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TWO-MAGNON ABSORPTION AND THE MAGNETOELECTRIC EFFECT IN A LINEAR CHAIN OF SPINS

L. N. BULAEVSKIĬ

Institute of Chemical Physics, USSR Academy of Sciences

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An estimate is made of the intensity of two-magnon absorption in crystals with linear chains of localized spins, and the frequency dependence of the intensity of this absorption is investigated. It is shown that in crystals with a one-dimensional system of spins and with symmetry that allows a vector, a spontaneous polarization, dependent on the spin state of the crystal, is possible. In this case the polarization depends on the magnetic field, and this effect can be observed experimentally in iminoxyl radicals. Similar effects are considered in polyradical molecules.

THIS article considers two-magnon absorption[1] and the nonlinear magnetoelectric effect[2] in crystals and molecules with one-dimensional systems of localized spins. We consider only the case of antiferromagnetic interaction of nearest neighbors in the chain. Such a system, even in the case of an infinite number of spins, differs significantly in its properties from a three-dimensional antiferromagnet, since at all finite temperatures there is an absence of ferromagnetic ordering in it. Consequently, the calculation of the two-magnon absorption spectrum and of the characteristics of the magnetoelectric effect in such systems presents a special problem. At present it is becoming timely because of the appearance of a large number of crystals, synthesized on the basis of radicals or ion-radicals of the type TCNQ$^-$ (or TCNE$^-$)[3], in which, apparently, there are one-dimensional systems of localized spins. Thus in systems of the type (dye)$^+$TCNQ$^-$, the TCNQ$^-$ ion-radicals, possessing one unpaired electron, form a system of filaments, in which exchange interaction of unpaired electrons in different filaments is practically absent, while along a chain the exchange interaction should be much stronger for neighboring radicals than for electrons of radicals that are not neighbors. In iminoxyl radicals, the presence of a one-dimensional system of spins with antiferromagnetic interaction of nearest neighbors is confirmed by measurements of the magnetic susceptibility of the crystals[4]. Finally, we remark that two-magnon absorption in a broader sense is the excitation of spin states by an alternating electric field, and in this sense it exists also in polyradical molecules with a finite number of spins[5]. In them there can also be a dependence of the dipole moment of a molecule on its spin state; that is, a nonlinear magnetoelectric effect.

We shall suppose that in all these systems, just as in antiferromagnets[1], the spin Hamiltonian and the effective dipole-moment operator, which determine the two-magnon absorption and the magnetoelectric effect, are described in terms of a spin-½ operator in the form

$$\mathscr{H} = \sum_n I_{n,\,n+1}\left(\mathbf{S}_n\mathbf{S}_{n+1} - \frac{1}{4}\right), \tag{1}$$

$$\mathbf{D}_{\text{eff}} = \sum_n \mathbf{d}_{n,\,n+1}\left(\mathbf{S}_n\mathbf{S}_{n+1} - \frac{1}{4}\right. \tag{2}$$

The operator $\mathbf{D}_{\text{eff}}$ is different from zero only in crystals without a center of inversion between nearest radicals of the linear chain. This condition is satisfied by crystals in which different radicals, for example TCNQ$^-$ and TCNE$^-$, alternate along a filament. In this case, in crystals of any symmetry, nondiagonal matrix elements of the operator $\mathbf{D}_{\text{eff}}$, which lead to two-magnon absorption, are allowed. In crystals whose symmetry allows a preferred direction (a vector), diagonal elements are also allowed, corresponding to the occurrence of a spontaneous polarization dependent on the spin state of the system. (Finally, in crystals of this type there can also be present the usual polarization, independent of the spins.) In crystals of equivalent radicals, $\mathbf{D}_{\text{eff}}$ is allowed only in the case of a symmetry that permits a vector. An example of such crystals is the iminoxyl radical[6]. In these systems, two-magnon absorption is absent, and $\mathbf{D}_{\text{eff}}$ leads only to a magnetoelectric effect.

