Zeitschrift: Archives des sciences [1948-1980]

Herausgeber: Société de Physique et d'Histoire Naturelle de Genève

Band: 27 (1974)

Heft: 2-3: EPR of magnetic ions in metals

Artikel: Magnetic resonance in 3d impurities in metals

Autor: Hirst, L.L.

DOI: https://doi.org/10.5169/seals-739313

Nutzungsbedingungen

Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften auf E-Periodica. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. Das Veröffentlichen von Bildern in Print- und Online-Publikationen sowie auf Social Media-Kanälen oder Webseiten ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. Mehr erfahren

Conditions d'utilisation

L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. La reproduction d'images dans des publications imprimées ou en ligne ainsi que sur des canaux de médias sociaux ou des sites web n'est autorisée qu'avec l'accord préalable des détenteurs des droits. En savoir plus

Terms of use

The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. Publishing images in print and online publications, as well as on social media channels or websites, is only permitted with the prior consent of the rights holders. Find out more

Download PDF: 14.07.2025

ETH-Bibliothek Zürich, E-Periodica, https://www.e-periodica.ch

MAGNETIC RESONANCE IN 3d IMPURITIES IN METALS

BY

L. L. HIRST

Institute Laue-Langevin, 8046 Garching, West Germany *

I am happy to be able to speak near the end of this conference, because so many of the preceding speakers have discussed effects relevant to those which I am to discuss. This makes my job much easier. So I should like to express my thanks to the other speakers and also to those who have done such an excellent job of organizing this conference.

1. THE BOTTLENECK EFFECT

As is well known, the phenomenon of *EPR* of $3d$ impurities in metals is intimately connected with the bottleneck effect [1-5]. This effect is implicit in the phenomenological equations of motion for the coupled macroscopic magnetizations, which are used in the direct analysis of the experimental data. Here we can only summarize this effect very briefly, our main aim being to identify the important parameters which we hope to understand via the microscopic theory.

Let us first consider the case when we have a single species of impurities, with d and s denoting the magnetization of the impurities and the spin magnetization of the conduction electrons respectively. The various cross relaxation and spin-lattice relaxation rates for this system are indicated schematically by the left-hand portion of Figure 1. The essential point of the bottleneck effect is that the cross relaxation rates $1/T_{ds}$ and $1/T_{sd}$ tend to cancel out of the linewidth when they are large, whereas the spin-lattice relaxation rates $1/T_{dL}$ and $1/T_{sL}$ do not. Practically, the question of whether a given species of d-impurity can show an *EPR* which is narrow enough to be observed under the usual conditions will depend mainly on whether it has a large spin-lattice relaxation rate $1/T_{dL}$.

It is also often useful to study alloys in which we have a primary impurity species, denoted d and usually *Mn* in practice, which is a good bottlenecking impurity, together with an additional impurity species, denoted a, whose behavior is to be investigated [4-6]. The equations of motion for the coupled d, s, and a magnetizations can be solved and the solution can be interpreted in terms of two bottlenecking

---

* Present address: Institut für Theoretische Physik der Universität Frankfurt, Frankfurt a. m., West Germany.

conditions [6]. It is found that if the *a*-impurities have a sufficiently rapid spin-lattice relaxation rate they will remain near thermal equilibrium and have a strong broadening effect on the resonance; if not, the *a* magnetization will tend to move in phase with the coupled *d* and *s* magnetizations and have little broadening effect, a situation which is referred to as double bottlenecking. The Darmstadt group was recently able to observe [6] this double bottlenecking phenomenon for the first time in *Cr-Mn-Cu*.

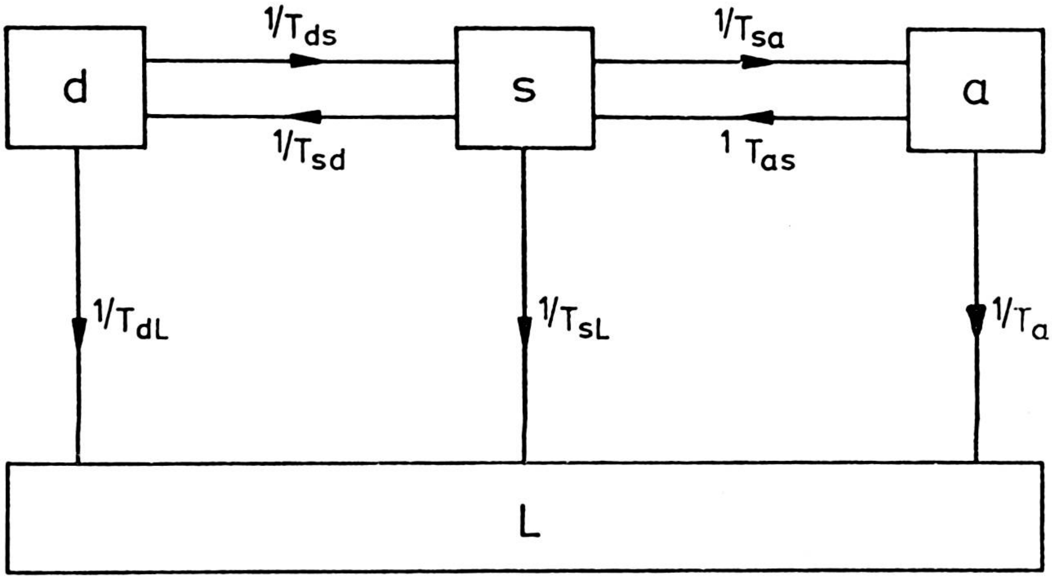

FIG. 1. — Schematic diagram of relaxation processes in bottlenecked *EPR*. The primary *3d* impurities, the conduction-electron spin magnetization, and the additional *3d* impurities are denoted *d*, *s* and *a* respectively, and the temperature bath ("lattice") is denoted L.

