

CONCLUSIONS

The electron-beam method, which can reversibly introduce and remove positive charge near the Si-SiO₂ interface of an MOS structure, has been used to study the effects of positive charge on the surface mobility. The experimentally observed changes in the mobility were compared to the theoretical predictions of I, and good agreement was found. The slow decrease in mobility observed may be correlated to the decrease

in mobility of commercial MOS devices. This decrease is much slower than predicted by a theory which assumes constant diffusivity. It has been found that effects due to fast surface states can be separated from effects due to the positive charge by an initial electron bombardment. Although several approximations were necessarily used in the analysis, a definite correlation between theory and experiment was found for surface charge scattering, one important mechanism of surface-mobility reduction.

Absorption Spectrum of Nickel in Gallium Phosphide*

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Optical absorption due to transitions within the d shell of Ni(d^8) as an impurity in GaP has been observed and interpreted. The crystal-field parameters deduced are $B=310\text{ cm}^{-1}$, $\Delta=5500\text{ cm}^{-1}$. An apparent reduction of the first-order spin-orbit interaction in the ${}^3T_1(P)$ state is taken to be a manifestation of the Ham effect.

1. INTRODUCTION

THE absorption spectra of $3d^n$ transition metal impurities in II-VI and III-V semiconductors are of interest because the environment has largely covalent bonding. They are also of use in indicating the electronic configuration of the impurity, and the empirical crystal-field parameters may be used in the prediction of ionization energies and other properties. Weakliem¹ and others have measured such spectra in a variety of II-VI compounds. In a previous paper² we extended this work to the III-V semiconductors and presented data for the absorption of ${}^1\text{Fe}(d^6)$ and $\text{Co}(d^7)$ in a variety of host crystals. In this paper the absorption spectrum of Ni(d^8) in GaP is presented. It is found that the empirical rules given in the previous paper apply to the nickel spectrum. In addition the spectrum shows unusual features in its fine structure, which may be interpreted as a manifestation of the Ham effect.³

2. SPECTRA

Slices of n -type GaP were cut from solid polycrystalline ingots, grown from the melt by S. J. Bass of Services Electronics Research Laboratory. Nickel was

evaporated onto a slice and then diffused in at 1250°C for 24 hours. The slices were optically polished to a thickness of 1.5 mm and mounted on a cold finger in a cryostat, and spectra were measured with a Cary 14IR spectrophotometer. A carbon resistance thermometer was used to monitor the specimen temperature, which was about 8°K.

A typical absorption spectrum in the region 5000–17 000 cm^{-1} is shown in Fig. 1. There is a strong broad absorption with two edges, which probably correspond to the thresholds for photoionization transitions from the impurity to the conduction band and from the valence band to the impurity. Superposed on this is the weaker, sharp line absorption due to transitions within the d shell. The structure near 11 500 and 5700 cm^{-1} , shown in the insets of Fig. 1, was very weak but reproducible.

Electrical measurements prove nickel to be a deep-lying acceptor in GaP. The arguments given by Loescher *et al.*,⁴ for GaP:Co show, when applied to GaP:Ni, that the nickel atoms are in a d^8 configuration and are on substitutional gallium sites in the crystal. The absorption spectrum is in fact similar to that of Ni(d^8) in II-VI compounds with tetrahedral co-ordination.¹ Liehr and Ballhausen⁵ give the energy matrices for the crystal-field splitting of the d^8 configuration in cubic environments. The ground state is ${}^3T_1({}^3F)$ and is split into four components by spin-orbit interaction, while the excited triplet states are ${}^3T_2(F)$, ${}^3A_2(F)$ and

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⁴ D. H. Loescher, J. W. Allen, and G. L. Pearson, J. Phys. Soc. Japan, Suppl. **21**, 239 (1966).

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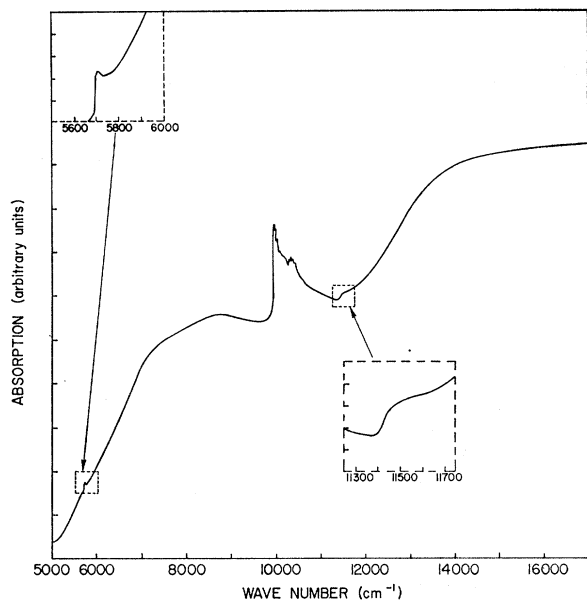


FIG. 1. Absorption spectrum of Ni(d^8) in GaP at liquid-helium temperature.

