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# OPTICAL AND ESR STUDIES OF IRON DOPED LEAD AZIDE POWDERS

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Picatinny Arsenal
Dover, New Jersey

June 1974

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Optical reflectance and electron spin resonance spectra have been obtained for iron doped lead azide prepared by several different procedures. The results indicate that iron is incorporated in lead azide as either $Fe^{2+}$ or $Fe^{3+}$ depending upon the method of preparation. Based upon the electron spin resonance data, it is suggested that $Fe^{3+}$ ions in the lead azide lattice are in a highly perturbed environment and are probably closely associated with the charge compensating defect. Models are proposed for the various types of defect associates which can occur.

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# OPTICAL AND ESR STUDIES OF IRON DOPED LEAD AZIDE POWDERS

## Introduction

Impurities and native atomic imperfections in inorganic solids have been observed to produce changes in many of the solid state phenomena such as luminescence, optical absorption, photoconductivity and others. The inorganic azides exhibit, in addition to these more common solid state phenomena, the unusual property of decomposing to form metal and nitrogen gas. This decomposition can be initiated by a variety of stimuli including heat, light, shock and ionizing radiation, and for many of the heavy metal azides may be highly exothermic leading to the initiation of explosion or detonation.

The effects of impurities on the solid state properties, and particularly on the slow decomposition reactions of lead azide have received some attention[1-8]. However, in most cases the valence state of the impurity and the atomic nature of the impurity center was not directly established, and the determination of the role of the impurities in the decomposition process was therefore subject to this limitation.

In the specific case of iron impurities in α-lead azide, several phenomena have been observed:

(1) The onset in the optical absorption spectrum[4] of a broad plateau at 6500A which extends to the fundamental absorption edge.

(2) A corresponding peak in the photocurrent spectrum[4] in the neighborhood of 6500A.

(3) Extrinsic photolytic decomposition in which nitrogen gas is evolved with irradiation in the 6500A impurity absorption region[4].

(4) A change in the "reactivity" by the inclusion of $10^{-2}$ mole per cent of iron impurities[2].

In order to understand in more detail the role of iron impurities in producing these effects in lead azide, we have performed optical and electron spin resonance (ESR) measurements on α-lead azide powders doped with varying concentrations of iron. Evidence of several different iron impurity centers has been obtained for different methods of preparation, and the valence state of several of the iron centers has been identified. In addition, preliminary evidence is presented for the observation of a complex impurity associate of the donor-acceptor pair type.

## Experimental

### A. Material Preparation

Ferric azide was obtained in solution by the reaction of a 5% hydrazoic acid solution with either pure metallic iron or with reagent grade ferric or ferrous halide salts. The reaction of the ferric ion with hydrazoic acid is readily identified by the intense red color produced by the presence of the ferric azide complex which is formed according to the reaction[9],

$$Fe^{3+} + HN_3 \rightarrow (FeN_3)^{2+} + H^+.$$

The coloration was observed in solution obtained by reacting metallic iron with $HN_3$ or by acidifying iron halide salt solutions with the same acid.

Several different techniques were employed for the preparation of iron doped lead azide powders. The procedures are presented below and the types of lead azide obtained by these techniques are arbitrarily labelled Type I through IV for reference in the discussion which follows.

## $Pb(N_3)_2$ : Fe(Type I)

A lead nitrite solution was obtained by swirling "spec-pure" (Johnson and Mathey Ltd.) lead oxide, PbO, in water while bubbling in a 50/50 weight percent mixture of nitrous oxide and nitric oxide gases. The reaction was monitored visually to prevent the formation of $HNO_2$ (characterized by a blue coloration) due to excess addition of the gases, and the solution was maintained at icebath temperature since lead nitrite is somewhat unstable and decomposes slowly at room temperature.

Quantitative amounts of the ferric azide solution were added to the lead nitrite solution and subsequently gaseous $HN_3$ was bubbled through the solution[10]. The resulting precipitate was lead azide with a yellow coloration characteristic of the ferrous ion. The

reduction of the iron occurs in the solution through reaction with the nitrite ions prior to the addition of gaseous $HN_3$.

It should be noted that if the procedure is reversed by adding lead nitrite solution to an $HN_3$ solution containing the ferric azide complex the resulting precipitate is reddish in color and similar in all respects to the Type II samples discussed below. Both variations result in a high purity precipitate since the reaction products, other than the doped lead azide, are all gaseous.

