

Specific Heat of Dilute Alloys

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Recently Zimmerman has observed that the addition of Mn to Cu produces a large contribution to the specific heat which, at low temperatures, is linear in temperature and *independent* of Mn concentration. It is shown that: (1) this remarkable result can be explained in terms of the well-known Ruderman-Kittel-Yosida spin-spin coupling via conduction electrons; (2) the specific heat results of Beck *et al.* on FeV and FeCr alloys are probably of essentially the same origin as those of Zimmerman on Cu Mn; (3) that there are serious objections to the mechanism of antiferromagnetism postulated by Overhauser and used by him to explain the specific heat results. In contrast to the Overhauser theory, no new concepts are involved and it is suggested that the large specific heat comes from a small fraction of Mn spins which, because of the random nature of the alloy, happen to be in small effective fields and therefore not strictly aligned. The theory depends on two plausible assumptions which have not, at present, been proved rigorously valid.

RECENTLY Zimmerman¹ has observed that the addition of Mn to Cu produces a large contribution to the specific heat which, at low temperatures, is linear in temperature and independent of Mn concentration. (The experiments were performed over the range of concentration 0.17 to 4.00%) At a higher temperature the specific heat falls rapidly to the pure Cu value. This fall-off temperature is proportional to the Mn concentration so that the entropy associated with the extra specific heat is proportional to concentration as it must be if it is to be attributed to the disordering of spins on the Mn atoms. The same effect has been observed by De Noble and Du Chatenier² for Mn in Ag. To explain Zimmerman's remarkable results Overhauser³ has postulated a new mechanism for antiferromagnetism invoking the concept of a spin density wave in the conduction electrons. It is our purpose to point out: (1) that Zimmerman's results can be explained using the well known and established interaction derived by Ruderman and Kittel,⁴ Kasuya,⁵ Yosida,⁶ and Blandin and Friedel⁷ (2) that the specific heat results of Beck *et al.*⁸ on FeV and FeCr alloys are probably of essentially the same origin as those of Zimmerman on Cu Mn; (3) that there are serious objections to the Overhauser theory.

We assume that in Cu-Mn the Mn spins interact according to the Ruderman-Kittel-Yosida Hamiltonian:

$$H = \sum_{n < m} f(n-m) \mathbf{S}_n \cdot \mathbf{S}_m, \quad (1)$$

where

$$f(R) = (9\pi G^2/2E_0)(2k_0R)^{-4} \times (2k_0R \cos 2k_0R - \sin 2k_0R). \quad (2)$$

Here the summation goes over all Mn spins, G is the $4s-3d$ exchange interaction, E_0 the Fermi energy and k_0 the Fermi wavevector. For simplicity take S to be $\frac{1}{2}$ (magnetic susceptibility measurements⁹ show S is $\frac{5}{2}$ or 2 but this produces no qualitative difference) and assume the interaction may be replaced by an Ising term. This Ising approximation is reasonably good provided that the spin arrangement in the ordered state has a unique orientation axis which we call the Z axis; it would certainly fail if there were spiral spin arrangements and of course, it cannot possibly give spin-wave effects. This Ising interaction produces an effective field H in the Z direction acting on each spin. In the presence of this field a spin makes a contribution to the thermal energy of

$$-\mu H \tanh \mu H / kT.$$

The total number of spins is Nc , where c is the concentration, and if $p(H, T)$ is the probability distribution of H at temperature T then an exact expression for the total thermal energy is

$$E(T) = -\frac{1}{2}Nc \int_{-\infty}^{\infty} dH p(H, T) \mu H \tanh \mu H / kT. \quad (3)$$

The factor $\frac{1}{2}$ has been introduced into this expression because otherwise in constructing the thermal energy from the effective field we would have included each pair interaction twice. Differentiating to get the specific heat gives

$$C_M(T) = \frac{1}{2}Nc \int_{-\infty}^{\infty} dH p(H, T) (\mu^2 H^2 / kT^2) \times \operatorname{sech}^2 \mu H / kT - \frac{1}{2}Nc (\partial / \partial T) h(T) + \frac{1}{2}Nc \int_{-\infty}^{\infty} dH \{ \mu |H| - \mu H \tanh \mu H / kT \} \times (\partial / \partial T) p(H, T), \quad (4)$$

¹ J. E. Zimmerman (to be published).

