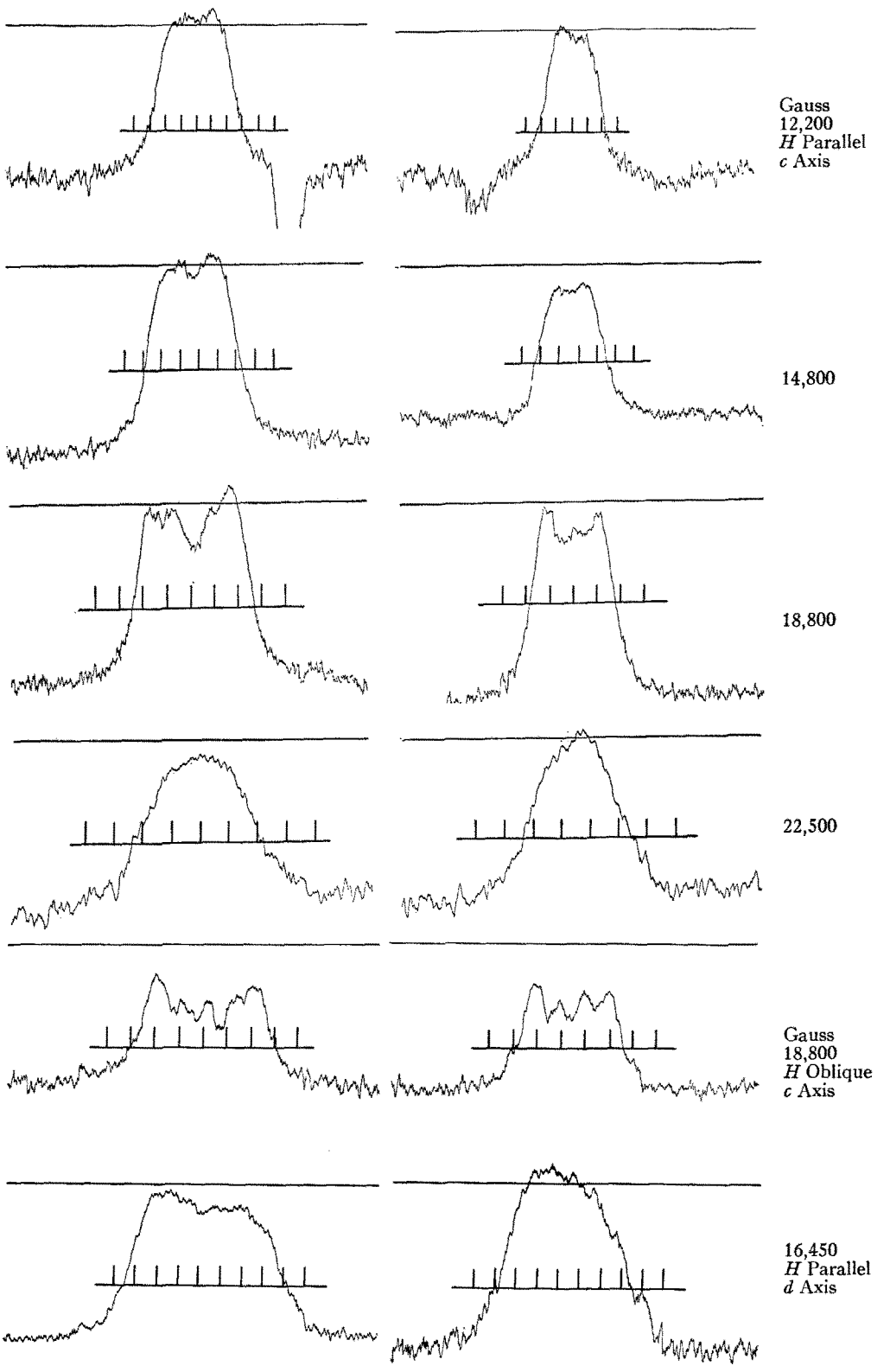

FIG. 7. Transverse Zeeman effect in $GdCl_3 \cdot 6H_2O$. Light ray parallel to b axis. (Magnification $\times$ 21.)