The order of magnitude of $\mathbf{d}_{n,\,n+1}$ in crystals can be estimated by considering the mechanisms that lead to the relation (2)[1,2]. Paper[1] takes account of the contribution to $\mathbf{D}_{\text{eff}}$ from virtual transitions of an electron of an unfilled shell to excited levels of the same radical because of the dipole moment, and of the Coulomb interaction of the excited electron with an unpaired electron of the neighbor radical, which leads to exchange of spins and to return of the excited electron to a lower unfilled shell. Paper[2] takes account of virtual transitions of an electron of an unfilled shell to a neighbor radical; the parameters of (1) and (2) are determined by the relations

$$\begin{gathered}
I_{n,\,n+1} = 2\beta^2_{n,\,n+1}(1/E_{n,\,n+1} + 1/E_{n+1,\,n}),\\
\mathbf{d}_{n,\,n+1} = 2\mathbf{D}_{n,\,n+1}\beta_{n,\,n+1}(1/E_{n,\,n+1} + 1/E_{n+1,\,n})\\
+ \beta_{n,\,n+1}(\mathbf{D}_{n+1,\,n+1} - \mathbf{D}_{n,\,n})(1/E^2_{n,\,n+1} - 1/E^2_{n+1,\,n}),\\
\mathbf{D}_{n,\,m} = \int w_n(\mathbf{r})e\mathbf{r}\,w_m(\mathbf{r})\,d\mathbf{r},
\end{gathered} \tag{3}$$

where $\beta_{n,\,n+1}$ is the resonance integral for transition of an electron from radical n to neighbor radical n + 1, $w_n(\mathbf{r})$ is the Wannier function of an electron localized on radical n, and $E_{n,\,n+1}$ is the energy of the system in the excited state, which is equal to the energy of ionization of radical n without the energy of affinity to the electron of radical n + 1 and the energy of repulsion of unpaired electrons n and n + 1. If there is no center of inversion between neighboring radicals, $D_{n,n+1}$ or $(E_{n,n+1} - E_{n+1,n})$ are different from zero, and $d_{n,n+1} \approx$ (0.1 to 1) $\times d_0 I_{n,n+1}/E_{n,n+1}$, where d_0 is the atomic dipole moment and $E_{n,n+1} \approx 1$ eV. Mechanism[1] leads approximately to the same estimate of $d_{n,n+1}$. The value of $d_{n,n+1}$ for molecules will be estimated below.

TWO-MAGNON ABSORPTION IN CRYSTALS WITH LINEAR CHAINS OF SPINS

Allowing for the possibility of alternation in the system of spins (the interaction parameter alternates along the chain: I, γI, I, ..., $\gamma \leq 1$), we write (1) and (2) in the form

$$\mathscr{H} = I \sum_n \left[\left(\mathbf{S}_{2n}\mathbf{S}_{2n-1} - \frac{1}{4} \right) + \gamma \left(\mathbf{S}_{2n}\mathbf{S}_{2n+1} - \frac{1}{4} \right) \right], \qquad (4)$$

$$\mathbf{D}_{\text{eff}} = \mathbf{d} \sum_n \left[\left(\mathbf{S}_{2n}\mathbf{S}_{2n-1} - \frac{1}{4} \right) - \gamma' \left(\mathbf{S}_{2n}\mathbf{S}_{2n+1} - \frac{1}{4} \right) \right] \qquad (5)$$

and we find the dependence of the intensity of two-magnon absorption on frequency in the Hartree-Fock (HF) approximation for the four-fermion Hamiltonian equivalent to the spin Hamiltonian (4)[7,8].