$Pb(N_3)_2$ : Fe (Type II)

Lead azide doped with iron was prepared by dropwise addition of a high purity lead acetate (Johnson Mathey - Grade I) solution to a continuously stirred 5% $HN_3$ solution which contained a quantitative amount of ferric azide complex (obtained as discussed under Type I). The resulting precipitate was reddish colored α-lead azide.

$Pb(N_3)_2$ : Fe (Type III)

Quantitative amounts of iron azide solutions were added to a 5% $HN_3$ solution. Nitric acid was then added until the red coloration disappeared indicating the destruction of the ferric azide complex[9]. Lead acetate solution was added dropwise to this colorless solution and the precipitated lead azide was also colorless.

$Pb(N_3)_2$ : Fe, Ag. (Type IV)

(a) Quantitative amounts of iron azide solution were added to a 1M $HN_3$ solution. A lead acetate solution containing a small quantitative amount of dissolved silver acetate was added to precipitate lead azide containing iron and silver.

(b) Quantitative amounts of iron azide solution were added to a 1M $HN_3$ solution which also contained small quantitative amounts of dissolved silver acetate. Lead acetate solution was then added dropwise to precipitate lead azide containing silver and iron. This procedure was applicable only for low silver concentratons. High concentrations ($>10^{-3}$ mole fraction) of silver acetate produced a haze in the $HN_3$ solution. The solution could be cleared by the addition of a small quantity of $HNO_3$, however, it was preferred not to have $NO_3^-$ ions present during precipitation.

The methods of preparation are summarized in Table 1.

TABLE 1

| Type | Method of Preparation |
|---|---|
| I | $[Pb(NO_2)_2 + Fe^{2+}] + HN_3$ (gaseous) |
| II | $Pb(Ac)_2 + [HN_3 + (FeN_3)^{2+}]$ |
| III | $Pb(Ac)_2 + (HN_3 + Fe^{3+} + HNO_3)$ |
| IVa | $[Pb(Ac)_2 + AgAc] + [HN_3 + (FeN_3^{2+})]$ |
| IVb | $Pb(Ac)_2 + [HN_3 + AgAc + (FeN_3^{2+})]$ |

The concentration of the iron impurity using all these techniques was, in most cases, varied over the range of $10^{-6}$ to $10^{-2}$ mole fraction; and the amount of silver added in Type IV was calculated to maintain a 1:1 or 2:1 atomic ratio of silver to iron. The high solubility of ferric azide in water prevents its co-precipitation, and the precipitates were washed in triply distilled water to eliminate any adsorbed ferric azide.

Undoped lead azide samples were also prepared by each of the different techniques for use as comparison standards. Several of the lead azide samples, both pure and doped, were submitted for mass spectrographic and quantitative chemical analysis, but because of the inherent explosive properties of lead azide the samples had to be thermally decomposed prior to analysis by mass spectrographic techniques. The procedure followed was to first convert the lead azide to PbO by decomposing it in air at approximately 200°C and then to increase the temperature to 390°C over an eight hour period. It was assumed from known conversion temperatures and the coloration of the sample that the final product was $Pb_3O_4$, and the fractional weight analyses were based upon this assumption.

In several cases both undecomposed doped lead azide samples and their corresponding decomposed samples were both analyzed for iron and silver using standard colorimetric and gravimetric techniques.

B. Apparatus

Diffuse reflectance measurements were performed on a Perkin-Elmer Model 350 Spectrophotometer equipped with a diffuse reflectance accessory. The powder samples were spread evenly over the bottom of a Suprasil-A quartz sample holder which was then mounted into the integrating sphere. Since the quartz sample holder acts as a window which can contribute to the reflectance, the magnesium carbonate standard was mounted in an identical holder; and the baseline for 100% reflectance was established by using two magnesium carbonate standards in identical sample holders.

The electron spin resonance spectra of the powders were measured using Varian E-3 and V-4500 spectrometers. The samples were contained in evaucated quartz tubes which could be immersed in liquid nitrogen for low temperature studies.

## Results

Representative samples of the materials prepared by each method were analyzed; the diffuse reflectance was measured; and the ESR absorption spectra were obtained. The results are presented according to the method of preparation.

