This seems to be an averaging which produces behavior like that in the elements which are intermediate in the periodic table. The large solubility of Mo in Ru enables us to simulate technetium quite closely both in crystal structure and superconducting transition temperature, thus strengthening our faith in the validity of this point of view.

An additional remark may be justified concerning these alloys: previously superconductivity had only been observed, apart from the elements, in either well defined compounds with very small homogeneity ranges or in solid solutions. We believe this is the first time that disordered alloys of nonsuperconducting elements have become superconducting and it may indicate that superconductivity is a long-range order effect rather than a short-range one.

CONCLUSION

There seems to be a rule linking the superconducting transition temperatures to the number of electrons outside filled shells, the valence electrons. At present we do not understand the theoretical implications of this. It seems, however, reasonable to suggest that a large number of valence electrons is quite favorable for the occurrence of superconductivity. Then why is there a dip for a value near six valence electrons? The answer to this may be roughly that this dip corresponds to the dip in paramagnetic susceptibility and in electronic specific heat for the same elements, which is commonly supposed to be due to a low effective number of free electrons.

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Paramagnetic Resonance Absorption in Praseodymium Trichloride*

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Paramagnetic resonance absorption in crystalline solutions of $PrCl_3$ in $LaCl_3$ has been investigated at a frequency of 2.32×10^{10} sec^{-1} and at the boiling point of He. The apparent g's, when H is parallel and perpendicular to the c axis have been found to be 1.79 and 3.98 respectively. The results have been discussed in terms of the known crystalline structure and Stark splittings.

INTRODUCTION

THE static magnetic and optical spectroscopic properties of crystalline praseodymium compounds have been successfully interpreted, at least in general outline, by Van Vleck,[1] Penney and Schlapp,[2] Kynch,[3] Spedding,[4] Hellwege and Hellwege,[5] and others. The ground state of the trivalent magnetic ion is the Hund state, $^3H_4$, for two $4f$ electrons[1] and Russell-Saunders coupling is obeyed approximately. The perturbations by the crystalline electric field play an important role in determining the temperature variation of the magnetic susceptibility and the details of the optical absorptions. The magnitudes of these perturbations are found generally to be considerably smaller than the spin-orbit coupling energies as is to be anticipated on the basis of the theoretical expectation that $4f$ orbitals lie deep inside the magnetic ion.

Recently Davis, Kip, and Malvano,[6] Altshuler, Kurenev, and Salikhov,[7] and Bleaney and Scovil[8] have observed magnetic resonances in compounds of praseodymium. The general theory of the paramagnetic resonance absorption in rare-earth salts has been given in great detail by Elliott and Stevens[9–12] although they have given only brief consideration to the specific case of Pr^{+3}.

In this paper experimental results of an investigation of paramagnetic resonance in a solution of $PrCl_3$ in $LaCl_3$ are presented and their interpretation discussed.

EXPERIMENTAL

Preparation of Crystals

The crystals employed for the measurements were right circular cylinders with their crystallographic c axes perpendicular to their cylinder axes. These were cut

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from irregularly shaped single crystals prepared by cooling fused $PrCl_3$ and $LaCl_3$ in a Pt crucible in an HCl atmosphere from a temperature approximately 50°C above the melting point of the mixture (about 820–830°C) to room temperature. The melts were cooled at rates of from 40° to 80°C per hour. Single crystals were selected from the irregular pieces so produced and these were oriented by means of polarized light and ground to shape on a lathe. All cutting, grinding, and orienting operations were performed in an atmosphere of carefully dried N_2. The $PrCl_3$ in $LaCl_3$ was prepared by heating the hydrated salts in a Pt boat from room temperature to the melting point over a period of about 48 hr. The heating was done in an HCl atmosphere. The very slow heating and the HCl atmosphere were necessitated by the very strong tendency toward hydrolysis to the oxychloride. Crystals of $LaCl_3$ prepared by this method contained 0.1 percent of material insoluble in H_2O and identified by Professor W. H. Zachariasen by x-ray diffraction as LaOCl. The hydrated $LaCl_3$ was prepared by evaporation of an aqueous solution of La_2O_3 and HCl, and the hydrated $PrCl_3$ by evaporation of a solution of Pr_6O_{11} and HCl. The La_2O_3 was prepared by the Lindsay Light and Chemical Company and found by them to contain 99.99 percent La_2O_3. The Pr_6O_{11} was Baker and Adamson brand and was stated to contain 99.8 percent Pr_6O_{11}. Spectrophotometric analyses showed that the crystals which were used contained 11 ± 0.5 mole percent $PrCl_3$. The amount of $NdCl_3$ was found to be about 0.07 mole percent and there was about 0.1 weight percent oxychloride.