With some oversimplification (ignoring for example the dependence upon *g* values, which however is usually less important) we can say that *EPR* with bottlenecking is primarily a measure of the spin-lattice relaxation of the 3*d* impurities. The available experimental data for 3*d* impurities with strongly paramagnetic behavior indicates a qualitative distinction between bottlenecking impurities, such as *Mn* and *Cr* in *Cu*, which have relatively small spin-lattice relaxation rates, and non-bottlenecking impurities, such as *Fe* and *Co* in *Cu*, which have relatively large spin-lattice relaxation rates. We shall seek to explain this empirical distinction microscopically in the following sections.

Before turning to the microscopic theory, we want to make sure that the meaning of the above-mentioned parameters is clear. The bottleneck effect corresponds to a fusion of the impurity *EPR* and the conduction-electron spin resonance, so the *s* magnetization is literally a spin magnetization (aside from some very small *g* shifts). On the other hand, the term "spin-lattice relaxation", as applied to the impurities, is a piece of standard jargon which must not be understood literally. Here the "spin" stands for a *fictitious spin* describing the degrees of freedom, whether spin or orbital, of the impurity in some appropriate ground level; and the "lattice" refers not necessarily to phonons but to any thermal bath which may be assumed to remain at thermal equilibrium while exchanging relaxation flips with the impurity "spin". In fact, in the spin-lattice relaxation mechanism to be calculated below the "lattice" will be the orbital motion of the conduction electrons, which may be assumed to remain at thermal equilibrium even though s is participating in the resonance. This is a situation familiar from conduction-electron spin resonance [7].

2. THE GENERALIZED *s-d* INTERACTION MODEL

Our microscopic theory will be based upon the generalized *s-d* interaction model [8], an impurity model which is derived from a generalized Anderson model [9] by a Schrieffer-Wolff transformation. It is found to be absolutely essential to take into account the orbital magnetization and orbital degrees of freedom of the impurity [10], which means that we must use a generalized Anderson model corresponding to a full 10-electron $3d$ shell, as opposed to the simplified spin-only version where the "$3d$" shell contains only 2 electrons. The "generalization" consists in the fact that we deal accurately with the finer intra-impurity splittings, in contrast to the original 10-electron version of the Anderson model, where these splittings were included only in a schematic and incomplete fashion [11].

Let us briefly review the various splittings which are included in the Hamiltonian of the isolated $3d$ impurity ion [12]. At least for mnemonic purposes these may be characterized in descending orders of magnitude as follows:

i) The competition between the principal part of the Coulomb energy, U, and the one-electron binding energy, tends to stabilize a configuration $3d^n$, the stabilization energy being typically $U \sim 10\ eV$.

ii) The remaining parts of the Coulomb interaction, described by the higher Slater integrals F^2 and F^4, give a splitting into L-S terms of typically $1\ eV$.

iii) The crystalline electric field (*CEF*) splits the orbital states by $\sim 0.1\ eV$.

iv) The spin-orbit interaction, provided it is not forbidden within the *CEF* orbital ground level, provides a spin-orbit splitting $\sim 0.01\ eV$.

There are also various finer splittings, here omitted, some of which will be mentioned later on. The splitting scheme as listed above corresponds to the intermediate-*CEF* scheme. (Actually, it appears that the *CEF* in some host metals may be up to 10 times larger than the nominal value of $0.1\ eV$ given above, but this does not make much difference for what follows since for most cases, in cubic symmetry, the intermediate-*CEF* Scheme and the strong-*CEF*, high-spin scheme coincide.) The standard literature informs us how such splitting schemes can be worked out in detail for free ions [13] or for ions in a *CEF* [12]. We certainly do not need to repeat all this work by going through the exercise of deriving the splittings from some fully explicit model Hamiltonian.

We complete our generalized Anderson model Hamiltonian by adding to the impurity part a conduction-electron Hamiltonian and an Anderson-Schrieffer [11, 14] mixing interaction. The generalized *s-d* interaction model [8] is derived as follows: We take the impurity as being in a pure configuration $3d^n$ in the zero-order approximation; we treat the mixing interaction as a perturbation in second order to obtain a Schrieffer-Wolff effective interaction within the ground configuration; and we project this interaction successively onto the Hund's-rule *L-S* ground term, onto the *CEF* orbital ground level, and onto the spin-orbit ground level when appropriate. To carry out these projections conveniently it is necessary to make use of symmetry methods, and the couplings so obtained can be expressed most conveniently by means of the irreducible-tensor method. Since in the present discussion we want only to emphasize the main qualitative features, we shall omit the irreducible tensors (which are really quite simple but may be a bit forbidding to those who are not familiar with the method) and instead write the generalized *s-d* interaction, as it appears after projection onto the *L-S* ground term, in terms of angular-momentum operators:

$$H_1 = J_S \mathbf{S} \cdot \mathbf{s} + J_L \mathbf{L} \cdot \mathbf{l} + J_{LS} \mathbf{L} \cdot \mathbf{l} \mathbf{S} \cdot \mathbf{s} + \ldots \tag{1}$$

Here $\mathbf{l}$ is an orbital angular momentum operator for conduction electrons within the $\mathbf{l} = 2$ partial wave. The omitted terms stand for **L-l** operator products going up to order 4 in the **L** and **l** operators, which either stand alone or are multiplied by $\mathbf{S} \cdot \mathbf{s}$. The coupling constants J_S, J_L, ... are all of comparable importance and have the magnitude of a few tenths of an *eV* (The corresponding coupling constants in the irreducible-tensor formulation are a few times larger due to differences in normalization [8].)