### TYPE I

Powders obtained by this method were analyzed for iron content by both mass spectrographic and colorimetric techniques. As an

example, addition of ferric azide solution in quantities calculated to produce $2.6 \times 10^{-3}$ mole fraction of iron impurity resulted in a product containing $1.9 \times 10^{-3}$ mole fraction of iron.

The diffuse reflectance spectrum (Figure 1) shows an onset in absorption at 600 nm which increases gradually to the sharp edge at 420 nm corresponding to the fundamental absorption of lead azide. No ESR absorption was observed in these powders at either room or liquid nitrogen temperature.

## TYPE II

Several iron doped lead azide samples were prepared using this method, and the amount of iron present was varied from $10^{-6}$ to $10^{-1}$ mole fraction. A typical analysis shows $6 \times 10^{-4}$ mole fraction of iron in a product where $2 \times 10^{-2}$ mole fraction was available in solution. The coloration of the powders varied from pink, for low iron concentration, to reddish brown for the heavily doped samples. The diffuse reflectance spectra of samples prepared by methods IV (a) and (b) are qualitatively the same, and in the wavelength region studied they are not distinguishable from spectra of Type II samples with similar concentrations of iron. The typical diffuse reflectance spectrum, Figure 1, showed a long absorption tail, the onset of which occurs at approximately 800 nm. The fundamental absorption was again observed at 420 nm. These samples have a characteristic ESR spectrum which appears at liquid nitrogen

temperature, and is shown in Figure 2. The absorption is centered at approximately 1500 gauss at X-band frequencies. The position of the effective g-value, 4.27, is indicated in the figure. Increasing the concentration of iron produced a corresponding increase in the intensity of the ESR signal.

## TYPE III

The preparation of $Pb(N_3)_2$:Fe from low pH solutions yields a white precipitate which was shown, by colorimetric analysis, to contain iron. The diffuse reflectance spectrum is qualitatively the same as that obtained from undoped lead azide; and there is no ESR absorption at room or liquid nitrogen temperature. When the powders were irradiated with ultraviolet light at 77°K an ESR absorption was obtained at approximately g = 2.0. Undoped powders were subsequently prepared under the same conditions of low pH and irradiated in the same way. The u.v. induced resonance appeared in these samples as well. This resonance probably arises from one or more paramagnetic species produced from nitrate ions by u.v. irradiation. Similar effects have been observed with u.v. irradiated $KN_3$ which contained $NO_3^-$.[11] It should be noted that this resonance was not obtained in either the doped or undoped powder samples prepared by any of the other procedures.

## TYPE IV

The addition of silver and iron to lead azide represents an attempt to incorporate both donors, $Fe^{3+}$, and acceptors, $Ag^{+}$, in the crystal lattice. It is possible that $AgN_3$ was co-precipitated in preparation (a), however in preparation (b) where the silver acetate is added to the ferric azide solution no precipitate is observed prior to the addition of the lead acetate solution. Two typical samples were analyzed for silver and iron content by both mass spectrographic and wet chemical techniques: (1) Quantitative amounts of silver and iron calculated to give $2 \times 10^{-2}$ mole fraction silver and $1 \times 10^{-2}$ mole fraction iron were available in solution. Analysis showed $2 \times 10^{-2}$ silver and $1 \times 10^{-3}$ iron in the final product. (2) The calculated amounts of silver and iron available were $10^{-1}$ mole fraction for both dopants. Analysis showed that $1 \times 10^{-1}$ mole fraction of silver and $5 \times 10^{-3}$ mole fraction of iron were present in the precipitate.

The typical ESR spectrum obtained from these samples at 77°K is shown in Figure 3. The field position and extent of the resonance absorption are the same as observed for samples of Type II, but the structure associated with the resonance absorption is modified considerably by the addition of the silver.

## Discussion

The preparation designated as Type I was devised to incorporate $Fe^{2+}$ into the lead azide lattice. Partial evidence that this does occur is provided by the yellow color of the sample as compared to the reddish color of the Type II powders. We assume that the $Fe^{2+}$ is incorporated at $Pb^{2+}$ sites since this requires no charge compensating defect. (The ionic radius of $Pb^{+2}$ is 1.20 A and the radius of $Fe^{2+}$ is .76 A.) The formation of some other defect would be necessary if the iron were incorporated at a different site. For example, an interstitial $Fe^{2+}$ might be compensated by two interstitial azide ions or a lead vacancy.

