

are properties of the host lattice in which the ion is embedded. This dependence on host lattice is reflected in the reported⁵⁰ minimum energy gap required for the appearance of Er^{3+} fluorescence which ranges from $\approx 900 \text{ cm}^{-1}$ in LaCl_3 to $\sim 4000 \text{ cm}^{-1}$ in some glasses.

SUMMARY

Excited rare-earth ions in crystals relax in general by a combination of radiative and nonradiative processes. The present investigation has demonstrated that the individual rates of these processes and the quantum efficiencies for specific levels can be determined from measurements of excited-state lifetimes and calculated spontaneous emission probabilities. The latter are predominantly electric-dipole in nature for $\text{LaF}_3:\text{Er}^{3+}$ and were calculated from the phenomenological treatment of Judd and Ofelt and experimental oscillator strengths. To get truly quantitative results, calculations using crystal-field eigenstates are obviously needed. However, even though the use of intermediate coupled states, the assumption of equally populated crystalline Stark manifolds, neglect of J -state mixing, and the

⁵⁰ G. H. Dieke, in *Paramagnetic Resonance*, edited by W. Low (Academic Press Inc., New York, 1963), Vol. I, p. 237.

approximations inherent in the Judd-Ofelt theory limit the accuracy of the present results, they are, nevertheless, valuable in explaining the relaxation and spectral properties. The rates of nonradiative transitions between J multiplets, obtained from comparison of measured lifetimes and total calculated radiative lifetimes, are found, as expected, to be very sensitive to the energy of the transition to the next-lower multiplet. These processes are attributed to multiphonon emission and appear to make significant contributions to the lifetimes of fluorescent states of rare earths in LaF_3 even for large transitions corresponding to the simultaneous emission of 5-6 phonons. A study of the dependence of the nonradiative probabilities on the properties of the host lattice would be of interest to further the understanding of multiphonon processes.

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Magnetic Resonance of Mn^{++} in PbS , PbSe , and PbTe †

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The paramagnetic resonance of Mn^{++} in various lead salts has been observed at 1.3 and 77°K. The spectrum shows hyperfine splitting, but no crystal-field splitting. The hyperfine constant of Mn^{++} in PbS , PbSe , and PbTe is 71.8, 67.6, and $61.2 \times 10^{-4} \text{ cm}^{-1}$, respectively. An anomalous g shift of the hyperfine lines is attributed to the electronic equivalent of the Knight shift. Electronic inhomogeneity in PbSe results in two separate sets of hyperfine lines. It is suggested that the inhomogeneity is due to a clustering of lead vacancies. The spectrum of Eu^{++} in PbSe is also reported.

I. INTRODUCTION

THE paramagnetic resonance of manganese in a cubic environment has been studied in a very large variety of insulators and semiconductors.^{1,2} It has also been seen in metals as a broad featureless line.³ We

report here the magnetic resonance of Mn^{++} in the degenerate semiconductors PbSe , PbS , and PbTe . In PbSe and PbTe (and probably PbS) we observe anomalies which we attribute to free-carrier effects. We have also observed the resonance of Eu^{++} in PbSe , and an unknown resonance at $g=2$ in all three materials.

II. SAMPLE PREPARATION AND APPARATUS

The single crystals were grown by a modified Bridgman technique, following the procedure described by Lawson.⁴ The starting materials for the PbSe crystals were 99.999% pure ASARCO Pb and Se. In the PbS and PbTe crystals, 99.9% S and Te were used. All the samples used had 0.01% Mn added to the elements

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¹ G. W. Ludwig and H. H. Woodbury, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1962), Vol. 13, p. 223.

² W. Low, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 2, Suppl., pp. 118-119.

³ J. Owen, M. Browne, W. D. Knight, and C. Kittel, *Phys. Rev.* **102**, 1501 (1956).

⁴ W. D. Lawson, *J. Appl. Phys.* **22**, 1444 (1951).

before reaction. The crystals, which have the NaCl structure, were oriented by cleaving.