It may be supposed that the HF approximation gives correctly the qualitative characteristics of two-magnon absorption. A basis for such optimism is provided by a comparison of the results obtained in the HF approximation with those exact results that have been obtained recently for the Hamiltonian (4). In fact, the HF approximation reproduces quite accurately the triplet excitation spectrum ϵ(k) (the single-magnon spectrum). For $\gamma = 1$, we get $\epsilon_{HF}(k) = (1 + 2/\pi)\,|\cos k|$[7,8]; the exact value $\epsilon(k) = (\pi/2)\,|\sin k|$[9] differs from the Hartree-Fock value only by 4%. For $\gamma < 1$, there are only numerical calculations of the single-magnon spectrum for ten spins[10], and a comparison of them with the HF approximation ([10], Fig. 6) shows that it is more accurate, the smaller γ, and that it becomes exact for $\gamma = 0$. Furthermore, the results of a numerical calculation of the magnetic susceptibility for 10 and 11 spins with $\gamma = 1$[11] show that the HF approximation satisfactorily reproduces the behavior of the susceptibility at temperatures T > 0.3 I. The dependence of the magnetic moment of the system on the magnetic field[12] at T = 0 also turns out to be qualitatively correct in the HF approximation. Quantitatively, the HF result is least accurate for the susceptibility at T = 0, but even in this case we get for the susceptibility per spin in units $4\mu^2/I$ (μ is the Bohr magneton) the value 0.140, whereas the exact value is 0.101. Finally, the energy of the ground state is determined in the HF approximation with an accuracy of about 5%.

And so, we go over in (4) from the Pauli spin operators to the Fermi operators α_k and β_k, which in the HF approximation for an infinite chain of spins are the operators of annihilation of quasiparticles with momentum k and energies

$$\varepsilon_\alpha(k) = -\varepsilon_\beta(k) = \varepsilon(k) = \frac{a_1 + a_2\cos^2(k/2)}{\sqrt{1 + \gamma^2 + 2\gamma\cos k}},$$

$$a_1 = \frac{1}{2}(1-\gamma)^2\left[1 + \frac{2}{\pi}K(x)\right], \qquad x = \frac{2\sqrt{\gamma}}{1+\gamma},$$

$$a_2 = 2\gamma + \frac{1}{\pi}(1+\gamma)^2 E(x) - \frac{1}{\pi}(1-\gamma)^2 K(x), \qquad (6)$$

where E(x) and K(x) are elliptic functions. The spectrum of quasiparticles α and β consists of a lower β-band, filled in the ground state, and an upper α-band, empty in the ground state. For $\gamma < 1$, there is between these bands a gap $\Delta = a_1(1 + \gamma)$. To a magnon—an excitation with z-projection of the total spin $S_z = +1\ (-1)$ and impulse k—corresponds an extra quasiparticle (hole) in the upper (lower) band; the energy of the magnon is ϵ(k). The quadratic part of the expression (5), which determines the two-magnon absorption at temperature T = 0, has the form

$$\mathbf{D}_{\text{eff}} = \sum_k i\boldsymbol{\pi}(k)\,(\alpha_k^+\beta_k - \beta_k^+\alpha_k),$$

$$\boldsymbol{\pi}(k) = \frac{\mathbf{d}\xi\sin k}{\sqrt{1 + \gamma^2 + 2\gamma\cos k}}$$

$$\xi = \gamma + \nu' - \frac{1}{2\pi}\int_0^\pi \frac{\gamma(1+\gamma') + (\gamma^2 + \gamma')\cos k}{\sqrt{1 + \gamma^2 + 2\gamma\cos k}}\,dk. \qquad (7)$$

It is evident from (7) that excitation by an electric field with a wavelength larger than the period of the lattice leads to transition of the quasiparticle from the lower band to the higher band without change of momentum. This process corresponds to creation of two magnons with momenta ±k and energy 2ϵ(k). Thus the frequencies of two-magnon absorption lie in the interval from 2Δ to $2(a_1 + a_2)/(1 + \gamma)$ ($\hbar$ is taken equal to 1). The imaginary part of the dielectric permittivity has the form

$$\varkappa''(\omega) = \frac{N}{2\pi}\int_0^{2\pi} \pi^2(k)\,\delta[2\varepsilon(k) - \omega]\,dk = \frac{N}{2\pi}\frac{\pi^2(k)}{d\varepsilon/dk}, \qquad (8)$$

where N is the spin density, and where the value of k is related to the frequency ω by the equation $\omega = 2\epsilon(k)$. For a uniform chain ($\gamma = \gamma' = 1$), the frequency interval of absorption extends from 0 to $\omega_0 = 2(1 + 2/\pi)I$, and

$$\varkappa''(\omega) = \frac{8Nd^2(1 + 1/\pi)^2}{\pi\omega_0}\sqrt{1 - \frac{\omega^2}{\omega_0^2}}. \qquad (9)$$

