secondary could not be more than about $2\times10^{-29}$ cm$^2$/nucleon. If the cross section were as high as $5\times10^{-29}$ cm$^2$/nucleon, the chances of obtaining the present results would be only about three percent.

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# Dipolar Broadening of Magnetic Resonance Lines in Magnetically Diluted Crystals

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Calculations are given for the frequency moments associated with the dipolar broadening of magnetic resonance lines in crystals having lattice points populated at random by identical paramagnetic ions or nuclei. It is found that for fractional magnetic population $f>0.1$ the line shape is approximately Gaussian with a width proportional to $f^{\frac{1}{2}}$; for $f<0.01$ the line shape is approximately Lorentzian with a width proportional to $f$.

We have solved rigorously by the method of moments the problem of magnetic dipolar broadening of magnetic resonance lines in crystals having lattice points populated at random by identical paramagnetic ions or nuclei, the remaining equivalent lattice sites being populated by diamagnetic ions or nuclei with spin zero. Such a situation often occurs in paramagnetic resonance research by design in order to improve resolution, or it may arise naturally as in crystals with color centers or as in nuclear resonance experiments when only one of the isotopes has a magnetic moment. The dipolar broadening problem when all lattice sites are populated identically has been solved by Van Vleck.[1] For random population there have been published two apparently conflicting arguments, one[2] suggesting that the line width is proportional to the square root of the concentration of magnetic systems, the other[3] suggesting that at low concentrations the width is directly proportional to the concentration and that the line has a Lorentz shape. The result of our exact treatment is that in the absence of exchange and hyperfine interaction the line width for random occupancy is proportional to the square root of the concentration, if more than about 0.1 of the lattice sites are filled magnetically, while for appreciably lower concentrations the width is proportional to the concentration.

The result follows easily from the equations of Van Vleck in the paper cited. We consider first the second moment. From his Eqs. (9) and (10) the mean square deviation of the frequency from the Larmor value may be written

$$\langle\Delta\nu^2\rangle_{\mathrm{Av}}=[S(S+1)/3N\hbar^2]{\textstyle\sum_{j,k}}'\,B_{jk}^2, \tag{1}$$

where $N$ is the actual number of magnetic ions and

$$B_{jk}=-3g^2\mu_B{}^2r_{jk}{}^{-3}[\tfrac{3}{2}\gamma_{jk}{}^2-\tfrac{1}{2}], \tag{2}$$

$\gamma_{jk}$ being the direction cosine of $\mathbf{r}_{jk}$ with the static field. If $f$ is the probability that a lattice site is occupied by a magnetic system, the number of $k$ sites occupied at a displacement $\mathbf{r}_{jk}$ from the occupied $j$ sites is, after summing over $j$, simply $Nf$, as $N$ sites $j$ are occupied and $f$ is the probability that any other site is occupied. Hence the sum $\sum_{jk}'$ over all occupied sites ($j\neq k$) is just $Nf\sum_k'$, where we now sum over *all* $k$ sites, whether or not occupied. Thus Eq. (1) becomes

$$\langle\Delta\nu^2\rangle_{\mathrm{Av}}=[S(S+1)/3\hbar^2]f{\textstyle\sum_{k}}'\,B_{jk}^2, \tag{3}$$

where the sum is over all lattice sites, so that the second moment is always proportional to the concentration.[4] It is necessary, however, to examine the fourth moment before any conclusions may be drawn regarding the apparent width of the line. Van Vleck's Eq. (24) for the fourth moment involves sums of the form

$$\text{(I)}\ {\textstyle\sum_{jk}}'\,B_{jk}^4;\quad \text{(II)}\ {\textstyle\sum_{jkl}}'\,B_{jk}^2B_{jl}^2;$$

and

$$\text{(III)}\ {\textstyle\sum_{jkl}}'\,B_{jk}^2B_{jl}B_{kl}.$$

It is readily seen that these sums over randomly filled sites are equal to the following sums over all sites (with

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[1] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

[2] Whitmer, Weidner, Hsiang, and Weiss, Phys. Rev. **74**, 1478 (1948).

[3] P. W. Anderson, Phys. Rev. **82**, 342 (1951).

[4] It may be noted that this differs from the result one would obtain if the effect of dilution were to expand the magnetic lattice uniformly.

$jkl\neq$):

$$\text{(I)}\ Nf\textstyle\sum_k{}' B_{jk}^4;\quad \text{(II)}\ Nf^2\textstyle\sum_{kl}{}' B_{jk}^2B_{jl}^2;$$
$$\text{(III)}\ Nf^2\textstyle\sum_{kl}{}' B_{jk}^2B_{jl}B_{kl}.$$

We find for a simple cubic lattice with the static field directed along the 100 axis:

$$\langle\Delta\nu^4\rangle_{\mathrm{Av}}=3[\langle\Delta\nu^2\rangle_{\mathrm{Av}}]^2 \times\{0.742+f^{-1}[0.098-0.021(S^2+S)^{-1}]\}, \quad (4)$$

which, when all sites are occupied ($f=1$), is equal to Van Vleck's Eq. (25). If the line shape were Gaussian, the term is the curly brackets above would be equal to one. For $S=\frac{1}{2}$ the expression in the brackets is

$$0.742+0.070f^{-1},$$

so that the line may be considered to be approximately Gaussian for values of the fractional concentration $f>0.1$.