PbSe tends to crystallize with a large excess of Se, which results in a *p*-type crystal with resistivity on the order of 0.003 Ω -cm. The stoichiometry can be adjusted, as described by Brebrick and Scanlon,⁵ and by Bloem,⁶ by placing the sample at one end of a close-fitting quartz tube, which is put into a 730°C furnace. The other end of the tube, which contains a piece of Se, projects into a low-temperature furnace. The vapor pressure of the Se over the sample is determined by the temperature of the piece of Se. The sample is kept in the furnace until it reaches equilibrium with the Se atmosphere, and then is quenched in water to preserve the high-temperature vacancy concentration. Stoichiometry corresponds to 212°C with a maximum resistivity of about 0.2 Ω -cm. Lower temperatures produce *n*-type material, and higher temperatures, *p*-type. It was difficult to get uniform samples; the resistivity, as measured by a four-point probe, typically varied by a factor of 2 at different places on the sample. Near stoichiometry, the samples would frequently have both *n*- and *p*-type regions. PbSe is quite volatile at 730°C, so the treatment time could not be increased to improve uniformity. It is possible that some of the sample variation was due to poor resistivity measurements caused by the rough surface produced by evaporation. This growth technique tends to produce a large number of dislocations and small angle grain boundaries. In addition, the crystals were probably strained by the quenching from 730°C following the heat treatment.

The spectrum was measured at 77 or 1.3°K on a superheterodyne ESR spectrometer which has been described elsewhere.⁷ The samples were held by Styrofoam in the center of a rectangular full-wave cavity. Added sensitivity was obtained by use of field modulation and lock-in detection. To make measurements of the *g* shift easier, the lock-in was set to detect the second harmonic of the modulation frequency.

The Pb nuclear resonance was performed on pure heat-treated powder samples, which were passed through a 325 mesh (44 μ) sieve, and then suspended in paraffin. The NMR spectrometer was a fairly conventional cross coil rig.

III. DATA

A. The Mn^{++} Spectrum at 1.3°K

We will see in this section that the spectrum of Mn in PbSe, PbTe, or PbS at 1.3°K has two features not

⁵ R. F. Brebrick and W. W. Scanlon, Phys. Rev. **96**, 598 (1954); W. W. Scanlon, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1959), Vol. 9, pp. 98–102.

⁶ J. Bloem, Philips Res. Rept. **11**, 273 (1956).

⁷ W. C. Holton and H. Blum, Phys. Rev. **125**, 89 (1962).

TABLE I. Comparison of the hyperfine constants of various materials having the NaCl structure.

Material	$A \times 10^{-4} \text{ cm}^{-1}$	T °K	Reference
NaCl	−82.3	300	a
MgO	−81.0±0.2	290	b
SrS	77.0±0.2	77	c
CaO	−80.8±0.2	290	d
PbS	71.8±0.4	1.3	
PbSe	67.6±0.3	1.3	
PbTe	61.2±0.4	1.3	

^a G. D. Watkins, Phys. Rev. **131**, 79 (1959).

^b W. Low, Phys. Rev. **105**, 793 (1957).

^c A. A. Manenkov and A. M. Prokhorov, Zh. Eksperim. i Teor. Fiz. **40**, 1606 (1961) [English transl.: Soviet Phys.—JETP **13**, 1129 (1961)].

^d A. J. Shuskus, Phys. Rev. **127**, 1529 (1962).

observed in other materials—anomalous structure and a large *g* shift. We attribute the structure to two sets of Mn ions with different *g* values. The meaning of these two sets of ions and the origin of the *g* shift will be discussed in Sec. IV.