${}^3T_1(P)$. The strong crystal-field peak near $10\,000\text{ cm}^{-1}$ is characteristic of the ${}^3T_1(F)\text{-}{}^3T_1(P)$ absorption in nickel. We then attribute the weak absorption peak at $11\,500\text{ cm}^{-1}$ to the ${}^3T_1(F)\text{-}{}^3A_2(F)$ transition, and that at 5700 cm^{-1} to ${}^3T_1(F)\text{-}{}^3T_2(F)$. In order to obtain values of the crystal-field parameters Δ and B it is necessary to assume a value for the splitting of the ground state. The spin-orbit stabilization of the lowest component is approximately $2.7|\lambda|$. Taking the free-ion value of $|\lambda|$ gives a stabilization of 900 cm^{-1} . The best fit to the spectrum, ignoring interaction with singlet states, is then given by $B=310\text{ cm}^{-1}$, $\Delta=5500\text{ cm}^{-1}$, for which the calculated transition energies are ${}^3T_1(F)\text{-}{}^3T_2(F)=5900\text{ cm}^{-1}$, ${}^3T_1(F)\text{-}{}^3T_1(P)=10\,000\text{ cm}^{-1}$, ${}^3T_1(F)\text{-}{}^3A_2(F)=11\,400\text{ cm}^{-1}$. Interaction with nearby singlets arising from 1D will depress the true value of ${}^3T_1(F)\text{-}{}^3T_2(F)$ below this calculated value. The agreement with experiment is therefore good. If we take a slightly reduced value for the stabilization, say 700 cm^{-1} , which is similar to that used by Weakliem for II-VI compounds, then the fit is about as good, with B still 310 cm^{-1} but Δ slightly increased to 5600 cm^{-1} .

In a previous paper² on the spectra of $\text{Co}(d^7)$ in various semiconductor compounds, it was shown that a correlation exists between the value of B and the refractive index n of the host crystal. Figure 2 is a plot of β , namely the ratio of B to the free-ion value, against n^{-2} , for Ni(d^8) in GaP, ZnSe⁶, ZnS,¹ CdS^{1,7} and ZnO.^{1,8} It is seen that the points lie on a smooth curve. The curve is close to that obtained for $\text{Co}(d^7)$, i.e., the

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⁷ R. Pappalardo and R. E. Dietz, Phys. Rev. **123**, 1188 (1961).

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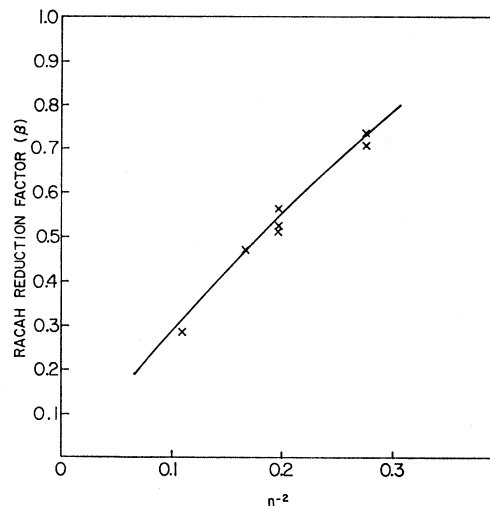


FIG. 2. Variation of the Racah parameter reduction factor β with n^{-2} , where n is the infrared index, for Ni(d^8).

dielectric screening is not greatly dependent on the configuration. This fact suggests that the same curve may be valid for other d^n configurations, thus allowing one to estimate the value of B in systems in which it is not known from experiment.

The value of Δ , $5500\text{--}5600\text{ cm}^{-1}$, is only slightly higher than that found for GaP:Co, namely 5400 cm^{-1} . It is greater than that for the II-VI compounds (4500 cm^{-1}) as is expected because Ni(d^8) in GaP is charged with respect to the host crystal.

3. ${}^3T_1(F)\text{-}{}^3T_1(P)$ ABSORPTION

Figure 3 is a plot, on an expanded scale, of the characteristic absorption peak near $10\,000\text{ cm}^{-1}$. Both the initial and final states are 3T_1 and are split into four components by spin-orbit interaction. At the temperature of measurement only the lowest level of the ground state is populated, so the absorption spectrum should consist of four lines. In fact two groups of four lines are seen. The spacings between corresponding members of the two groups are given in Table I. The spacings are

TABLE I. Fine structure in the ${}^3T_1(F)\text{-}{}^3T_1(P)$ absorption peak of GaP:Ni(d^8).