² J. De Noble and F. J. Du Chatenier, *Physica* **25**, 969 (1959).

³ A. W. Overhauser, *Phys. Rev. Letters* **3**, 414 (1959).

⁴ M. A. Ruderman and C. Kittel, *Phys. Rev.* **96**, 99 (1954).

⁵ T. Kasuya, *Progr. Theoret. Phys. (Kyoto)* **16**, 45 (1956).

⁶ K. Yosida, *Phys. Rev.* **106**, 893 (1957).

⁷ A. Blandin and J. Friedel, *J. phys. radium* **20**, 160 (1959).

⁸ C. T. Wei, C. H. Cheng, and P. A. Beck, *Phys. Rev. Letters* **2**, 95 (1959).

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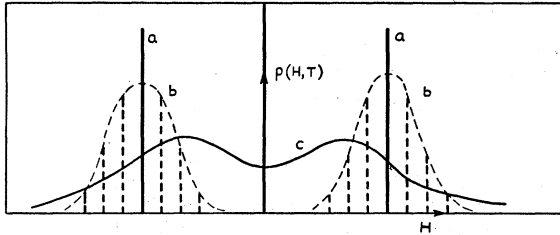


FIG. 1. $p(H, T)$ at low T for various cases (schematic): (a) Regular lattice, Weiss molecular field; (b) Regular lattice, Bethe-Peierls method; (c) Dilute alloy.

where $h(T)$ is the mean magnitude of H

$$h(T) = \int_{-\infty}^{\infty} dH |H| p(H, T). \quad (5)$$

In order to estimate $p(H, T)$ for this problem it is necessary to consider first the simpler problem of a regular cubic array of spins with antiferromagnetic Ising interaction of strength J between nearest neighbors only. The simplest order-disorder approximation for this latter problem is given by the Weiss molecular field method which determines self-consistently an effective field which acts on all the spins and no allowance whatever is made for fluctuations in this field; hence the molecular field approximation gives

$$p(H, T) = \frac{1}{2} \delta[H - h(T)] + \frac{1}{2} \delta[H + h(T)], \quad (6)$$

where $h(T)$ is defined by (5) and determined by the well known self-consistency equation. Above the critical temperature $h(T)$ is zero and (4) gives zero specific heat. This is a direct result of having no fluctuations in H .

A better order disorder approximation, which does allow for fluctuations in H , is given by the Bethe-Peierls method which considers a central spin and the surrounding r nearest neighbors. The effective field acting on the central spin is

$$H = (N_{\beta} - N_{\alpha})J/2\mu, \quad (7)$$

and N_{β} and N_{α} are the number of β and α spins in the shell of r nearest neighbors. The difference $N_{\beta} - N_{\alpha}$ can take all integer values from $-r$ to r and the probability for each value is easily calculated using standard Bethe-Peierls theory. Hence $p(H, T)$ is obtained as a sum of δ functions at the discrete field values given by (7). Schematically we can replace this by the continuous curve b of Fig. 1. Notice that $p(H, T)$ has sharp maxima and in particular $p(H, T)$ is exponentially small [$\sim \exp(-T_c/T)$] for small H and for temperatures below the critical temperature T_c . As a result (4) gives an exponentially small specific heat at low T .

Now consider the form of $p(H, T)$ for the more difficult dilute alloy problem where we must extend this discussion to take account of the random distribution of Mn atoms and of the dependence of the interaction

parameter (2) on distance. The effective field acting on any given spin will again be the sum of contributions coming from all other spins. The sum will be dominated by the few spins which happen to be the closest; hence the mean magnitude at low T is

$$h = \lambda |f(\bar{R})|/4\mu, \quad (8)$$

where λ is a number of order unity representing the effective coordination number and \bar{R} is the mean distance from any Mn atom to the nearest Mn atom. This expression for h is very important and we shall discuss it fully later.