If the Mn^{++} spectrum is observed without too much care, it is found to consist of six equally spaced isotropic lines centered near *g*=2. The lines are symmetric due to a mixture of absorption and dispersion produced by skin effect. The six lines are due to the hyperfine interaction of the Mn^{++} *d* shell with its spin- $\frac{5}{2}$ nucleus, and can be fit by the Hamiltonian

$$\mathcal{H} = g\beta\mathbf{H} \cdot \mathbf{S} + A\mathbf{I} \cdot \mathbf{S}. \quad (1)$$

Table I compares the values of *A* we obtain in the lead salts with previous values in other materials. Note that *A* decreases as one moves from PbS to PbTe. The elements O, S, Se, and Te form a series with increasing covalency of bond from left to right. Thus the data illustrate, as has been frequently noted before,^{2,8} that the hyperfine constant in solids is reduced from its “free-ion” value by covalent bonding of the *d* shell with neighboring ions. The large reduction of *A* in the lead salts indicates that the bond is quite covalent.

If the spectrum of Mn:PbSe is studied more carefully, each hyperfine line is found to have structure. Similar structure has been seen in two samples of PbTe. The one PbS sample observed was of very low resistivity and showed no structure. There was, however, a large *g* shift, and we expect structure would appear in higher-resistivity samples. The remainder of the data apply only to PbSe.

The structure on each hyperfine line in the Mn:PbSe spectrum can be divided into two types—isotropic and nonisotropic. The nonisotropic structure varied greatly from sample to sample. The splitting was never greater than 10 G (which is much less than the hyperfine

⁸ J. Van Wieringen, Discussions Faraday Soc. **19**, 118 (1955).

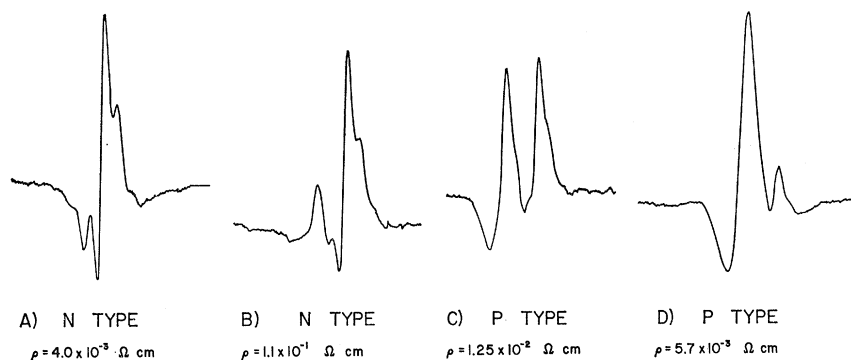


FIG. 1. Second derivative of the lowest-field hyperfine absorption line of Mn: PbSe at 1.3°K. The magnetic field is oriented along a $\langle 100 \rangle$ crystal axis. The field increases from left to right.

splitting) and never showed the five-line pattern of a ${}^6S_{5/2}$ ion in a cubic field. We feel that this structure is due to association of the Mn^{++} with Pb or Se vacancies. Since the structure was different for every crystal, and absent in some, we will not consider it further.

The second type of structure is isotropic as the magnetic field is rotated with respect to the crystal axes. There is a slight broadening of the lines as the field is rotated from along the $[100]$ crystal axis to along the $[110]$ axis. There is no other indication of crystal-field effects. In every sample the structure consisted of two lines, which we shall call the n - and the p -type lines. Figure 1 shows the lowest-field hyperfine line for four different samples. The recorder trace is the second derivative of the absorption signal. The second derivative is narrower than the absorption with a peak at the center and small negative wings. The admixture of a dispersion signal by the skin effect makes the line slightly asymmetric. We see in Fig. 1 that the n -type line, which occurs on the high-field side of the hyperfine line, is large in n -type material and decreases in size as the PbSe becomes p -type. The p -type line shows the opposite behavior. Note that the lines persist even in very low resistivity material of the opposite type, and are of equal intensity, not at stoichiometry, but in fairly low-resistivity p -type PbSe. (We recognize that the relationship of the "intensity" of the second derivative curves to the number of centers giving rise to the absorption depends on detailed knowledge of the line shape which we do not have.) Note also that both type lines have a small satellite line on the high-field side. The satellites are well resolved only in n -type material and disappear as the main line broadens when the field is rotated away from the $[100]$ direction. These satellites are not understood.