The electronic ground state of $Fe^{2+}$ is $^5D$, and in the weak-field limit the spin quantum number S=2 is expected. The paramagnetic resonance from this configuration is highly anisotropic therefore not easily observed in powders.

The reddish appearance and the long wavelength decrease in reflectance for samples of Type II are evidence for the presence of iron in a different charge state than obtained by the procedure of Type I. The iron is present in solution as $[FeN_3]^{2+}$ and may be incorporated into the lead azide lattice as $Fe^{3+}$ or it may maintain its close association with the azide ion and be incorporated as the doubly charged impurity complex $[FeN_3]^{2+}$.

In the Type II powders the electron spin resonance which occurs at low magnetic field has an effective g value of 4.3 and is

dependent upon the iron concentration. According to the analyses there are no other extrinsic impurities which should give rise to a resonance of this magnitude. The ground state electronic configuration of the $Fe^{3+}$ ion is $^6S_{5/2}$, and unless the local site symmetry of this ion is especially low or there is some degree of covalent bonding a paramagnetic resonance is expected to occur at approximately g=2. Similar low field ESR spectra have been observed in several other materials, including glasses, natural quartz, polycrystalline biological materials and some II-VI compounds[12-16]. These spectra, all of which exhibit a resonance at an effective g-value[17] of approximately 4.3 at X-band frequencies, have been attributed to the $Fe^{3+}$ ion in an environment of low symmetry and in either strong local crystalline fields or in a site where there is some degree of covalent bonding to the ligands or to a closely associated impurity. In these situations the $^6S_{5/2}$ state can be split into three Kramer's doublets, and in many cases the resonance transition arising from the central doublet is isotropic or nearly isotropic and gives rise to the absorption observed at or near $g_{eff}$ = 4.3 at X-band frequencies. The spin Hamiltonian which describes the resonance is

$$H = g_o\beta H + D\left(S_Z^2 - \frac{S(S+1)}{3}\right) + E\left(S_x^2 - S_y^2\right)$$

where $g_o$ is assumed to be 2.0, S = 5/2 and D and E are large compared to $g_o\beta H$. Dowsing and Gibson have predicted the ESR transitions

at X-band for several values of the ratio E/D[16]. According to their calculations the absorption which we observed at $g_{eff} = 4.27$ indicates that $E/D \simeq 1/3$ and $D \sim 0.23\ cm^{-1}$.

The way in which the $[FeN_3]^{2+}$ complex is incorporated into the lead azide lattice is not fully established experimentally. If it maintains its identity as a complex, it can be situated at either of the two types of $Pb^{2+}$ sites[18] and would require no compensating defect.

The complicated structure observed in the powder spectrum could arise from the fact that there are two inequivalent sites, and in addition, if the $Fe^{3+}$ remains complexed as $[FeN_3]^{2+}$ there could be a strong hyperfine interaction with the nuclear spin ($I = 1$) of one or more of the nitrogen atoms in the associated azide ion.

The preparation of Type III lead azide represents an attempt to incorporate uncomplexed $Fe^{3+}$ into the lead azide lattice. As mentioned in the results this method leads to incorporation of $NO_3^-$ as well. The precipitate has a diffuse reflectance spectrum which is the same as undoped lead azide. However, presence of iron in these materials was established by analysis, and the concentration was as great or greater than that obtained by other methods of preparation. The reduction of the ferric ion or formation of the iron complex during precipitation showed a yellow or reddish precipitate respectively, as observed for Type I and Type II samples.

We conclude from these observations that the iron is present in Type III samples and is incorporated as $Fe^{3+}$.

Assuming that the iron is incorporated at a cation site, one would predict an ESR absorption at approximately $g = 2$ arising from the $^6S_{5/2}$ state of the unassociated $Fe^{+3}$ or at $g \simeq 4.3$ (similar to that observed in type II samples) if the $Fe^{+3}$ is closely associated with a compensating defect such as interstitial $N_3^-$ or $NO_3^-$.

The states of $Fe^{+3}$ ions substituted at $Pb^{+2}$ cation sites are donor states. Charge compensation may occur by the formation of negatively charged interstitial defects or by the formation of lead vacancies. It must be emphasized that this material is formed in aqueous solution at room temperature so that the coulomb interaction between charged defects over a distance of more than a few lead azide lattice constants is effectively screened by the large dielectric constant of the medium. Thus closely associated defects are statistically favored over the formation of more distant charge compensating defects.