3. IMPURITY LEVEL WIDTHS AND RELATED CONCEPTS

The reason for our use of a generalized *s-d* interaction model is that it permits us to build the finer details of the ionic-type splitting (crystal-field splitting, spin-orbit splitting, etc.) into the theory with a high degree of accuracy. Our experience with the *EPR* of 3*d* impurities in insulators [12] informs us that it is absolutely essential to include these features correctly in order to arrive at any microscopic understanding of the results, so to use a generalized *s-d* interaction model of the above type might seem like a very obvious thing to do. Nevertheless, more than 10 years went by after the first observation of *EPR* of a 3*d* impurity in a metal [1] before the full logical consequences were drawn from such a model. The main reason for this situation was the misguided application of the concept of a virtual bound state width, which seemed to indicate that the *CEF* splitting and other finer splittings must be smeared out and hence meaningless for a $3d$ impurity in a metal. The situation was complicated by the fact that there was also a "commutation" argument, equally misguided, which seemed to explain how one could observe a narrow *EPR* line despite the large v.b.s. width. Before proceeding to apply the generalized *s-d* interaction model, we shall review these historically important questions.

Our treatment based upon the generalized *s-d* interaction model applies to strongly magnetic impurities, for which the mixing tendency is weak compared to the intra-impurity energies tending to stabilize a single impurity configuration $3d^n$. More precisely, let $E_{exc}^{\pm}$ be the minimum energy necessary to excite the impurity from its ground level in the configuration $3d^n$ to a level in the configuration $3d^{n\pm 1}$, where the absorbed or emitted electron is placed in the conduction band at the Fermi energy. Let E_{exc} be the smaller of E_{exc}^{+} or E_{exc}^{-}. We also define $\Delta = \pi \mid V_{mix} \mid^2 \rho\,(\varepsilon_F)$, the so-called virtual bound state width, which is always an appropriate measure of the strength of the mixing tendency, regardless of whether it is actually appropriate to interpret it as a level width. Then the generalized *s-d* interaction model is applicable when Δ is small compared to E_{exc}, which more formally can be recognized as the condition for convergence of the Schrieffer-Wolff transformation. This case can be recognized phenomenologically by a Curie-Weiss impurity susceptibility, and evidently applies to such alloys as *Cu-Mn* or *Cu-Fe*.

An alternative approach to *EPR* in dilute alloys based upon the Friedel-Anderson virtual-bound-state theory [11, 15, 16] was discussed in an earlier talk by Dr. Yafet. This approach represents an opposite extreme to the generalized *s-d* interaction model, since it treats the mixing accurately but treats the intra-impurity interactions only in a rather crude approximation. We agree that this approach is the appropriate one to use for impurities which are not strongly magnetic, such as *Cu-Ti* and *Cu-Ni*, for which Δ is evidently not small compared to E_{exc}, and which the present theory does not pretend to describe. However, to use the Friedel-Anderson approach for strongly magnetic impurities such as *Cu-Fe* would amount to making an inappropriate perturbation development. In such cases the v.b.s. picture may reflect some aspects of the truth but has to be regarded with skepticism because it is not really the physically natural description. In our view, much confusion has resulted from uncritical reliance upon v.b.s. concepts as applied to strongly magnetic impurities.

Let us consider in more detail the energy-level scheme of a strongly magnetic impurity, as indicated schematically in Figure 2. Since by definition for such an impurity the mixing strength is weak compared to the energies necessary for inter-configuration excitation, the physically natural description is the configuration-based one shown on the right, in which one includes all the ionic-type splittings before considering mixing as a weak perturbation [9]. Including the mixing gives