The use of the second derivative gives a sharp peak which enables us to accurately determine the position of the line, provided we ignore the asymmetry due to skin effect. We find that the six p -type and six n -type lines can be separately fit using Eq. (1). To obtain an accurate fit, it is necessary to use third-order perturbation theory and to include a third-order term hidden, and usually neglected, in the denominator of the second-

order term. We estimate the accuracy of the fit to be $\pm 0.1 \times 10^{-4} \text{ cm}^{-1}$. In all samples the value of A for the p - and n -type lines differs at most by two or three times this error. The error of $\pm 0.3 \times 10^{-4} \text{ cm}^{-1}$ given in Table I represents the spread in A for both types of lines in many different samples.

Although A is almost the same for both type lines, the g value is very different. The structure is due to two sets of hyperfine lines centered at different positions and must represent two sets of Mn^{++} ions which are nonequivalent. Since the structure depends upon the resistivity, the nonequivalence is probably related to the free carriers. In an attempt to relate the g shift to the free-carrier concentration, we prepared a large number of different resistivity samples of PbSe. The p -type lines had a g shift running from $+0.0030$ to -0.0070 , while the n -type ran from -0.0010 to -0.0110 . There was little correlation with resistivity and little reproducibility in the samples. The difference between the g shifts of the p - and n -type lines was somewhat more reproducible from sample to sample with a value of 0.0055 ± 0.0015 in moderately high-resistivity samples. In very low-resistivity samples of either type, the difference was less. The fitting error is ± 0.0002 .

We feel that the sample variation is due to a strong dependence of the g shift upon the Mn concentration. The Mn concentration might vary even in samples taken from the same boule. Hence it would be desirable to re-use the same sample. But due to sample evaporation during heat treatment, it is difficult to retreat the sample many times. One large sample, however, was retreated five times. The g shift decreased (toward zero) after each treatment. This could be due to evaporation or precipitation of the Mn during the heat treatment.

Although we have not been able to unravel the parameters which determine the g shift, we do emphasize that ordinarily a g shift for an ion is unique for a given host. One is thus almost forced to conclude that the continuously variable shifts are related to the carriers.

The Mn spectrum could not be saturated except

at high power (5 mW) in high-resistivity *p*-type material, where the *p*-type line decreased relative to the *n*-type.

B. The Mn^{++} Spectrum at 77°K

At 77°K the hyperfine lines are lifetime broadened and the structure is hidden. In one PbSe sample the 1.3°K splitting was great enough that the structure was partly resolved at 77°K. In all three lead salts, the hyperfine structure is unchanged from the low-temperature value. However, the broadening makes the fitting error rather large. In PbSe, the *g* shift varied from slightly positive to -0.0110 , with most occurring near -0.0090 . At room temperature the spectrum is not visible.

C. The Eu^{++} Spectrum in PbSe

The Eu^{++} spectrum is not visible in PbSe at room temperature or 77°K. At 1.3°K the spectrum is strong, and in contrast to Mn^{++} , is very easily saturated. In the [100] direction, the spectrum is the characteristic seven-line pattern of a $^8S_{7/2}$ ion in a cubic field. The central $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition is resolved to reveal the 12-line hyperfine pattern of the two equally abundant spin- $\frac{5}{2}$ isotopes. The hyperfine constants are $A_{151} = (29.2 \pm 0.3) \times 10^{-4} \text{ cm}^{-1}$ and $A_{153} = (12.7 \pm 0.3) \times 10^{-4} \text{ cm}^{-1}$. The other transitions are broadened and the hyperfine lines are only partly resolved. When the field is rotated away from the [100] direction, "forbidden" transitions produce many lines in addition to the hyperfine lines. The "forbidden" transitions arise since the cubic field is strong enough to compete with the external field to determine the quantization. The crystal-field Hamiltonian is diagonalized by the magnetic quantum numbers only when the external field is along a crystal axis. Off the crystal axis the "forbidden" lines rapidly become very intense and at 5° from the [100] axis, the hyperfine pattern can no longer be resolved. In the [110] direction the lines are again resolved on the $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition. The crystal field is very strong; the pattern is a little wider than the one Ryter⁹ observed in CaF_2 and may contain a noncubic contribution.