One very plausible type of associate defect is a lead vacancy with two ferric ions at two of the nearest neighbor lead sites, $[Fe^{3+} - V_{Pb}^{2-} - Fe^{3+}]$. In this case, however, a contribution from the exchange coupling between the ferric ions could perturb the magnetic interactions to produce a highly anisotropic spectrum and prohibit the observation of any ESR absorption in the powder samples.

The electron spin resonance for an unassociated, substitutional $Fe^{+3}$ ion should result from the + 1/2 - 1/2 transitions in the $^6S$ state. This resonance should be isotropic and easily observable even in powder samples. Failure to detect such a resonance in Type III samples strongly supports the identification of a more complex anisotropic defect such as the $[Fe^{3+} - V_{Pb}^{2-} - Fe^{3+}]$.

The Type IV samples were prepared in an attempt to incorporate defect associates of the donor-acceptor pair type in lead azide. This type of defect in other semiconducting materials, has produced several interesting phenomena involving radiative electron transfer between donors and acceptors[19].

The effects of the addition of $Ag^+$ on the thermal decomposition, electrical conductivity and photoconductivity of lead azide powders have been studied[5], and it was assumed, although not explicitly demonstrated, that silver can be incorporated in lead azide as $Ag^+$.

Analyses of the Type IV samples showed that the silver and iron are both present in the precipitate. We have not shown directly that the silver was incorporated into the crystal lattice of the lead azide; it may be present as co-precipitated silver azide. However, indirect evidence that silver was incorporated appears in the ESR absorption spectrum. A low field electron spin resonance occurs as in Type II powders, but its structure is considerably different. We identify the resonance, from its effective g-value

of 4.27, as arising from the perturbed $^6S_{5/2}$ state of the $Fe^{3+}$, and suggest that the perturbation may arise in this case from a $Ag^+$ ion at a nearest neighbor lead site. Closely associated Fe-Ag and Fe-Cu pairs have been observed in several II-VI compounds[15]. Associate formation of this type depends on the total concentration and the relative number of donors and acceptors present. If the concentrations of the iron and silver are $10^{-4}$ mole fraction for each impurity ion an electron spin resonance identical to that observed in Type II samples is observed. If the impurity concentration is raised to $10^{-2}$ mole fraction or greater, the electron spin resonance is observed with approximately the same effective g-value but the structure in the resonance is considerably modified. Further, it is observed that the amount of iron incorporated, compared to that available in solution, is greater when $Ag^+$ is present than when it is not as in samples of Type II. These observations are consistent with the idea that $Ag^+$ at a neighboring lead site provides the charge compensation for an $Fe^{3+}$ ion, also at a lead site. The diffuse reflectance spectra of Type II and Type IV are not distinguishable and therefore only confirm the presence of $Fe^{3+}$ in a strongly perturbed environment.

## Summary

We have used four methods to prepare lead azide doped with iron and have performed analyses to show that iron is present in the

product in all cases. The observations and proposed models of the iron impurity centers are compiled in Table 2.

TABLE 2

| Type | Onset of Diffuse Reflectance | ESR | Proposed Defect |
|---|---|---|---|
| I | ∿600nm | Not observed | $Fe^{2+}$ |
| II | ∿800nm | $g_{eff}$ ∿4.3 | $[FeN_3]^{2+}$ |
| III | ∿420nm | Not observed | $[Fe^{3+}-V_{Pb}^{2+}-Fe^{3+}]$ |
| IV | ∿800nm | $g_{eff}$ ∿4.3 | $Fe^{3+}-Ag^{+}$ Pair |

The coloration of the powders follows a chromophoric series which corresponds to that of the iron ion in solution. Type I, Type III, and Types II and IV correspond to the ferrous (yellow), ferric (colorless), and ferric complex (red) respectively.

By diffuse reflectance measurements we observed the characteristic fundamental absorption edge of lead azide at 420 nm in samples prepared by the four methods. In addition the Type I and Type II and IV spectra show characteristics which depend upon the method of doping and therefore the charge state of the incorporated iron.

We identify the paramagnetic ion responsible for the ESR spectra of Type II and Type IV samples as $Fe^{3+}$ in an environment of low symmetry. The details of the main ESR absorption in Type II are interpreted as arising from some degree of covalent bonding between the ferric ion and an associated azide ion and a hyperfine

interaction with at least one of the nitrogen nuclei. The modifications in the spectra of the $Ag^+$ - $Fe^{3+}$ doped samples of Type IV are interpreted as being due to an association of the $Fe^{3+}$ ion with a charge compensating $Ag^+$ ion at a nearest neighbor lead site.