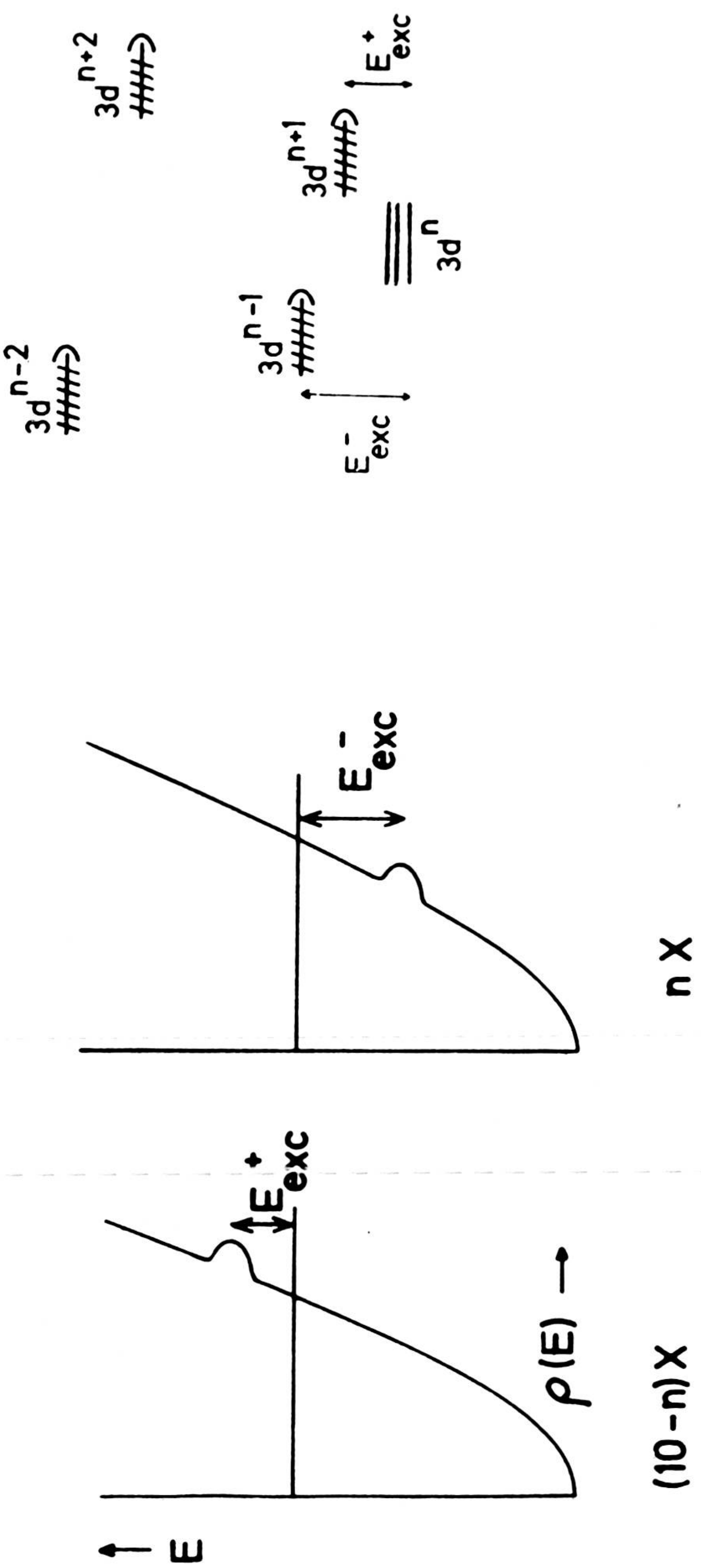

FIG. 2. — Energy levels of a *3d* impurity according to the virtual-bound-state picture (left) and the configuration-based picture (right).

the levels belonging to the configurations $3d^{n\pm1}$ a width Δ. This corresponds to the fact that the impurity, if put into such a level, will spontaneously decay back to the ground configuration by emitting or absorbing a conduction electron, with a transition rate of approximately Δ/h.

However, the levels of the ground configuration are energetically stable, do not have such a decay channel open to them, and hence do not have such a width [1]. The levels belonging to the ground configuration do of course have finite widths, but these result from higher-order processes (to be discussed in more detail in later sections) and are much smaller than Δ.

If we attempt to describe this same impurity in v.b.s. terms, we get the picture shown on the left of Figure 2. There are 10 scattering channels in the $l = 2$ partial wave, of which n exhibit a v.b.s. well below the Fermi energy and $10 - n$ exhibit a v.b.s. well above it. There is an n-fold and $(10-n)$-fold degeneracy in the absence of intraconfiguration splitting, which is lifted when such splitting is included; however, the v.b.s. picture is very ill-suited to exhibiting and dealing with the effects of intraconfiguration splitting. The v.b.s. energies are single-electron Hartree-Fock energies, which by Koopmans' theorem have the significance of being the energies necessary to add or remove single electrons from the system. The v.b.s. thus have an intimate relation to the interconfiguration excitations of the configuration-based picture.

To the extent that we are dealing with phenomena in which electrons are added to or removed from the impurity, the v.b.s. picture is essentially equivalent to the configuration-based picture and may be used. Thus, we could expect to see resonances corresponding to the v.b.s. energies E_{exc}^{+} and E_{exc}^{-} in idealized optical-absorption experiments, and resonances corresponding to E_{exc}^{-} in *ESCA* or the photo-electric effect. Such resonances ideally would have a width $\sim \Delta$, which in the configuration-based picture would be described as broadening due to final-state decay. However, in *EPR* we are dealing with transitions among low-lying levels within the impurity's ground configuration. It should be clear that the v.b.s. description is completely unsuited for the discussion of such an effect. The generalized *s-d* interaction model, which is a more quantitative version of the configuration-based description as specialized to the lowest-lying impurity levels within the ground configuration, provides the only appropriate framework for the discussion of *EPR* in a strongly-magnetic impurity.

Despite the elementary and fundamental nature of the above arguments, many workers have persisted in trying to interpret *EPR* from a v.b.s. point of view. The most obvious apparent difficulty with such an interpretation, namely the fact that

---

[1] Here we are assuming that, when the intraconfiguration splitting is included, all the levels of the ground configuration lie below the lowest level of any excited configuration. If this condition were not satisfied for some of the higher intraconfiguration levels of the ground configuration, then such levels would show a width $\sim \Delta$.

the observed resonance linewidths are many orders of magnitude smaller than the v.b.s. width, is alleged to be removed by a "commutation" argument which may be stated as follows: Since the Anderson-Schrieffer mixing interaction commutes with the total magnetization, it cannot cause any broadening. From this argument the conclusion is drawn that *EPR* lines should be narrow, but that the finer impurity splittings should be smeared out over an energy range corresponding to the v.b.s. width, so that for example crystal-field and spin-orbit splittings should have no significant effect for $3d$ impurities. Now, such commutation arguments are valid if carefully used, and amount essentially to a restatement of the bottlenecking phenomenon, namely of the fact that large cross-relaxation rates can cancel out of the observed linewidth. However, in order to apply such an argument correctly one has to consider carefully the specific microscopic structure of the system at hand, and also the specific type of resonance measurement being made. The discussion given in following sections will indicate that the Anderson-Schrieffer mixing interaction, when converted into a generalized *s-d* interaction by a Schrieffer-Wolff transformation, gives relaxation rates which may or may not cancel out of the *EPR* linewidth depending upon the details of the electronic ground level of the impurity. (It should also be emphasized that the same relaxation rates which cancel out of the *EPR* width may contribute to the observed width in other resonance measurements, e.g. in the Mössbauer effect.) Consequently, the commutation argument as a broadside argument to explain generally the existence of narrow *EPR* lines is fallacious. The error it makes is to implicitly assume that *EPR* can be interpreted as an observation of the dynamic response of the total magnetization, whereas in fact it involves the total magnetization of the impurity but only the spin magnetization of the conduction electrons.