Notice that in the previous example there was a strong tendency for the r nearest neighbors to be all alike (all α or all β) and hence their contributions to H tended to add up "in phase" to give large values of h and a sharp peak to $p(H)$. But in the dilute alloy the tendency for the "nearest neighbors" to be alike is greatly reduced because they have mutual interactions which are equally likely to be of either sign; also they will not all be at the same distance and therefore have the sign interaction with the "central" ion. As a result h will be smaller and the width of the $p(H)$ peaks larger. It is therefore reasonable to postulate that this width becomes comparable to h and hence we get the $p(H)$ curve as shown schematically in Fig. 1 (curve c). The precise shape of this curve is not important for our immediate purposes; the only essential points to note are that $p(H, T)$ is now a continuous function (whereas previously it was a sum of δ functions) and that $p(0)$ is not exponentially small but of order $1/h$.

Consider the value of (4) at low temperatures $T \ll h/k$ where most of the spins are rigidly aligned because they are in effective fields much larger than kT/μ . The second term of (4) may be neglected because only the rigidly aligned spins make an appreciable contribution to h and hence h is temperature insensitive. In both the first and third terms the integral is dominated by contributions from the range of H values from roughly $-kT/\mu$ to kT/μ so in both $p(H)$ can be replaced by $p(0)$. Furthermore for any reasonable variation of $p(0)$ with T the third term is negligible compared to the first. Hence (4) reduces to

$$C_M(T) \simeq \frac{1}{2} N c p(0, 0) \times \int_{-\infty}^{\infty} dH (\mu^2 H^2 / kT^2) \operatorname{sech}^2 \mu H / kT. \quad (9)$$

We may easily understand this result as follows. The majority of the spins are rigidly aligned in strong ($\gg kT/\mu$) fields and therefore make a negligible contribution to the specific heat themselves but serve merely to produce a temperature insensitive effective field to which the partially aligned spins are subjected. In this approximation the specific heat arises solely from those spins which are only partially aligned because

they happen to lie in a small field $\approx kT/\mu$ and each gives a Shottky-like contribution to C_M .

Setting $p(0,0)$ equal to $1/4\lambda'h$ where λ' is a number of order unity, and using (8) gives

$$C_M(T) \simeq [Nck^3T/2\lambda\lambda'f(\bar{R})] \int_{-\infty}^{\infty} dx x^2 \operatorname{sech}^2 x. \quad (10)$$

Now for dilute alloys the dominant term in the interaction constant (2) is that of order $\approx R^{-3}$, hence

$$|f(\bar{R})| \simeq (9\pi G^2/2E_0)(2dk_0\bar{R})^{-3} \\ \simeq (9\pi G^2/2E_0)(2dk_0)^{-3}c, \quad (11)$$

where d is the nearest neighbor distance and c the concentration. Substituting into (10) and remembering $(2dk_0)^3$ is $24\sqrt{2}\pi^2$ for Cu, gives

$$C_M(T) \simeq (Nk^2TE_0/G^2)(8\pi\sqrt{2}/3\lambda\lambda') \int_{-\infty}^{\infty} dx x^2 \operatorname{sech}^2 x, \quad (12)$$

which is linear in T and independent of c in agreement with experiment. The integral in (12) is a number of order unity. This expression for C_M is remarkably similar to that given by Overhauser: both are inversely proportional to G^2 and proportional to T and E_0 (Overhauser's constant C is of the order of E_0). But the derivation given here has not introduced any new concepts as Overhauser's theory does.

At higher temperatures ($T \approx T_c$) the approximation leading from (4) to (9) is no longer valid and C_M deviates from (12). It is not possible at present to estimate in detail the dependence of C_M on T in this higher temperature region but it is obvious that the specific heat will begin to deviate from the linear law at a temperature proportional to $\mu h/k$. This temperature is linear in the concentration. At very high temperatures ($T > T_c$), C_M falls like T^{-2} .

We therefore conclude that, subject to certain simple assumptions, the specific heat results of Zimmerman can be qualitatively explained in terms of the Ruderman-Kittel-Yosida spin-spin interaction. The other properties of Cu-Mn alloys are not sensitive to the precise origin of the antiferromagnetism and it does not seem necessary to invoke any new mechanisms to explain them. The most serious weakness of the theory described here is probably the use of the Ising model. We must expect an additional specific heat coming from the spin waves and we have assumed this additional term is small at low temperatures without giving any proof.