For $f<0.01$ the deviations from Gaussian shape become very marked: the fourth moment increases relative to the square of the second moment just as in motional or exchange narrowing. Anderson and Weiss[5] have given compelling reasons for believing that the line shape with motional and exchange narrowing is Lorentzian, and Anderson[3] has suggested that the shape is approximately Lorentzian (with a cutoff) also in the random dilution problem. We can show that at small $f$ Eqs. (3) and (4) above are compatible with a cut-off Lorentzian line. They are incompatible with a cut-off Gaussian line.

We take a Lorentzian line with cut-off frequencies $\nu_0\pm\alpha$ and half-width at half-maximum intensity $\Delta$:

$$\begin{aligned} &I(\nu)d\nu=d\nu/(\nu^2+\Delta^2) && |\nu-\nu_0|\leq\alpha,\\ &I(\nu)d\nu=0 && |\nu-\nu_0|>\alpha. \end{aligned}$$

In the approximation $\Delta/\alpha\ll 1$ the second and fourth moments for this line are

$$\langle\Delta\nu^2\rangle_{\mathrm{Av}}=2\Delta\alpha/\pi,\quad \langle\Delta\nu^4\rangle_{\mathrm{Av}}=2\Delta\alpha^3/3\pi.$$

For $f\ll 1$ and the field along the 100 axis in a simple cubic lattice Eqs. (3) and (4) give second and fourth moments of $7.47fA^2$ and $11.7fA^4$, respectively, where $A=g\mu^2{}_B/ha^3$. These moments are thus compatible with a Lorentzian line with cut-off frequency $\alpha=2.2A$ and a half-width at half-maximum intensity of $\Delta=5.3fA$. At low concentration the width would then appear to be linearly proportional to the concentration. The maximum intensity is independent of concentration, as the integrated absorption must be proportional to the concentration.

It is of some interest to check the Lorentz line against the sixth moment, although we should bear in mind that the higher moments give us progressively less information about the central portion of the line. We have succeeded in finding a general expression for the term of the $2n$th moment which is linear in the fractional concentration $f$. This will be the dominant term at low concentrations. The result is for spin $\frac{1}{2}$

$$h^{2n}\langle\Delta\nu^{2n}\rangle_{\mathrm{Av}}=(\tfrac{1}{2})^{2n}f\textstyle\sum_k{}' B_{jk}^{2n}+\cdots. \quad (5)$$

This result is easily derived by a subterfuge. It is obvious that the term containing $\sum' B_{jk}^{2n}$ is the only term linear in $f$. We note that each element in the summation refers only to a pair of atoms, so that the moment will be given by an expression of the identical form, if we treat only two atoms as if we treat a large number of atoms. We can, moreover, easily find an explicit solution for the absorption frequencies in the two atom problem; having the frequencies, we can calculate any desired moment. With the Hamiltonian as truncated by Van Vleck we find the two transition frequencies $\nu_0\pm\frac{1}{2}B_{jk}$ for two atoms with spin $\frac{1}{2}$. The expression Eq. (5) for the moments follows directly. We find on comparing sixth moments that $\langle\Delta\nu^6\rangle_{\mathrm{Av}}{}^{1/6}$ for for the Lorentz line is about 15 percent too high (for a simple cubic lattice in the 100 direction). This difficulty with the Lorentz line is not surprising in view of the overwhelming importance of nearest neighbor atoms in the higher moments, giving rise to satellites.

The problem of spin-lattice relaxation in dilute salts is also of interest. An inspection of the Waller[6] calculation suggests that for dipolar interactions the spin-lattice relaxation time should be inversely proportional to the fractional concentration $f$.

At present there do not appear to be available quantitative data taken under controlled conditions to test our theoretical conclusions in detail. It is possible to contemplate tests with both electronic and nuclear systems, although with electrons one must be alert to recognize the effects of exchange and hyperfine interactions[7] as well as of the effects of nonrandom arrangements caused by elastic forces.

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[5] P. W. Anderson and P. R. Weiss, Revs. Modern Phys. (to be published).

[6] I. Waller, Z. Physik **79**, 370 (1932).

[7] It is shown by C. Kittel [Bull. Am. Phys. Soc., **28**, No. 2, 21 (1953)] that the shape and width of the resonance line observed by Hutchison and Noble in KCl colored with excess potassium may be accounted for by hyperfine structure, rather than by dipolar interactions.