Even aside from the theoretical considerations which we have reviewed, it should have been obvious long ago that something was wrong with the traditional interpretation of impurity *EPR* in terms of v.b.s. concepts, from consideration of the experimental observations in the case of $4f$ impurities. Although the Δ value for $4f$ impurities is much smaller than in the $3d$ case, it is generally agreed that it cannot be assigned a value less than about 100° K. Hence the discovery by Griffith and Coles [17] of an *EPR* line in *Ag-Er* showing precisely the properties of the Γ_7 *CEF* ground level, even though this level is separated from higher levels [18] by only about 35° K, was in conflict with the v.b.s. interpretation. Since that time similar observations have been made for many non-S-state $4f$ ions, often involving still smaller splittings. Furthermore, the beautiful work on the fine-structure splitting of S-state $4f$ ions which was reviewed by Prof. Orbach, shows that even impurity energy levels with splittings of a fraction of a degree Kelvin can be perfectly well defined.

Our conclusion therefore is that the v.b.s. width Δ is not directly relevant to the *EPR* of strongly-magnetic impurities; it gives neither the *EPR* linewidth nor a limitation on the amount of ionic-type fine structure which can be resolved. In fact the correct lower limit on the resolution of fine structure is provided by the generalized Korringa relaxation discussed in the next section, or when the Kondo effect is important by a larger value approaching T_K at low T.

4. RELAXATION IN THE GENERALIZED *s-d* INTERACTION MODEL

In the present section we discuss the magnetic relaxation of $3d$ impurities as calculated in second order from the generalized *s-d* interaction [19]. This is a generalization of the familiar Heitler-Teller-Overhauser-Korringa relaxation obtained from the simple spin-only *s-d* interaction model, and yields rates proportional to the temperature with typical magnitude $5x\ 10^{10}$ sec $^{-1}/°\ K$. The important new feature is that the present rates may have the significance of either cross relaxation $1/T_{ds}$ or spin-lattice relaxation $1/T_{dL}$, depending upon the nature of the impurity degrees of freedom. As noted in Section 1, large cross relaxation rates can cancel out of the observed *EPR* linewidth due to the bottleneck effect, but large spin-lattice relaxation rates cannot. The contributions here considered are sufficiently large that they will essentially wipe out the resonant behavior, under the usual experimental conditions, of those impurities for which they have the significance of spin-lattice relaxation. This, we believe, is the explanation of the empirical observation that some strongly-magnetic $3d$ impurities show resonant *EPR* behavior while others do not. In our discussion we will not repeat the details of the calculation [19] but will only seek to clarify the qualitative distinction between cases where the generalized *s-d* interaction does or does not give spin-lattice relaxation contributions.

Let us consider various $3d$ impurities in *Cu*, for which the most experimental data is available. We can consider the impurities *V*, *Cr*, *Mn*, *Fe* and *Co* as being sufficiently strongly magnetic to be described by the generalized *s-d* interaction model, with some possible reservations in the case of *V* and *Co*. The first point we must settle is the ground configurations $3d^n$ to be assigned to these impurities. From considerations of the screening energy we certainly expect n to increase by 1 when the atomic number increases by 1; that is, all impurities should correspond to ions of the same valency. From consideration of the trend in experimentally-measured Curie effective moments, which fall off on either side of *Mn*, it is clear that *Mn* should be assigned $3d^5$, i.e. that the configuration assignments are those corresponding to the divalent ions. We emphasize here that what is important is to look at the trend to identify the ground configuration rather than attempting to directly identify the observed moment with $2\sqrt{S(S+1)}$. This is so because S is only the bare impurity spin, whereas the observed effective moment may be appreciably reduced by an antiferromagnetic induced conduction-electron spin polarization, as was discussed in an earlier talk by Dr. Walstedt. (The orbital contribution to the effective moment should also be taken into account, but this usually turns out to be rather small even in cases where the impurity orbital moment is not fully quenched [10].)

Having identified the ground configurations, we assign the various impurities L and S values according to Hund's rules. We next introduce the *CEF* splitting according to the intermediate *CEF* scheme. For 3*d* ions in cubic point symmetry, this splitting is determined by a single *CEF* parameter, whose sign we take from a point-charge estimate. (The correctness of this sign choice is confirmed by the results.) This produces electronic states for the various impurities as follows, where the last column gives the symmetry label of the *CEF* orbital ground state, followed by its degeneracy in parentheses [10]:

	V	*Cr*	*Mn*	*Fe*	*Co*
n	3	4	5	6	7
S	3/2	2	5/2	2	3/2
L	3	2	0	2	3
CEF	$A_2(1)$	E(2)	—	$T_2(3)$	$T_1(3)$

The distinction between spin-lattice and cross relaxation results from the fact, discussed in Section 1, that only the spin magnetization of the conduction electrons can participate in bottlenecked *EPR*, whereas their orbital states remain in thermal equilibrium and may be supposed to constitute a thermal bath. Thus a scattering process by which the impurity "spin" (in the sense of fictitious spin) exchanges a flip with the orbital magnetization of the conduction electrons provides a spin-lattice relaxation contribution. Let us now see how this works out in detail for specific impurities:

Mn-Cu: In this case we have an *S*-state ($L = 0$) ground term according to Hund's rules. Hence all the interaction contributions involving L in the generalized *s-d* interaction, eq. (1), vanish when projected onto the ground term and we are left only with an $\mathbf{S} \cdot \mathbf{s}$ coupling. Consequently we obtain only cross relaxation and no spin-lattice relaxation, in agreement with the experimental fact that *Mn-Cu* shows a narrow bottlenecked *EPR* [1, 4].

V-Cu: In this case we have finite L in the Hund ground term but a singlet *CEF* orbital ground state. Thus the generalized *s-d* interaction again reduces to an $\mathbf{S} \cdot \mathbf{s}$ coupling after projection and yields no spin-lattice relaxation. Experiments are not available due to the low solubility.