MICROWAVE EXPERIMENTS

The paramagnetic resonance absorption was investigated at 2.32×10^{10} sec^{-1} and at the boiling point of He. The crystals were mounted on a polyethylene post with their cylinder axes parallel to the rf magnetic field and perpendicular to the static magnetic field. They were rotated about their cylinder axes and thus any desired angle between the crystallographic c axis and the static field could be obtained. A polyethylene cap was placed over the crystal and thermally sealed to the post in a helium atmosphere. The resonant reflection cavity was evacuated but because of possible very small leaks probably contained a low pressure of He. A single resonance absorption peak was observed. The spectroscopic splitting factor for one crystal as a function of angle θ between the c axis and the static field is presented in Fig. 1. The measurements on a second crystal were in agreement with these. The largest errors were in the determination of the angles of orientation of the crystal and were not greater than $\pm0.015\pi$. The apparent g's, when H is parallel and perpendicular to the c axis are 1.791 and 3.975 respectively.

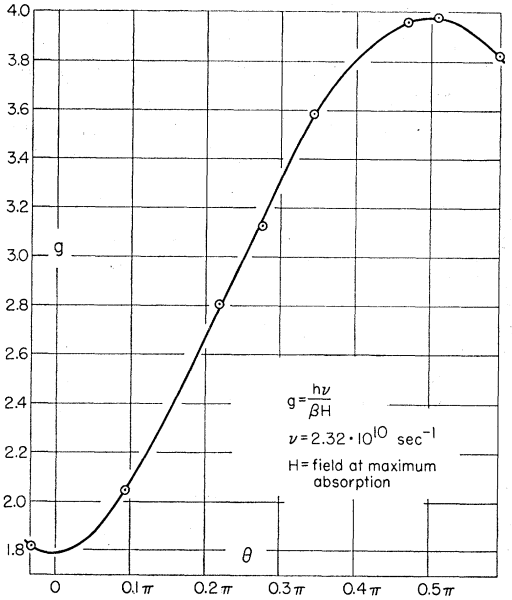

FIG. 1. g *vs* θ for $PrCl_3$.

No nuclear hyperfine structure was observed at the concentration of $PrCl_3$ used in these experiments. The absorptions were narrowest, about 25 gauss, when the c axis made an angle $\pi/2$ with the static magnetic field and widest, about 180 gauss, when the angle was 0.

A very weak resonance with an intensity not greater than ~0.01 of the intensity of the main absorption was observed at $g\sim2$ independent of θ and was attributed to traces of impurities on the walls of the cavity or to unoriented oxychloride in the sample.

DISCUSSION

The crystal structures of $LaCl_3$ and $PrCl_3$ are known to be of the UCl_3 type[13] belonging to the space group $C6_3/m$. The nearest neighbors of the Pr^{+3} ion are nine Cl^- ions, each at a distance of about 2.9A. These nearest neighbors lie in a configuration with C_{3h} symmetry. The point group of the symmetry at a Pr^{+3} considering the whole crystal is also C_{3h}. When such a potential is expanded in spherical harmonics one need consider no l values greater than 6 (because one is dealing with f electrons) and no odd l if one is dealing with a single configuration. The only m values involved are consequently 0 and 6, and therefore the only nonzero matrix elements of the electrostatic potential in the J,J_z representation are those for which $\Delta M=0, 6$. The secular problem therefore consists of three quadratics involving the pairs of states $-4, 2$; $-2, 4$; $-3, 3$; the three states $-1, 0, 1$ are not connected by any elements of the potential. The diagonalization of the electrostatic energy gives rise to two twofold-degenerate states from the quadratics -4, 2 and -2, 4 (denoted by Hellwege by the quantum numbers $\mu=\pm2$) and one twofold-de-