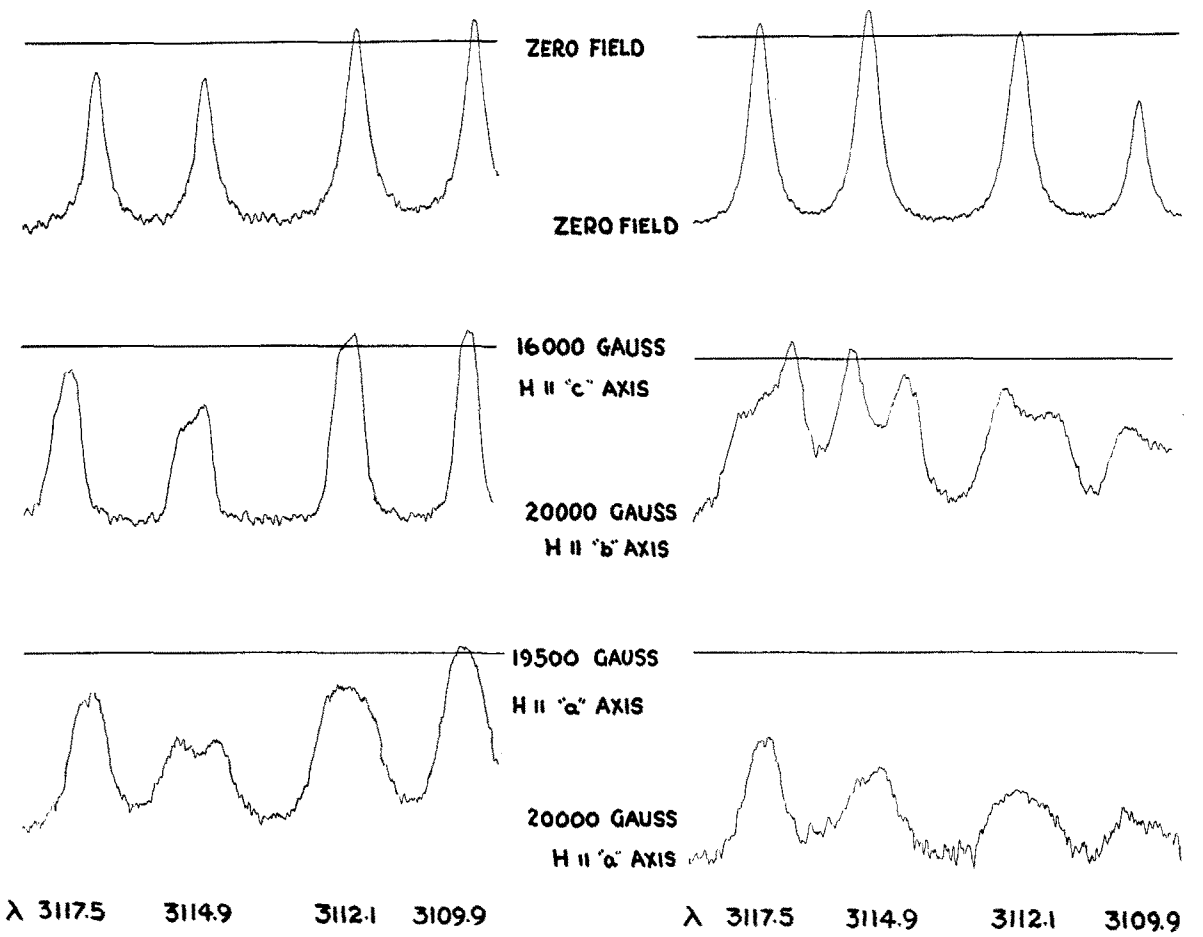

FIG. 8. Transverse Zeeman effect in $GdCl_3 \cdot 6H_2O$. Temperature, 298°A. (Magnification × 21.)

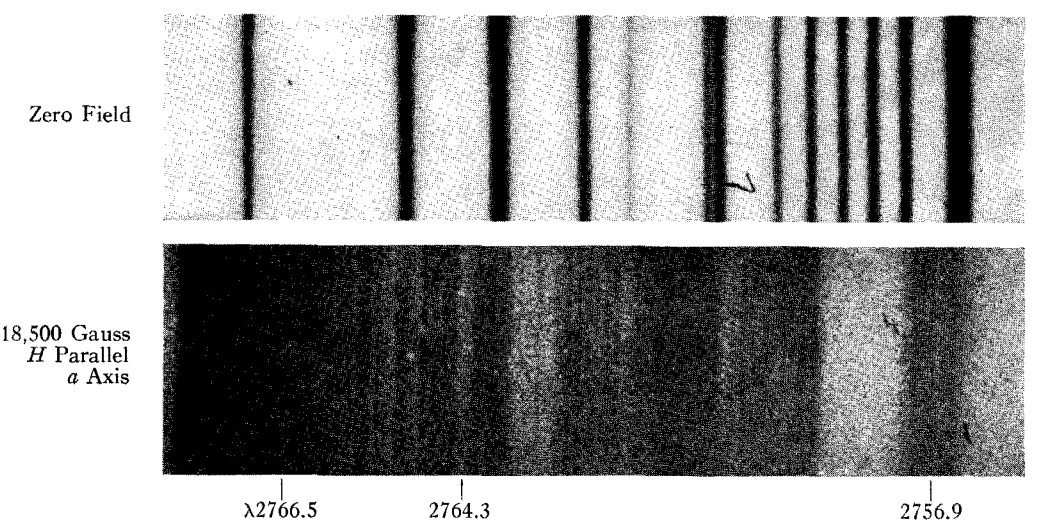

FIG. 9. Transverse Zeeman effect in $GdCl_3 \cdot 6H_2O$. Light ray parallel *b* axis.