Equation (8) deserves further discussion because it is essential for the theory that h be proportional to c as (8) indicates. Kittel has brought to the author's attention the close analogy between this problem and that of computing the line shape for nuclear magnetic resonance on a dilute sample of nuclear spins distributed randomly

in a crystal and coupled only by their magnetic dipole interactions. The latter problem has been discussed by Anderson¹⁰ and by Kittel and Abrahams¹¹ and it was concluded that for very dilute samples the line shape is a cut-off Lorentzian with width proportional to concentration (whereas if the line shape were Gaussian a width proportional to the square root of the concentration would be expected). A similar treatment to that of Kittel and Abrahams demonstrates immediately that $p(H,T)$ also has a width proportional to the concentration for dilute alloys. This justifies (8) which is the only assumption it is essential to make about $p(H,T)$. I am grateful to Dr. Kittel for suggesting this argument.

The foregoing argument is sufficient to fix the width of the $p(H,T)$ curve but not sufficient to determine its precise shape. But it is worthwhile to consider why the cut-off Lorentzian of the nuclear problem is distorted into the shape of curve c in Fig. 1 for this electron spin problem. Using the Ising approximation to the Hamiltonian (1) we can write the effective field acting on spin S_n as

$$H_n = (1/2\mu) \sum_{\mathbf{m}} f(\mathbf{n}-\mathbf{m}) S_{\mathbf{m}}^z, \quad (13)$$

and hence we can write the moments of the distribution $p(H,T)$ as

$$\langle H^2 \rangle = (1/4\mu^2) \sum_{\mathbf{l}, \mathbf{m}} f(\mathbf{n}-\mathbf{l}) f(\mathbf{n}-\mathbf{m}) \langle S_{\mathbf{l}}^z S_{\mathbf{m}}^z \rangle, \quad (14)$$

$$\langle H^4 \rangle = (1/16\mu^4) \sum_{\mathbf{l}, \mathbf{m}, \mathbf{p}, \mathbf{q}} f(\mathbf{n}-\mathbf{l}) f(\mathbf{n}-\mathbf{m}) f(\mathbf{n}-\mathbf{p}) f(\mathbf{n}-\mathbf{q}) \\ \times \langle S_{\mathbf{l}}^z S_{\mathbf{m}}^z S_{\mathbf{p}}^z S_{\mathbf{q}}^z \rangle, \quad (15)$$

where the sums go over the lattice points occupied by Mn. These may be written in terms of sums over all lattice points as

$$4\mu^2 \langle H^2 \rangle = (c/4) \sum_{\mathbf{l}} f^2(\mathbf{l}) + c^2/2 \sum_{\mathbf{l} < \mathbf{m}} f(\mathbf{l}) f(\mathbf{m}) \langle S_{\mathbf{l}}^z S_{\mathbf{m}}^z \rangle, \quad (16)$$

$$16\mu^4 \langle H^4 \rangle = (c/16) \sum_{\mathbf{l}} f^4(\mathbf{l}) + (3c^2/8) \sum_{\mathbf{l} < \mathbf{m}} f^2(\mathbf{l}) f^2(\mathbf{m}) \\ + (9c^3/2) \sum_{\mathbf{l} < \mathbf{m} < \mathbf{n}} f^2(\mathbf{l}) f(\mathbf{m}) f(\mathbf{n}) \langle S_{\mathbf{m}}^z S_{\mathbf{n}}^z \rangle \\ + c^4/24 \sum_{\mathbf{l} < \mathbf{m} < \mathbf{n} < \mathbf{p}} f(\mathbf{l}) f(\mathbf{m}) f(\mathbf{n}) f(\mathbf{p}) \\ \times \langle S_{\mathbf{l}}^z S_{\mathbf{m}}^z S_{\mathbf{n}}^z S_{\mathbf{p}}^z \rangle. \quad (17)$$

The first term of (16) is proportional to c and independent of temperature; the second term of (16) is temperature dependent and vanishes at high temperatures. At low enough concentrations the first term will dominate (16). The first two terms of (17) are temperature independent and at low enough concentration the

¹⁰ P. W. Anderson, Phys. Rev. **82**, 342 (1951).