In this case, the intensity of the absorption, which is proportional to $\omega\kappa''(\omega)$, has a broad maximum at frequency $\omega_0/\sqrt{2}$. In a strongly alternating system ($\gamma = \gamma' \ll 1$), the absorption curve has the form of a sharp peak in the interval $(2 \pm \gamma)I$,

$$\varkappa''(\omega) = \frac{9Nd^2\gamma}{4\pi I}\sqrt{1 - \frac{(\omega - 2I)^2}{I^2\gamma^2}}. \qquad (10)$$

Figure 1 shows the functions $\kappa''(\omega)$ for $\gamma = \gamma' = 1$, 0.8, 0.6, 0.4, and 0.2. For small $(1 - \gamma)$, the value of $\kappa''(\omega)$ is very large in the region $\omega \gtrsim 2\Delta$. This is due to the fact that when $\gamma \approx 1$, we get $d\epsilon/dk = 0$ not only at $k = \pi$, but also at some point near π. Presumably this peculiarity is due to the HF approximation, and it may be supposed that a more accurate calculation will greatly change the behavior of $\kappa''(\omega)$ in the region $\omega \gtrsim 2\Delta$. Therefore in Fig. 1 the curves for $\gamma \approx 1$ in the region $\omega \gtrsim 2\Delta$ are shown dashed. When $\gamma \lesssim 1$, just as in a uniform system, the absorption is greatest at a frequency of order $\omega_0/\sqrt{2}$ and decreases slowly with increase of frequency. But its drop at low frequencies (of order 2Δ) in this case is abrupt.

We note that if, in the linear spin system with uniform interaction ($\gamma = \gamma' = 1$), there are defects—sites

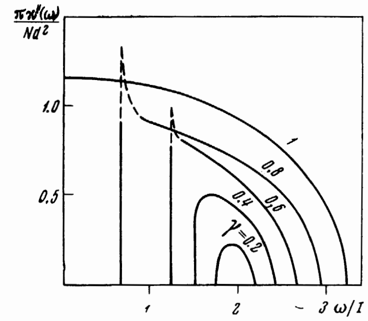

FIG. 1

without spin—of concentration c, then it is a statistical ensemble of chains of spins of finite length n, whose distribution function is $c(1-c)^n \approx c\exp(-cn)$ for $c \ll 1$. Therefore

$$\varkappa''(\omega) = Nc^2 \sum_{n=1}^{\infty} e^{-cn}\varkappa_n''(\omega), \tag{11}$$

where $\kappa_n''(\omega)$ is the contribution from a chain of length n. In a chain of n spins, the minimum energy of two magnons is of order 8I/n, and for such a chain $\kappa_n''(\omega) \approx 0$ for $\omega \lesssim 8I/n$. Then for small ω, the contribution to $\kappa''(\omega)$ is made by chains with $n > 8I/\omega$, whose contribution decreases as $\exp(-8cI/\omega)$ as $\omega \to 0$. Thus the left edge of the absorption in a chain with defects is abrupt in this case also.

We shall discuss only qualitatively the dependence of the two-magnon absorption on temperature. With increase of temperature, its intensity drops, and this drop is fastest in the temperature range near I/2. At $T \gg I$ the absorption disappears, since every level of the higher and of the lower band is filled uniformly with quasiparticles with probability ½. Thus the two-magnon absorption can be identified experimentally through the dependence of its intensity on temperature.

In systems with a center of inversion between neighboring radicals, the process of creation of two magnons may accompany the creation of optical phonons in an electromagnetic field[13]. The intensity of this process is about five orders smaller than the intensity of phonon absorption in crystals with spin interaction I ≈ 100°K, and the absorption frequencies corresponding to these two processes differ by a quantity of order I. This process changes with temperature in the same way as does the two-magnon absorption.