Line in first group	Line in second group	Difference
$9926 \pm 3\text{ cm}^{-1}$	$10\,288 \pm 3\text{ cm}^{-1}$	$362 \pm 5\text{ cm}^{-1}$
9970	10 331	361
10 000	10 368	368
10 070	10 406	336

almost constant and are close to the energy of the TO(Γ) mode in GaP,⁹ 366 cm^{-1} , so we believe the second group to be a phonon replica of the first group.

Within the first group there are four lines, as expected.

⁹ J. P. Russell, J. Phys. (Paris) **26**, 620 (1965).

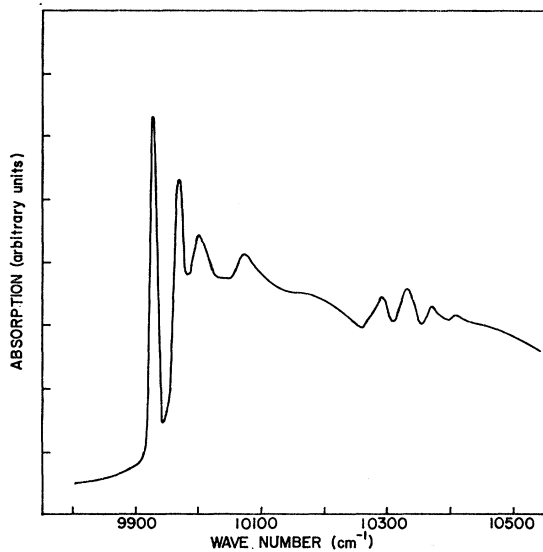


FIG. 3. ${}^3T_1(F)$ - ${}^3T_1(P)$ absorption at liquid-helium temperature.

The calculated width of the group is approximately $3|\lambda|$, i.e., $\sim 1000 \text{ cm}^{-1}$, but the observed spacings are only 44, 30, and 70 cm^{-1} . Although λ is reduced from its free ion value in solids, it is not reduced to this extent. Because the ${}^3T_1(P)$ state is orbitally degenerate it is liable to be split by a Jahn-Teller distortion. Ham⁸ has shown that under certain circumstances tunnelling between crystallographically equivalent distorted sites can lead to an apparent reduction of the spin-orbit coupling. Slack *et al.*¹⁰ have interpreted the spectra of $\text{Fe}(d^6)$ in II-VI compounds in terms of the Ham effect, and observe an apparent reduction of the first-order spin-orbit coupling of the same order of magnitude as we observe in GaP:Ni. We conclude that the ${}^3T_1(P)$ state in GaP:Ni also shows the Ham effect.

Since the ground state is also 3T_1 , the question arises whether the spin-orbit splitting is also quenched in this state. We have no direct experimental information on this, but if we assume the spin-orbit stabilization of the lowest level of the ground state is 100 cm^{-1} or less, it is

¹⁰ G. A. Slack, F. S. Ham, and R. M. Chrenko, *Phys. Rev.* **152**, 376 (1966).

no longer possible to obtain such a good fit to the positions of the 3T_2 , 3A_2 and 3T_1 absorptions with any value of B and Δ .

4. CONCLUSIONS

The absorption spectrum of GaP:Ni(d^8) falls into the same general pattern as those of other $3d^n$ impurities in the II-VI and III-V semiconductors. Despite the strong covalency, a simple crystal-field description is adequate to explain the observed spectrum, as long as the parameters B and Δ are regarded as empirical quantities. The correlation between B and the refractive index reported for Co(d^7) and interpreted as a dielectric screening effect also holds for Ni(d^8). The value of Δ is consistent with that observed in related systems.

Usually it is difficult to find an unambiguous interpretation of the fine structure in crystal-field spectra because energy separations due to phonon interactions and to spin-orbit interactions are of similar magnitude. Nickel in GaP is a special case in which the two types of interaction are clearly distinguished because the spin-orbit coupling is reduced by almost an order of magnitude by the Ham effect, and because only one phonon is dominant in the phonon interaction.

At the present time, there is insufficient knowledge of the parameters involved to predict for a given system whether there will be a Ham effect, a static Jahn-Teller effect or a negligible site distortion. We therefore cannot say, for instance, whether the ground state ${}^3T_1(F)$ is subject to an apparent reduction of the spin-orbit coupling. It is interesting in this respect that we have been unable to find any resolvable fine structure in the ${}^3T_1(F)$ - ${}^3T_1(P)$ absorption in ZnTe:Ni, even at liquid-helium temperature, which may be a manifestation of a dynamic distortion strong enough to wash out all structure. Weakliem¹ has observed extensive fine structure in the absorption spectra of Ni(d^8) in ZnO, ZnS and CdS, and Pappalardo *et al.*,⁸ for ZnO:Ni, but here the interpretation is complicated by the trigonal component of the crystal field in the wurtzite structure, and it is not possible to extract from the data an unambiguous value for the apparent spin-orbit coupling.