¹¹ C. Kittel and E. Abrahams, Phys. Rev. **96**, 238 (1953).

first term will dominate because it is linear in c . We now recognize that if we retained only the temperature independent terms of (16) and (17) then we could have the exact analogy of the nuclear line width problem and we could therefore, by analogy, assume $\phi(H, T)$ to be a cut-off Lorentzian, i.e.,

$$\begin{aligned} \phi(H, T) &= \frac{\Delta}{\pi} \frac{1}{H^2 + \Delta^2} \quad \text{for } |H| < \alpha \\ &= 0 \quad \text{for } |H| > \alpha, \end{aligned} \quad (18)$$

where Δ and α are determined by

$$\begin{aligned} \langle H^2 \rangle &= 2\Delta\alpha/\pi, \\ \langle H^4 \rangle &= 2\Delta\alpha^3/3\pi, \end{aligned} \quad (19)$$

and we have assumed $\alpha \ll \Delta$. From (16), (17), and (19) we deduce that Δ is proportional to c and α is independent of c at low concentrations. From (18) we find

$$h = (\Delta/\pi) \ln[1 + (\alpha/\Delta)^2], \quad (20)$$

which, ignoring the weak dependence of the logarithm on c , is proportional to concentration.

The temperature dependent "correlation terms" in (16) and (17) approach zero at high temperatures and therefore we may assume that at high temperatures $\phi(H, T)$ is a cut-off Lorentzian. We now have to consider how $\phi(H, T)$ is modified at low temperatures. We notice from (16) that H^2 is increased by an amount $\sim c^2$ above the value it has at high temperatures and one way of doing this is to decrease $\phi(H, T)$ near $H=0$ and increase it the corresponding amount near $|H| \approx h$, i.e., by distorting (18) into the shape of curve c in Fig. 1. We also recognize this is reasonable on physical grounds because the effect of correlation must be to reduce the energy and this can only be done by arranging for spins to sit in fields of larger magnitude. We therefore conclude that this approach using the moments of $\phi(H, T)$ is quite consistent with the postulate that $\phi(H, T)$ is as shown in Fig. 1(c) at low temperatures and as given by (18) at high temperatures. However it should be emphasized again that for our immediate purposes the precise shape of $\phi(H, T)$ is of no importance.

It is possible to define an "effective magnetic field" without making the Ising approximation and the subsequent analysis is exactly as we have given in this paper. But the concept of an effective magnetic field as used here is strictly valid only in the Ising approximation and so at low temperatures it is doubtful if this alternative approach would be of value (but at high temperatures it is certainly better than the theory based on the Ising approximation).

It seems very likely that the explanation given here for the Cu—Mn alloys may also be used in connection with the unusual specific heat results of Beck *et al.*⁸ for V—Fe and Cr—Fe alloys. Beck observed that the term

in the specific heat linear in T was extremely sensitive to alloy concentration and had very sharp maxima at certain concentrations. It is very hard to believe that these could be explained by any conventional electron band theory and it seems more natural to explain the results by the same kind of qualitative argument we have given here for Cu—Mn. That is, we suggest that in these alloys some spins sit in very small effective fields and therefore give a large contribution to the specific heat. Indeed it has been pointed out to the author by R. J. Weiss that the maxima in Beck's results occur very close to the concentrations at which the ferromagnetism of Fe is destroyed and this is strong evidence that the usual results are connected with a spin disordering.

Let us now comment on the Overhauser theory of Cu—Mn. The most serious objection to the Overhauser theory is that it is incomplete in the same way as the Zener theory of ferromagnetism is incomplete. Both theories give a coupling between the Mn spins which is of infinite range and this must be incorrect for fundamental reasons as Yosida⁶ and Friedel¹² have pointed out. The origin of this infinite range coupling is the same in both theories; the interaction between the localized spins and the conduction electrons is treated only in first order perturbation theory whereas the total energy change appears finally as a second order quantity in the interaction. As Yosida has carefully emphasized it is essential to work consistently to second order in the interaction.

Of course it may be true that exchange effects cause the Ruderman-Kittel-Yosida interaction to be modified and we may visualize this as follows. Consider the spin density of the conduction electrons in the vicinity of a Mn atom; in the presence of the Mn spin each single particle eigenstate becomes a superposition of a plane wave with an outgoing scattered wave. Because of the spin dependence of the scattering mechanism these eigenstates are different for α and β spins and hence a nonzero spin density is produced in the neighborhood of the Mn atom. Yosida has shown that this spin density oscillates in sign and falls off with distance in a well defined way. But strictly speaking this result is not self-consistent; because of the exchange interaction between the conduction electrons they are scattered both by the Mn spin and by the spin density variations. Hence to determine the precise form of the spin density variations it is necessary to solve this scattering problem self-consistently. We recognize that this problem is analogous to that of determining the charge density variations around an impurity atom and the latter has been discussed in detail by Friedel. The author believes that it is only to this extent that exchange between conduction electrons can affect the spin density and spin-spin coupling in metals.