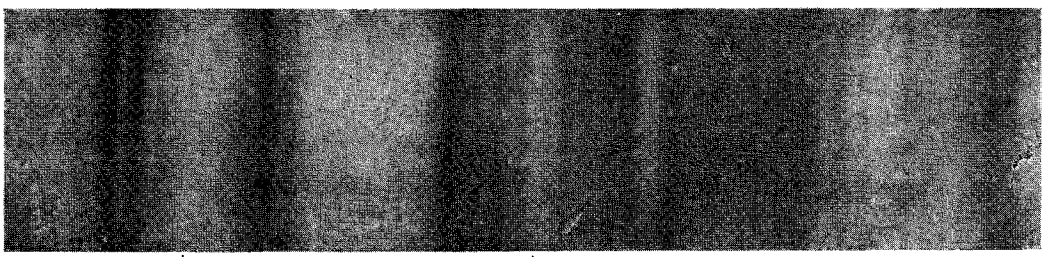

FIG. 10. Transverse Zeeman effect in $GdCl_3 \cdot 6H_2O$. High dispersion 78°A. Light ray parallel b axis. H parallel c axis.

levels regardless of their nature will split into two in a magnetic field with 2ω separation.

Bethe has shown that in the crossed electric and magnetic fields which are present in a crystal the selection rules $\Delta m = \pm 1$ or 0 breaks down. If all transitions are permitted, nine lines will be observed and this is just what is observed in most of the lines investigated. It should be mentioned that this type of coupling represents an ideal case and that the actual coupling will vary from level to level. In the case of Gd^{+++}, however, the actual case seems to be very close to the ideal one. (See Fig. 11.)

In strong fields where the magnetic field splitting becomes of the same order of magnitude as the crystal splitting a Paschen-Back effect will occur and the levels will split unsymmetrically. The observed lines will first blur and then resolve into two components. Also at low fields if the energy of coupling of the spin to the orbit is appreciable, dissymmetries will appear. A third factor which would tend to cause dissymmetries in the splittings is that if the second order terms of the crystal fields caused an appreciable splitting of the basic level the eight components would not be equally spaced in a magnetic field. The photographs seem to show such a condition to be present.

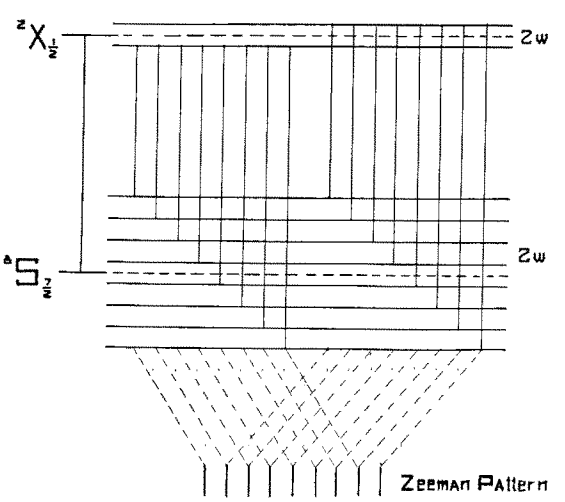

FIG. 11. Theoretical Zeeman effect in solids, Gd^{+++}.

Still another factor which becomes important as soon as the orbital moments begin to contribute to the splitting is that two or more types of gadolinium ions may be present in the crystal lattice. Thus if the unit cell contains more than one gadolinium ion (as it very likely does in $GdCl_3 \cdot 6H_2O$) the dissymmetries of the levels for the different atoms will be different. For even though the atoms are crystallographically identical, they no longer remain so when the external field is applied. The field vector will make different angles with the atoms which are mirror images of each other.[13]

As the lines arising from these levels are superimposed on each other when the dissymmetries occur the lines will blur very badly.

The writer wishes to thank the Chemistry Department for the fine cooperation it has shown him in these researches, and for obtaining the large spectrograph and magnet which made this work possible.

[13] Professor Pabst and the writer are investigating these crystals by x-ray means to determine the size of the unit cells and hope to have results soon.