Fe-Cu: In this case we have $L = 2$ and a triplet *CEF* orbital ground state, which supports an orbital moment and a spin-orbit coupling of $\sim 100° K$. The spin-orbit ground level is a triplet, and when we project the generalized *s-d* interaction onto it we obtain couplings of the fictitious spin to the orbital as well as the spin degrees of freedom of the conduction electrons. Consequently we expect a large spin-lattice relaxation which prevents *Fe* from showing significant resonant response under the usual experimental conditions, as is observed [4].

Co-Cu: This case is similar to *Fe-Cu* except that the situation is complicated by a high Kondo temperature.

Cr-Cu: In this case we have $L = 2$ and *E*-type doublet *CEF* orbital ground state. This means we have a twofold orbital degree of freedom. However, this doublet has the property of supporting neither an orbital moment nor a first-order spin-orbit interaction. Consequently, in a first approximation we may neglect the spin-orbit coupling entirely and regard the spin and orbital degrees of freedom of the impurity as independent. Then the generalized *s-d* interaction produces only cross relaxation of the impurity spin, which is thus predicted to show resonant *EPR* behavior in agreement with experiment [6, 20].

We would expect the electronic states of 3*d* impurities in *Ag* and *Au* to be the same as here discussed for *Cu*. However, in *Ag* there are solubility difficulties for impurities other than *Mn*. In *Au* one has seen only a very broad *EPR* for *Au-Mn* [5, 21], which probably is associated with the large spin-orbit coupling of the conduction electrons in the host due to the large atomic number of *Au*. Such a coupling, in conjunction with only a minute concentration of charge impurities, produces strong conduction-electron spin-lattice relaxation [7] and is assumed to be responsible for the fact that *CESR* cannot be observed in such heavy hosts.

I have learned from Dr. Narath in the course of this conference that on the basis of hyperfine data he has been able to conclude that *Co-W* has an A_2 singlet *CEF* orbital ground state. This indicates that the 3*d* impurities in *W* are divalent but that the sign of the *CEF* parameter in the cubic host *W* is reversed as compared to *Cu*, so that the *CEF* states of the above table are inverted about *Mn*. It would be extremely interesting if bottlenecked *EPR* could be detected in this system. However, the spin-orbit coupling of the conduction electrons in *W* may be too strong to permit this.

The situation for 3*d* impurities in h.c.p. hosts such as *Mg* or *Zn* is more complicated, since there are two *CEF* parameters and correspondingly more possibilities to consider [10]. Until now it has only been possible to establish that *Mn* impurities are $3d^5$ *S*-state ions.

5. FINE-STRUCTURE SPLITTING AND RELATED TOPICS

In the previous sections we have argued on theoretical grounds that strongly-magnetic 3*d* impurities in metals are not essentially different from 3*d* ions in insulators, and that the same types of ionic splittings in the intermediate *CEF* scheme which are familiar for the insulator case should be expected in metals. We showed also that including the *CEF* and spin-orbit splittings together with an appropriate generalized *s-d* interaction permitted us to understand in a very simple way the empirically-established distinction between bottlenecking and non-bottlenecking 3*d* impurities in *Cu*. Nevertheless, there remain big differences in the *EPR* between the metallic and insulator cases. If we consider the *EPR* of Mn^{++} in an insulator host, the last thing we would expect to see would be a single line at $g = 2$. We know that for the *S*-state Mn^{++} ion we have fine-structure splitting (*S*-state *CEF* splitting) as well as hyperfine splitting, both of which are an appreciable fraction of typical Zeeman energies, so that a complicated many-line *EPR* spectrum is expected [12]. Can one accuse us of being inconsistent in omitting these finer ionic-type splittings?

Fortunately, the answer to this question has been made clear by Prof. Orbach's talk on fine-structure splitting in 4*f* impurities. The answer is that bottlenecked *EPR* with a finite concentration of impurities is basically a collective effect, whereby cross relaxation between impurities via the conduction electrons tends to effectively wipe out the fine-structure splittings of individual impurities. For a long time $4f^7$ *S*-state ions seemed to show only a $g = 2$ line. A lot of hard work at low concentrations and low temperatures was necessary before the expected fine-structure effects could be detected, first as lineshape anomalies and shifts, more recently even as fully resolved splittings. The beautiful theoretical work on this phenomenon which has been done for 4*f* impurities should apply to the 3*d* case without essential modifications. Because the interactions in the 3*d* case are much stronger, it will be even more difficult to detect resolved fine-structure splittings in the 3*d* than in the 4*f* case. But even if this challenge proves too difficult, it should be possible to study lineshape effects associated with imperfectly resolved fine-structure splitting. It is to be assumed that the small but finite values of $1/T_{dL}$ which are obtained from fits to the phenomenological bottlenecking equations for impurities such as *Mn-Cu* or *Cr-Cu*, for which there are no plausible microscopic sources for significant spin-lattice relaxation rates at low temperatures, are actually due to unresolved fine-structure splittings.

Under the rubric of fine-structure splitting we include not only the *S*-state ion Mn^{++} but also the very interesting case of Cr^{++} in cubic surroundings (or Fe^{++} if the sign of the *CEF* is reversed as compared to *Cu*), where one has an *E*-type doublet *CEF* orbital ground level. In this case, the fine-structure splitting results from the spin-orbit coupling in second order via a virtual *CEF* excitation. This case has been studied in detail theoretically and has been observed experimentally in insulator hosts in a few cases, where fine-structure splittings as large as $10^\circ K$ have been found [12]. From the absence of a large negative *g* shift of the unsplit *EPR* line in *Cr-Cu*, it appears that its effective fine-structure interaction is smaller than in the insulator analogs which have so far been studied. On the other hand, a comparison of the *EPR* results for *Cu-Mn* and *Cu-Cr* suggests that the fine-structure splitting is larger in *Cr* than in the *S*-state ion Mn^{++}. We have suggested a mechanism involving spin-lattice relaxation of the orbital degree of freedom of

Cr which would tend to effectively reduce the fine-structure effects [19], but impurity-impurity interactions will also be important. Thus it seems likely that unresolved fine structure is contained in the *EPR* lineshape of *Cu-Cr* but the details of the interpretation are far from clear.