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generate state consisting of the pair $-1, 1$ (denoted by $\mu=\pm1$). The two states from the quadratic $-3, 3$ (denoted by $\mu=3$) and the 0 state (denoted by $\mu=0$) are all nondegenerate.

When a static magnetic field is applied the degeneracy of the doublets will in general be removed. There are however no matrix elements of the magnetic moment between the components of such a doublet and therefore no magnetic transitions are allowed and $g_\perp$ is 0. This situation has been discussed by Elliott and Stevens[12] and by Bleaney and Scovil.[8] They have assumed that the Jahn-Teller[14] effect will be operative to lower the symmetry and remove the degeneracy of a ground state such as $\mu=\pm2$. In this way other states which will permit transition will be mixed in, and if the separation so produced is small the value of $g_\parallel$ will still be near that for C_{3h} symmetry and $g_\perp$ will be small. In such a case the $g_\parallel$ would for example be $8/5=1.60$ for the doublet $\mu=\pm1$; or for $\mu=\pm2$ would be 1.69 if the states are assumed to be

$$\cos\varphi|J_z=\pm2\rangle-\sin\varphi|J_z=\mp4\rangle,$$

with $\varphi=0.15\pi$ as supposed by Elliott and Stevens.[12] $g_\perp$ would be close to 0. The behavior of g for $PrCl_3$ is obviously not in accord with such a model.

Another possibility that might be considered is that one of the crystal field levels to which transitions are possible from the ground state lies very close to the ground state. If the separation were of order 1 cm^{-1} then transitions would be observable at the frequencies employed in the present experiments. If, for example, the state $\mu=\pm2$ were separated from the state $\mu=\pm1$ by about 0.4 cm^{-1} and all the other states were much higher, then quite satisfactory agreement with experiment is obtained. The best fit in this case is for $\varphi=\pi/2$. There are undoubtedly several other satisfactory cases of this sort. Sayre and Freed[15] have, however, located the three doublet states (a $\mu=\pm2$ state is the ground state) and one of the $\mu=3$ states by means of polarization spectrum studies. Their results would indicate that neither the $\mu=\pm1$ state nor a $\mu=3$ state can lie near the ground state. An explanation of this type would therefore seem to be eliminated from consideration.

The crystal field splittings are found by Sayre and Freed[15] to be as large as 130 cm^{-1} and are hence not negligible compared with the spin-orbit splittings ($J=5$ is $\sim$2000 cm^{-1} higher than $J=4$).[11] However, as long as C_{3h} symmetry is maintained, the mixing of states of higher J with the state $J=4$ will not result in transitions between the components of the doublets. The case in which there is both lowered symmetry and mixing of higher J's has not been considered.

Other possibilities of interpretation lie in the consideration of configuration interaction or of large effects of departure from C_{3h} symmetry. It is probably doubtful that other configurations interact sufficiently to play an important part. On the other hand it may be true that at low temperatures there could be appreciable effects of lowering of the symmetry which might conceivably account for the magnetic observations (the optical data of Sayre and Freed at low temperatures are apparently in agreement with the assumption of C_{3h} symmetry).

The analyses mentioned above would indicate that quite pure crystals were used in the experiments. Any PrOCl would most probably have been randomly oriented since LaOCl is insoluble in $LaCl_3$[16] and presumably the same is true for PrOCl in $PrCl_3$. Moreover if all the oxychloride were present as PrOCl only 1 percent of the Pr^{+3} would be in that form.

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