THE NONLINEAR MAGNETOELECTRIC EFFECT IN CRYSTALS WITH LINEAR CHAINS OF SPINS

We consider only the most interesting case of a uniform spin interaction in crystals with equivalent radicals. Crystals of iminoxyl radicals belong to precisely this class[4]. The mean value of the operator D_{eff} makes a contribution to a spontaneous polarization **P** if the crystal symmetry permits a vector, and we get

$$\mathbf{P} = \mathbf{P}_0 + \langle \mathbf{D}_{\text{eff}} \rangle = \mathbf{P}_0 + \mathbf{d}\sum_n \left\langle \mathbf{S}_n\mathbf{S}_{n+1} - \frac{1}{4} \right\rangle, \tag{12}$$

where $\mathbf{P}_0$ is the usual spin-independent polarization, and where the second term is proportional to the exchange energy of the spins. Thus the polarization P contains a term that depends on temperature in the same way as does the mean exchange energy. Its change with temperature is most pronounced in an interval near I/2, and $\Delta P \approx 0.2\,Nd\,\Delta T/I$[8]. The dependence of the polarization on the magnetic field H, in the HF approximation, is determined by the expressions

$$\begin{gathered} \frac{|\mathbf{P}-\mathbf{P}_0|}{Nd} = \left\langle \mathbf{S}_n\mathbf{S}_{n+1} - \frac{1}{4} \right\rangle \\ = s^2 - \frac{\cos\pi s}{\pi} - \frac{\cos^2\pi s}{\pi^2} - \frac{1}{4}, \\ \frac{2\mu H}{I} = \left(1 + \frac{2}{\pi}\cos\pi s\right)\sin\pi s + 2s, \end{gathered} \tag{13}$$

where s is the mean value of spin at a site. The dependence of $|\mathbf{P}-\mathbf{P}_0|/Nd$ on $\mu H/I$ is shown in Fig. 2. In weak fields and in fields $H \approx I/\mu$, we get

$$\begin{gathered} \mathbf{P}(H) - \mathbf{P}(0) = \frac{2N\mathbf{d}\mu^2H^2}{I^2(\pi+4)}, \quad \frac{\mu H}{I} \ll 1, \\ \mathbf{P}(H) = -\frac{4N\mathbf{d}}{\pi}\sqrt{1-\frac{\mu H}{I}}, \quad 1-\frac{\mu H}{I} \ll 1. \end{gathered} \tag{14}$$

In the field range $H \approx I/\mu$, the change of polarization with change of field H is

$$\Delta P \approx Nd\frac{\mu\Delta H}{I} \approx (0.1-1)\frac{Nd_0\mu}{E_{n,\,n+1}}\Delta H \approx 10^{-5}\,\Delta H, \tag{15}$$

and in fields very close to I/μ one can get $\Delta P/\Delta H \approx 10^{-4}$. Such fields are attainable in iminoxyl radicals with I ≈ 2°K, and in them the dependence of polarization on magnetic field is presumably observable.

TWO-MAGNON ABSORPTION AND THE MAGNETOELECTRIC EFFECT IN POLYRADICAL MOLECULES

Excitation of spin levels by an electric field can be observed in polyradical molecules with a number of radical groups larger than two, in case neighboring radicals of a group are nonequivalent and the interaction between them is sufficiently large. Thus if radical fragments A and B are combined into a triradical of the type A—B—A′, the spin Hamiltonian and the effective dipole moment are determined by the expressions

$$\begin{aligned} \mathscr{H} &= I(\mathbf{S}_A\mathbf{S}_B + \mathbf{S}_{A'}\mathbf{S}_B) + I'\mathbf{S}_A\mathbf{S}_{A'}, \\ \mathbf{D}_{\text{eff}} &= \mathbf{d}(\mathbf{S}_A\mathbf{S}_B - \mathbf{S}_B\mathbf{S}_{A'}), \end{aligned} \tag{16}$$

and the vector **d** is directed along the line joining A and A′. The absorption due to transition between two levels with spin ½ (excitation energy I − I′) is determined by the imaginary part of the dielectric permittivity, $\kappa'' = 1.5\,Nd^2/\Delta\omega$ is the line width and N is the density of triradicals.