As noted above, cross relaxation and the bottleneck effect tend to oppose a resolution of the fine-structure splitting in the *EPR* spectrum. The way to overcome this is to go to low concentrations and low temperatures, insofar as the Kondo temperature is also low. More generally, we can say that in this limit, to the extent that it can be realized, we expect to see the typical *EPR* behavior of 3*d* ions in insulators. For example, the spin-orbit ground level which we have assigned to *Cu-Fe* implies a *g*-value of 7/2, or slightly less to the extent that a dynamic Jahn-Teller effect is present. If the Kondo temperature in this system were very low, then it would be possible to observe this resonance directly at sufficiently low temperatures, which of course would be of great interest. Possibly other analog systems can be found in which the Kondo temperature is sufficiently low to permit such an observation to be made.

6. THE KONDO EFFECT

As we heard from Prof. Götze, progress is being made in the theory of the Kondo effect and such difficulties as negative theoretical impurity susceptibilities, which formerly made the practical interpretation of experimental *EPR* data very problematic, seem to have been eliminated. Clearly the Kondo effect is important for *EPR* of 3*d* impurities at least in the qualitative sense that a sufficiently strong Kondo compensation will suppress the magnetic dipole strength of the impurity and finally make its truly magnetic effects on the *EPR* smaller than its effect simply as a charge impurity (which gives relaxation by providing spin-orbit scattering of the conduction electrons). Is there hope that *EPR* can be used to gain quantitative information about the Kondo effect and in particular to test the relaxation rates obtained from Kondo theories?

We want to emphasize again the importance of the distinction which was made earlier between spin-lattice and cross relaxation. Our remark that the generalized *s-d* interaction can give both of these, and our criteria for distinguishing cases for which it does or does not give spin-lattice relaxation, remain the same when one goes from second-order perturbation theory to a full Kondo theory. Since the cross relaxation tends to cancel out of the observed linewidth due to the bottleneck effect, *EPR* is usually not capable of measuring it accurately. On the other hand, spin-lattice relaxation of the impurity does give an observable broadening effect which can be measured in an arrangement where the impurity of interest is an additional impurity in a bottlenecking alloy such as *Mn-Cu*. Consequently, there is hope that Kondo relaxation rates can be measured for those impurities for which the generalized *s-d* interaction gives spin-lattice relaxation.

For understandable reasons Kondo theorists have preferred to work with an *s-d* interaction model of the simple $\mathbf{S} \cdot \mathbf{s}$ form. As we saw earlier, the cases where the generalized *s-d* interaction model reduces to this simple form are just those cases where no spin-lattice relaxation results. Hence if we want to test Kondo theories against *EPR* experiments, it will be necessary to generalize them corresponding to the generalized *s-d* interaction. It seems reasonable to hope that for most theories, with the aid of irreducible-tensor techniques, such a generalization can be achieved in a reasonable way [1]. This generalization is not merely a necessary chore but involves some interesting new physics regarding the relation between spin and orbital degrees of freedom in the Kondo compensation.

7. RELAXATION PHENOMENA IN THE MÖSSBAUER EFFECT

The Mössbauer effect in zero field, where the relaxation is sufficiently slow to permit the hyperfine splitting to be resolved, has proved to be a useful way of studying 4*f* impurities in metals [22, 23]. The information gained is similar to that which can be gained from *EPR*, but the two methods are sufficiently different to make them complementary. In view of the recent progress which has been made with this technique as applied to 4*f* impurities [24-26], we wish to comment briefly on the possibilities as to its use with 3*d* impurities.

The main point we wish to emphasize is that the bottleneck effect does not play a role in determining the Mössbauer relaxation. The bottleneck effect is connected with the fact that *EPR* constitutes a measurement of the dynamic response of the sum of the conduction-electron spin magnetization plus the impurity magnetization. Those relaxation processes which transfer spin flips without altering this total magnetization are classified as cross relaxation and cancel out of the *EPR* linewidth under appropriate bottlenecking conditions. In the Mössbauer effect, on the other hand, one is measuring a resonance localized at one impurity. Consequently all relaxation flips between the impurity moment and the conduction electrons will cause relaxation in the Mössbauer spectrum. There is no distinction to be made between spin-lattice relaxation and cross relaxation and no bottleneck effect.

Since there is no possibility that the relaxation via the *s-d* interaction can be short-circuited by bottlenecking, it will be very difficult to achieve relaxation rates sufficiently slow to permit a resolved hyperfine spectrum. However, this might be achieved by studying impurities in hosts with unusually low densities of conduction electron states, or also by going to very low temperatures so long as the Kondo temperature is also very low. The comparison of Mössbauer and *EPR* spectra for a given 3*d* impurity, if possible, would be very interesting in view of this difference as regards bottlenecking.

---

[1] Here we are referring to a generalized *s-d* interaction model with projection on to some appropriate impurity ground level. If one contemplates the stronger generalization of including finite impurity splittings, things are known to become much more difficult.

8. FUTURE PROBLEMS

The *EPR* of dilute magnetic impurities was first discovered [1] for a 3*d* impurity, *Cu-Mn*. This discovery initiated what we might call a first generation of investigations, in which the main impurities were *Mn* or *Gd* and the concentrations were rather high by current standards. Interest was centered mainly upon questions relating to the linewidth and to the *g*-shift or absence thereof, and the most important general result was the understanding of the bottleneck effect following Hasegawa's ideas.