D. Other Resonances in the Lead Salts

A featureless, isotropic resonance about 4 G wide was observed at $g=2$ in many of the PbSe samples at 1.3°K. A few of the samples also showed the resonance at 77°K. There was no correlation with its occurrence and the heat treatment. The resonance also appeared very strongly in PbTe and weakly in PbS. It is not due to impurities in the crystal, since non-*S*-state impurities deliberately added to PbSe either could not be observed or gave extremely broad lines. The resonance

⁹ C. Ryter, *Helv. Phys. Acta* **30**, 353 (1957).

might be due to the free carriers. However, it appears equally strong in *n*- and *p*-type material. In addition, Weinberg¹⁰ has calculated that the holes in PbTe should have a large *g* value. It is probably due to a defect in the crystal such as the *F* center.

E. NMR in PbSe

Sapoval¹¹ has recently observed the Pb^{207} nuclear resonance in very-low-resistivity PbTe by using helicon propagation through a single crystal. He observed a single narrow (4 G) line. He also observed the resonance in a powder by normal resonance techniques. This signal, however, is very broad (100 G). He ascribes the difference to the effect of powdering on the semi-conducting properties of PbTe.

Weinberg¹⁰ has observed the Pb^{207} nuclear resonance in PbSe at room temperature and above. We find that the resonance disappears at 77°K and reappears weakly at 1.3°K as a broad, sample-dependent line. We had hoped to observe nuclei whose Knight shift was affected by the electronic inhomogeneity which we believe exists in the crystal. But in view of Sapoval's results for powder samples, we can reach no conclusion. It would be interesting to use the helicon technique to examine the bulk Pb^{207} NMR in higher-resistivity PbSe or PbTe.

The Se^{77} NMR in PbSe could not be detected at any temperature.

IV. DISCUSSION

The very slight variation of *A* with free-carrier concentration and its regular variation with the covalency of the bond indicates that the electronic structure of the Mn ion and its bonds to neighboring ions are very little affected by the presence of even 10^{19} electrons/cm³.

The free carriers can, however, produce a *g* shift of the resonance. Yosida¹² has calculated that a *g* shift can be produced by exchange interactions of the unfilled shell with free carriers, provided that the carriers are polarized. For short electronic relaxation times, the ion sees the average polarization induced by the external field, and a shift analogous to the nuclear Knight shift occurs. The shift is proportional to n/E_F , where *n* is the free carrier concentration and E_F is the Fermi energy.

The presence in PbSe of two sets of hyperfine lines with different *g* shifts indicates that there are regions in the crystal where the free carrier concentration has two different values. This inhomogeneity can either be highly localized or spread over a large region.

¹⁰ I. Weinberg, *J. Chem. Phys.* **36**, 1112 (1962); I. Weinberg and J. Callaway, *Nuovo Cimento* **24**, 190 (1962); I. Weinberg, *J. Chem. Phys.* **39**, 492 (1963).

¹¹ B. Sapoval, *Phys. Rev. Letters* **17**, 241 (1966).

¹² K. Yosida, *Phys. Rev.* **106**, 893 (1957). Yosida's calculation applies strictly only to a metal. However, since PbSe is degenerate, its behavior is probably more metallic than semiconductorlike.

There is strong evidence in silicon to support the assumption that the electronic inhomogeneity in PbSe is large scale. Sundfors and Holcomb¹³ have studied the nuclear relaxation and Knight shift of B- and P-doped Si. They concluded that the P impurities are randomly distributed, but the boron clusters, to form dense uniform regions with greater than 8.5×10^{19} impurities/cm³. The clusters form, since the holes are able to form a metallic bond at such a high concentration. This results in a lower energy than for a random distribution.