The incorporation of iron in Type III samples was established by analysis, but this impurity does not produce observable effects in either the ESR or diffuse reflectance of these materials. We propose a model for a charge compensated associate involving two $Fe^{3+}$ ions and one lead vacancy. The principal justification for this model is the absence of an essentially isotropic ESR spectrum which should result from the $(+1/2 \rightarrow -1/2)$ transitions in the $^6S_{5/2}$ state of the isolated ferric ion and the fact that formation of associates of this type is favored in a medium with a high dielectric constant. The exchange coupling between two closely associated ferric ions would be expected to produce an anisotropic spectrum which cannot be observed in the powders. The presence of such associates could be verified by magnetic susceptibility measurements.

It is intended that this work will form a basis for interpreting the many phenomena observed in iron doped lead azide. Because of the complex structure of the lead azide lattice and the complexity of the impurity centers produced by iron doping, additional experimental work, particularly with doped single crystals, will be required to confirm the details of the defect associates suggested here.

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$$N_3^- + NO_2^- + 2H^+ \rightarrow N_2O + N_2 + H_2O.$$

Since the $NO_2^-$ is decomposed, $Pb(N_3)_2$:Fe is the only non-gaseous product.

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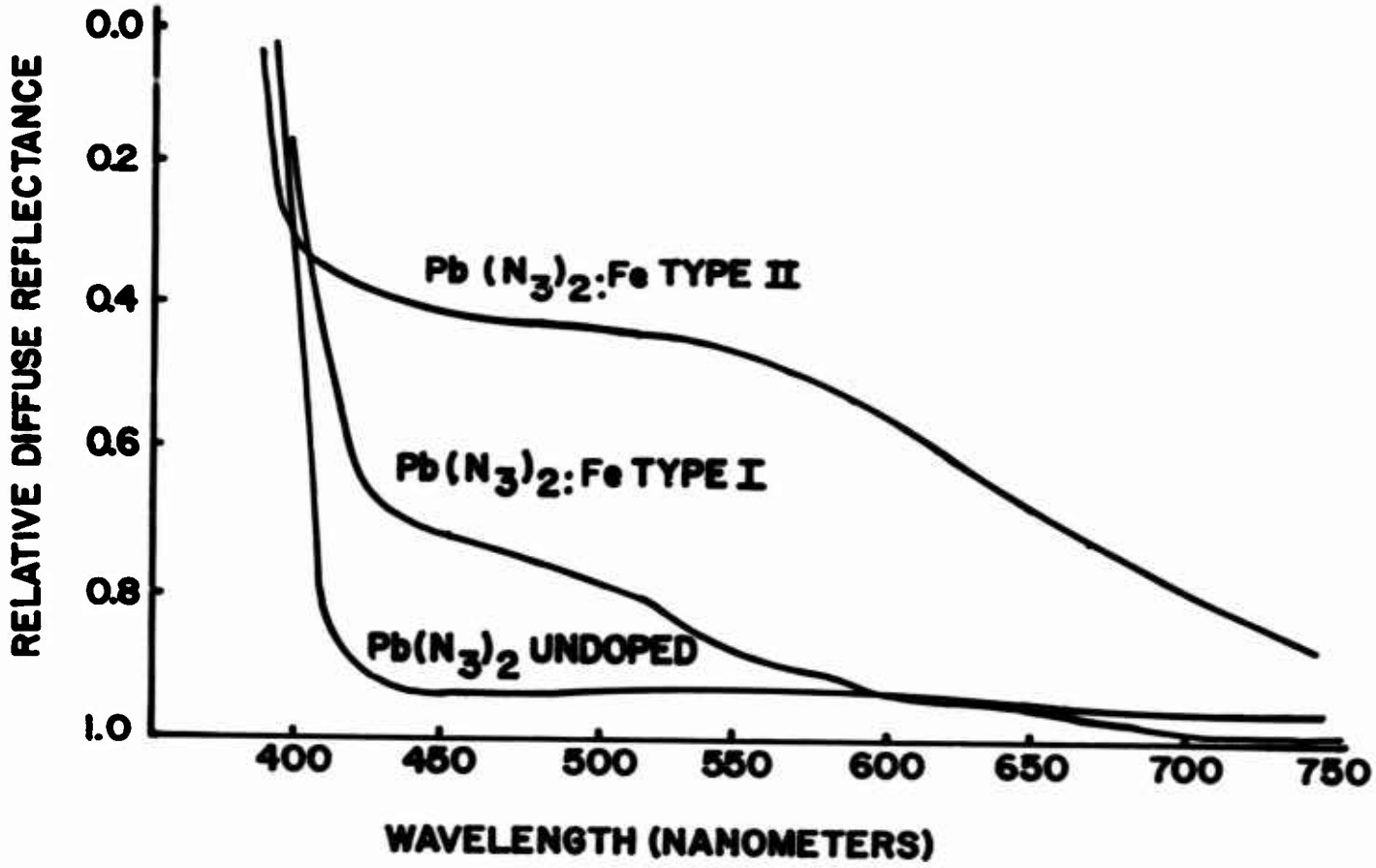