We shall estimate the value of d for radicals A—B joined to each other by a single σ-bond. The contribution

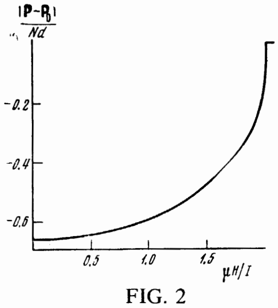

FIG. 2

to d comes from transitions of electrons from A and B on the σ-bond joining A and B, as a result of the Coulomb interaction of electrons of different bonds. In the case of degenerate (with respect to spins) levels, in the second order of perturbation theory with respect to $\mathcal{H}'$—the interaction between electrons of different bonds—the wave function contains the expression

$$\psi_i = \frac{1-\mathcal{P}}{\mathcal{H}_0 - E_0}\mathcal{H}'\frac{1-\mathcal{P}}{\mathcal{H}_0 - E_0}\mathcal{H}'\varphi_{i0}. \tag{17}$$

In (17), $\mathcal{P}$ is the operator of projection onto the space of the degenerate functions $\varphi_A(\pm\frac{1}{2})\varphi_B(\pm\frac{1}{2})\varphi_{A-B}(0)$, where $\varphi_{A,B}(\pm\frac{1}{2})$ is the ground-state function of radicals of groups A, B with spin projections $\pm\frac{1}{2}$, $\varphi_{A-B}(0)$ is the ground-state function of the σ-bond A – B (spin 0), and φ_{i0} are the stable combinations of degenerate-function space. In correspondence with (17), the effective dipole-moment operator for radicals A – B contains the expression

$$\mathbf{D}_{\text{eff}}^{A-B} = \mathcal{P}\mathbf{D}\frac{1-\mathcal{P}}{\mathcal{H}_0 - E_0}\mathcal{H}'\frac{1-\mathcal{P}}{\mathcal{H}_0 - E_0}\mathcal{H}'\mathcal{P} = \mathbf{d}\left(\mathbf{S}_A\mathbf{S}_B - \frac{1}{4}\right), \tag{18}$$

where $\mathbf{D}$ is the dipole-moment operator of electrons A – B. One of the terms in (18) consists of the matrix element of $\mathbf{D}$ for transition of electrons from A to the σ-bond A – B (of order d_0), exchange Coulomb interaction of electrons of bond A – B with electrons in B (of order 1 eV), and the reverse transition of an electron from bond A – B to A, caused by the Coulomb interaction of electrons of bond A – B with electrons A (of order 1 eV[15]). Intermediate states are states without an electron in A and with three electrons in bond A – B; their energies are of order 10 eV. Thus $d \approx (10^{-2}$ to $10^{-3})\rho^2 d_0$, where ρ is the spin density on atoms A and B, between which the σ-bond A – B exists. Each extra π- or σ-bond between A and B diminishes d by about an order. For two σ-bonds between A and B, $I \approx 10^{-3}$ to 10^{-4} eV, $d \approx (10^{-4}$ to $10^{-5})d_0$, and the absorption frequency may drop to the microwave range, in which the sensitivity of spectrometers is sufficient for observation of the absorption.

In biradicals without a center of inversion, the dipole moment $\mathbf{P}$ of the biradical depends on the spin state and changes with temperature according to the law

$$\mathbf{P} = \mathbf{P}_0 + \mathbf{d}\langle \mathbf{S}_1\mathbf{S}_2\rangle = \mathbf{P}_0 - \frac{\mathbf{d}}{1+3\exp(-I/T)}. \tag{19}$$

At low temperatures and magnetic field, the dipole moment changes suddenly by the amount $\mathbf{d}$ on increase of the field intensity above the value I/μ.

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