In PbSe the Pb and Se vacancies, which play the roles of the B and P, respectively, are simultaneously present; stoichiometry corresponds, not to an absence of vacancies but to equal numbers. If one type of vacancy clusters, while the other is randomly distributed, then one would expect to see two hyperfine lines. Since the clusters are quite dense, at stoichiometry the volume of the crystal occupied by clusters is considerably less than the volume free of clusters. Thus the hyperfine lines from Mn²⁺ located in the clusters should be considerably smaller than the lines from Mn²⁺ outside the clusters. Experimentally, the *n*-type line is large at stoichiometry (Fig. 1B). Thus the *p*-type line results from clusters and we conclude that the Pb vacancies cluster while the Se vacancies are random. (We caution that these remarks are based on the assumption that the peak heights of the second derivative curves are proportional to the number of centers with the *same* constant of proportionality for *both* the *n*- and *p*-type lines.)

There is independent evidence for clustering in *p*-type PbS. Snowden and Portis¹⁴ have observed anomalies in the dark and photoconductivities of PbS films. To explain these anomalies they assumed that the films have regions of photo-insensitive material surrounded by connecting photo-sensitive regions.

A second possible explanation is that the electronic inhomogeneity is localized and the hyperfine lines arise from Mn²⁺ located near a Pb vacancy, a Se vacancy, or isolated. Jerome, Ryter, and Winter¹⁵ have studied the low-temperature nuclear relaxation of Si²⁹ in heavily P-doped silicon. They conclude that, even though the doping is heavy enough to produce an impurity band, the carriers are still highly localized on the P impurity and the carrier density in the intervening regions is quite small. Thus in PbSe an Mn ion near a vacancy would see a considerably different electron density than an isolated one. However, one

has difficulty explaining the absence of noncubic crystal-field effects and the absence of three or more sets of hyperfine lines corresponding to the isolated Mn²⁺ as well as ions in various nonequivalent positions near the two types of vacancies. These nonequivalent positions may be the explanation of the small structure that we have not explained in Fig. 1. Our data do not enable us to differentiate between the two explanations, but we feel that clustering is the more likely explanation.

We have discussed the mechanism which could produce the observed splitting in the Mn hyperfine lines. The *g* shift responsible for the splitting only involves isolated Mn ions and is thus independent of concentration. If the Mn ions are close enough, the polarization induced in the conduction electrons by the exchange interaction already considered will extend to a second Mn ion. This additional polarization will produce a further "indirect exchange" *g* shift which is concentration-dependent.

The Mn concentration in the samples (0.01%) is quite small. Thus to produce a *g* shift of the observed magnitude, the indirect exchange coupling must be very long range. The variation of the samples is so great that we feel it cannot be entirely explained by this simple concentration dependence. The explanation probably involves the complex band structure of PbSe (ellipsoids at the $\langle 111 \rangle$ extremes of the Brillouin zone plus overlapping vacancy bands). There is a possibility that we are seeing the effect of electrons which are quasibound to vacancy levels that lie in the conduction band.

We finally discuss the absence of the cubic-crystal-field splitting. The most obvious explanation would be that the crystal is badly strained or has many small angle grain boundaries. This would average out the four angular-dependent lines of the cubic spectrum and leave only the isotropic $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition. However, the Eu²⁺ spectrum in PbSe crystals, grown in the same manner as those doped with Mn, shows large crystal-field effects. The total disappearance of the "forbidden" transitions when the crystal is accurately aligned along the [100] direction indicates that the crystal is of good quality. We must then conclude that the cubic crystal field is really small in the lead salts.

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¹³ R. K. Sundfors and D. F. Holcomb, Phys. Rev. **136**, A810 (1964).

¹⁴ D. P. Snowden and A. M. Portis, Phys. Rev. **120**, 1983 (1960).

¹⁵ D. Jerome, C. Ryter, and J. M. Winter, Physics **2**, 81 (1965).