Figure 1: Relative Diffuse Reflectance Spectra of Undoped, Type I and Type II Lead Azide

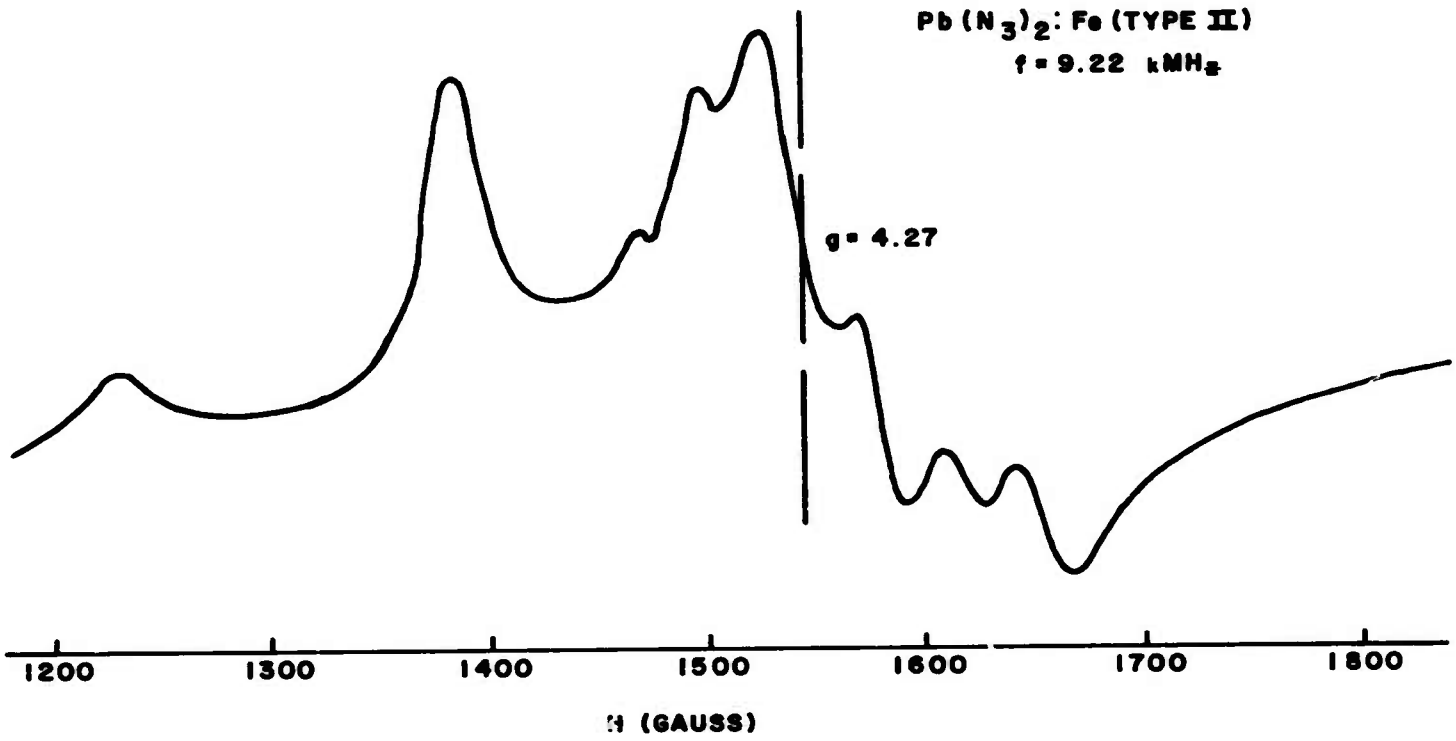