¹² J. Friedel, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1954), Vol. 3, p. 446.

In conclusion it should be emphasized again that the two basic assumptions of the theory presented here, namely the form of $\rho(H, T)$ and the use of the Ising approximation have not been rigorously proved valid but are put forward as extremely plausible assumptions which explain the experimental results.

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Spin-Lattice Relaxation of Shallow Donor States in Ge and Si through a Direct Phonon Process*

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The many-valley character of the conduction band edge of germanium and silicon causes an anisotropy of the g shift and of the deformation potential for the conduction electrons. It is shown that the combination of these two effects provides a mechanism for spin-lattice relaxations of the donor spins in germanium and silicon that yields $1/T_s$ proportional to the temperature T and to the fourth power of the static magnetic field H . Using known data about the deformation potential constant, the g shift, the energy of the intervalley splitting, and the elastic constants, the magnitude of T_s is found to be approximately 2×10^{-8} sec for phosphorus donors in germanium, and 1×10^4 sec for phosphorus donors in silicon. These values refer to $T = 1.25^\circ\text{K}$, $H = 3000$ gauss, with the field applied along the $[111]$ axis. Our mechanism fails to give a finite T_s for donors in silicon, when the field is applied along the $[100]$ axis.

1. INTRODUCTION

THE present investigation is concerned with a mechanism which may be responsible for spin-lattice relaxations of shallow donor spins in Ge and Si. We restrict our considerations to direct phonon processes, i.e., to processes which involve the absorption or emission of only one phonon.

The interaction of an electron with lattice vibrations in such a nonpolar crystal has been treated by many authors from the deformation-potential point of view.¹ In particular, a generalized theory of the deformation potential for many-valley semiconductors has been developed by Herring and Vogt.^{2,3} According to these authors, the shift of the electronic energy of the i th valley due to a strain \mathfrak{u} is given by

$$\epsilon^{(i)} = \sum_{\alpha, \beta} U_{\alpha\beta} (\Xi_d \delta_{\alpha\beta} + \Xi_u K_\alpha^{(i)} K_\beta^{(i)}), \quad (1.1)$$

where $U_{\alpha\beta}$ is the (α, β) component of the strain tensor \mathfrak{u} , $\mathbf{K}^{(i)}$ is the unit vector pointing from the origin to the bottom of the i th valley in the first Brillouin zone, and Ξ_d and Ξ_u are energy constants whose magnitudes are several eV. If one writes the displacement of the lattice at a position \mathbf{r} due to the lattice vibration as a

Fourier series:

$$\mathbf{Q}(\mathbf{r}) = \sum_{\mathbf{q}} \mathbf{Q}(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{r}}, \quad (1.2)$$

then, using Eq. (1.1), the corresponding Fourier component of the energy shift is given by

$$\epsilon_{\mathbf{q}}^{(i)} = \Xi_d (i\mathbf{Q}_{\mathbf{q}} \cdot \mathbf{q}) + \Xi_u (i\mathbf{Q}_{\mathbf{q}} \cdot \mathbf{K}^{(i)}) (\mathbf{K}^{(i)} \cdot \mathbf{q}). \quad (1.3)$$

The first and the second terms in the right-hand side of Eq. (1.3) represent the interaction of the electron with the lattice wave of a wave vector \mathbf{q} through the volume dilation, and the shearing strain, respectively.

In the present paper, we wish to show the importance of the second term of the expression (1.3) in the mechanism of spin-lattice relaxations of shallow donor states in Ge and Si. The effect of shearing strains on the ground state of donors has been discussed by Price⁴ and by Kohn.⁵ One interesting feature of these states, first pointed out by Kohn and Luttinger,⁶ is a splitting of the degenerate ground state through the intervalley interaction due to the impurity potential. The recent experiments on acoustoelectric effect (Ge),⁷ piezoresistance (Ge),⁸ Hall effect (Si),⁹ and spin resonance (Si, Ge)^{10,11} have confirmed this feature, and have

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