The discovery [17] of the non-*S*-state *EPR* of *Ag-Er* initiated what we might call a second generation of investigations, in which there was more interest in understanding the finer details of the states of the individual impurities. The investigations covered not only the *CEF* states of non-*S*-state 4*f* impurities but also hyperfine splittings and the fine-structure splittings of *S*-state 4*f* impurities. New and more subtile versions of the bottleneck theory had to be developed taking this splitting into account. It was necessary to go to temperatures and concentrations smaller than those previously used in order to see some of the effects of interest. The impurities used in this second-generation work so far have been exclusively 4*f*.

The very great progess which has been achieved in the recent work discussed at this conference encourages me to suggest that it is time for a second generation of experiments on 3*d* impurities. I believe that the bottleneck effect and the microscopic reasons for its presence or absence can be regarded as understood. What should be of interest in the future is the search for other effects which are more closely related to the electronic structure of individual impurities. These include:

1. Observation of resolved fine structure, or the effects of unresolved fine structure, in the *EPR* spectrum.
2. Direct observation (at very low temperatures) of the *EPR* of impurities having *CEF* states not suitable for bottlenecking.
3. Observation of resolved slow-relaxing Mössbauer spectra.
4. Study of Kondo relaxation rates in additional-impurity experiments.

Since the main point of these experiments is to study isolated or quasi-isolated individual impurities, very low concentrations are necessary. Furthermore, for all except the last of these proposals it is desirable to have a Kondo temperature not higher than the millidegree range. Thus for example *Ag-Mn* seems a likely candidate for 1. Since it is difficult to find elementary host metals in which impurities such as *Fe* and *Co* have very low Kondo temperatures, the use of intermetallic compounds or semimetals as hosts should be considered.

Only a short while ago, these proposals would have seemed utopian. Now they seem difficult but not impossible.

REFERENCES

[1] J. Owen, M. Browne, W. D. Knight, and C. Kittel, Phys. Rev. *102*, 1501 (1956).
[2] H. Hasegawa, Progr. Theor. Phys. *21*, 483 (1959).
[3] D. L. Cowan, Phys. Rev. Letters *18*, 770 (1967).
[4] A. C. Gossard, A. J. Heeger, and J. H. Wernick, J. Appl. Phys. *38*, 1251 (1967).
[5] Y. Oda and K. Asayama, J. Phys. Soc. Japan *29*, 869 (1970).
[6] L. L. Hirst, W. Schãfer, D. Seipler, and B. Elschner, Phys. Rev. B *8*, 64 (1973).
[7] Y. Yafet, Solid State Physics *14*, 1 (1963).
[8] L. L. Hirst, Z. Physik *244*, 230 (1971) (erratum *258*, 284 (1973)).
[9] L. L. Hirst, Phys. kondens. Materie *11*, 255 (1970).
[10] L. L. Hirst, Z. Physik *241*, 9 (1971).
[11] P. W. Anderson, Phys. Rev. *124*, 41 (1961).
[12] A. Abragam and B. Bleaney, "Electron Paramagnetic Resonance of Transition Ions", Clarendon Press, Oxford, (1970).
[13] E. U. Condon and G. H. Shortley, "The Theory of Atomic Spectra", Cambridge University Press, (1935).
[14] J. R. Schrieffer, J. Appl. Phys. *38*, 1143 (1967).
[15] J. Friedel, Nuovo Cimento Suppl. *7*, 287 (1958).
[16] A. Blandin and J. Friedel, J. Phys. Radium *20*, 160 (1959).
[17] D. Griffiths and B. R. Coles, Phys. Rev. Letters *16*, 1093 (1966).
[18] G. Williams and L. L. Hirst, Phys. Rev. *185*, 407 (1969).
[19] L. L. Hirst, Adv. in Physics *21*, 759 (1972).
[20] P. Monod and S. Schultz, Phys. Rev. *173*, 645 (1968).
[21] D. Shaltiel and J. H. Wernick, Phys. Rev. *136*, A245 (1964).
[22] L. L. Hirst and E. R. Seidel, J. Phys. Chem. Solids *31*, 857 (1970).
[23] L. L. Hirst, J. Phys. Chem. Solids *31*, 655 (1970).
[24] F. Gonzales Jiminez and P. Imbert, Solid State Comm. *11*, 861 (1972).
[25] F. Gonzalez Jiminez, P. Imbert, and F. Har4mann-Boutron, Phys. Rev., in press.
[26] G. K. Shenoy, J. Stöhr, and G. M. Kalvius, Solid State Comm., in press.

DISCUSSION

Giovannini: I would like to mention something that many people but perhaps not everyone knows. This is that for most effects the interaction $S.s$ and the rest that you have written just add up, as you showed for the relaxation time There is one effect that distinguishes between the two, the Hall effect. One could compare whatever number you get for T_{dl} with the Hall effect measurements in dilute alloys.

Hirst: I think this is something we should do.

Bleaney: How dilute?

Giovannini: Very dilute. It's a huge effect and so can be seen in very dilute alloys.

Orbach: In the double-bottleneck situation, say manganese and copper with iron, how would you distinguish between the exchange spin-flip scattering by the iron and the spin-orbit scattering by the iron which also leads to a lattice relaxation rate for the conduction electrons?

Hirst: The difference is in the order of magnitude. You have to compare manganese alone to manganese with iron. You can then fit T_{sl}. You assume that the additional T_{sl} you get for an additional manganese is comparable with that you would get for an additional iron.

Orbach: But that is not true.

Hirst: Well, it is not too bad an approximation if the effect is a charge scattering. It is just a scattering from a divalent impurity. It should be emphasized that the values of T_{sl} obtained in [4] resulted from a fit which didn't take into account the large temperature-dependent $1/T_{dl}$ rates which are expected for some *3d* impurities according to the present theory. The present interpretation of these measurements is consistent with a quite different set of T_{sl} values.