Figure 2: Electron Spin Resonance Spectrum of Type II Lead Azide

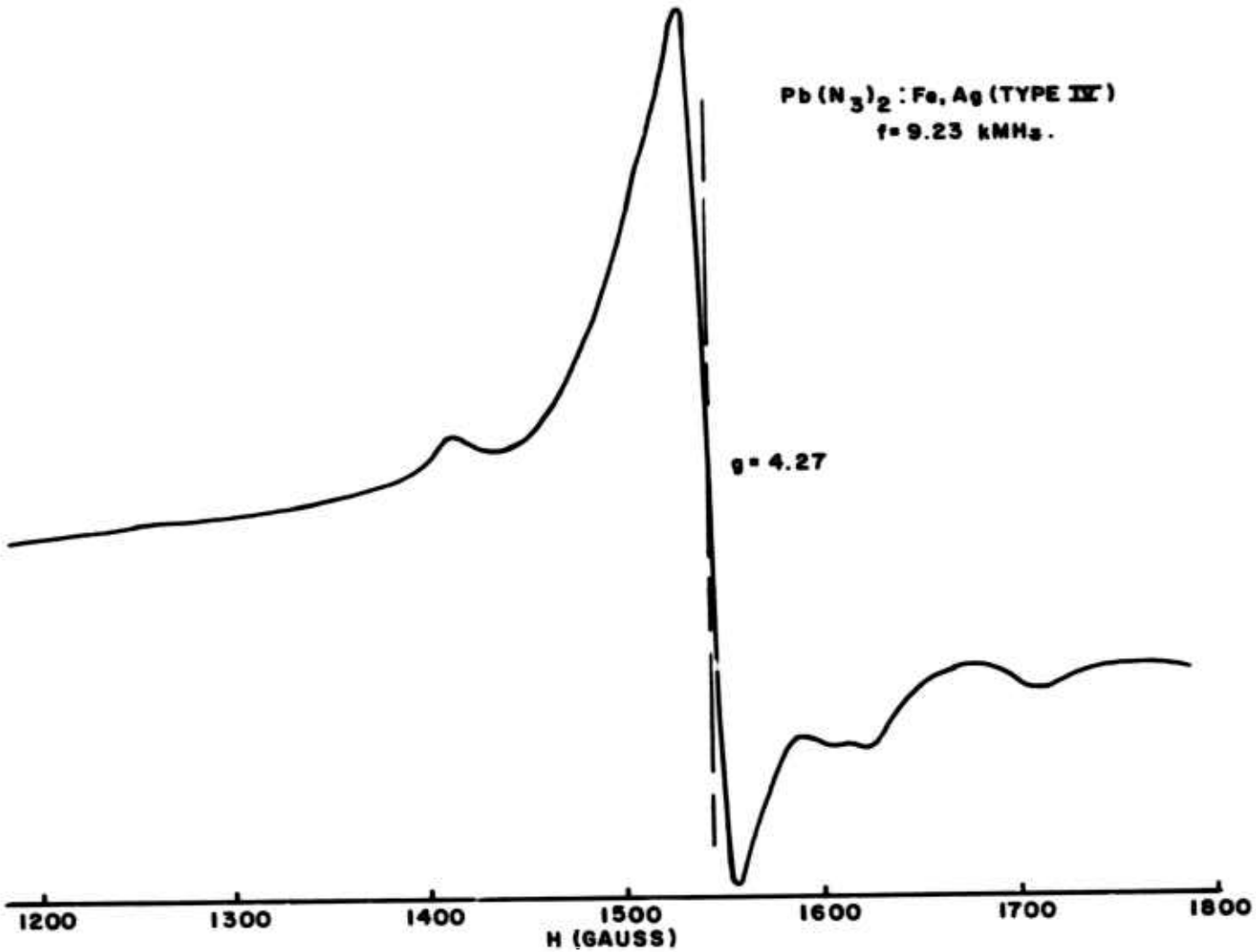


Figure 3: Electron Spin Resonance Spectrum of Type IV Lead Azide