SOVIET PHYSICS JETP VOLUME 5, NUMBER 1 AUGUST, 1957

On the Shape of Resonance Paramagnetic Absorption Curves in Crystals

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(Submitted to JETP editor November 2, 1955)
J. Exptl. Theoret. Phys. (U.S.S.R.) 32, 82–86 (1957)

The 6th order moment of the resonance paramagnetic absorption curve in crystals at high frequency has been calculated. Comparison of the computed 4th and 6th order moments with the experimental values confirms the theory of exchange narrowing. The exchange interaction coefficients thus obtained are smaller than those which are obtained by comparing the Van Vleck and Opechowski formulas for magnetic specific heat and Curie temperature with static susceptibility measurements.

THE calculation of moments of the resonance absorption curve in crystals at high frequencies (spin relaxation) was first carried out by Van Vleck[1]. He determined the 2nd and 4th moments considering dipole and exchange interactions of magnetic ions. It turned out that, with the existence of solely a dipole interaction, the resonance absorption curve has approximately a Gaussian shape. The experimentally observed absorption curves, however, are considerably narrower.

Taking exchange forces into consideration does not change the 2nd moment and strongly raises the 4th order moment. This shows that the exchange interaction of magnetic ions must lead to a narrower resonance absorption curve than is obtained in its absence. Consequently, through the effect of the exchange interaction, one can explain the shape of the experimental absorption curves. In the present work, the question of the adequacy of the narrowing effect of exchange forces is examined. To this end, the 6th moment of the resonance absorption curve is calculated for large static fields.

1. 6th MOMENT

Let us direct a static magnetic field H along the z axis and a high frequency field of frequency ν along the x axis.

For purposes of convenience one calculates the moments not of the curve $\chi''(\nu)$ (χ'' is the imaginary part of the complex magnetic susceptibility), but of the curve

$$f(\nu) = 2kT\chi''(\nu)/\pi\nu,$$

where T is the absolute temperature. In the calculation of moments of the resonance absorption curve in large static fields in a region far from a state of saturation, $f(\nu)$ can be represented in the form (see Ref. 2):

$$f(\nu) = g^2\beta^2(2S+1)^{-N} \times \sum_{n,m} |S_{xnm}|^2 \delta(|\nu_{nm}| - \nu). \qquad (1)$$

Here, n and m are indices of eigenvalues of the operator

$$\mathcal{H}' = g\beta H \sum_j S_{zj} + \sum_{j>k} B_{jk}S_{zj}S_{zk} + \sum_{j>k} (A_{jk} - {}^1/_3 B_{jk})(\mathbf{S}_j\mathbf{S}_k),$$

S_{xnm} is a matrix element of the projection of the spin of the system on the x axis, g is the Landé factor, β is the Bohr magneton, S is the spin quantum number of a magnetic particle, and

$$A_{jk} \text{ and } B_{jk} = -(3g^2\beta^2/2r^3_{jk})[3\cos^2(\widehat{Hr}_{jk}) - 1]$$

are the coefficients of the exchange and dipole interactions of the ions j and k, $\overline{\mathbf{S}}_j$ and $\overline{\mathbf{S}}_k$ their spins and r_{jk} the distance between them.

From Eq. (1) one obtains the expression

$$\nu_{2n} = \nu_{2n}/\nu_0 = (-1)^n \operatorname{Sp} U^2_{2n}/h^{2n} \operatorname{Sp} S^2_x \qquad (2)$$

$$U_{2n} = \mathcal{H}'U_{2n-2} - U_{2n-2}\mathcal{H}' \quad (U_2 = \mathcal{H}'S_n - S_x\mathcal{H}')$$

for the normalized moment of order $2n$ of the resonance absorption curve . In this way the normalized 6th order moment is determined by the formula

$$\overline{\nu}_6 = -\operatorname{Sp} U^2_6/h^6 \operatorname{Sp} S^2_x. \qquad (3)$$

In view of the unwieldiness we cannot completely work out the expression Sp U^2_6 within the confines of the present appper. Briefly, the 6th order moment can be written in the form

$$\nu_6 = \nu_z^6 + 15\nu_z^4\Delta\nu_2 + 15\nu_2^2\Delta\nu_4 + \Delta\nu_6,$$

where $\bar{\Delta}\nu_2$, $\bar{\Delta}\nu_4$ and $\bar{\Delta}\nu_6$ are the normalized moments of second, fourth and sixth orders relative to the Larmor frequency $\nu_z = g\beta H/h$. The numerical value of the 6th order moment relative to the Larmor frequency was determined for a crystal in which the magnetic ions form a simple cubic lattice, with the direction of the magnetic field H along a principal crystal axis.

The calculation for an arbitrary direction of the field H relative to the crystal axis and also for other crystal lattice types becomes highly complicated. For this reason the value of $\bar{\Delta}\nu_6$ averaged over direction of the field H, applicable for absorption curves in powders, was not calculated.

The exchange interaction, owing to the rapid decrease of exchange forces with distance, was considered only for neighboring particles. After rather laborious calculations, the numerical value of the 6th order moment was obtained equal to

$$\begin{aligned}\Delta\nu_6 = h^{-6}[&\varepsilon^2A^4(520\lambda^3 - 230\lambda^2 - 14\lambda)\\ &+ \varepsilon^3A^3(-31\lambda^3 + 18\lambda^2 - \lambda)\\ &+ \varepsilon^4A^2(1080\lambda^3 - 312\lambda^2 + 4\lambda)\\ &+ \varepsilon^5A(57\lambda^3 - 21\lambda^2 + 2\lambda)\\ &+ \varepsilon^6(665\lambda^3 - 181\lambda^2 + 2\lambda)],\end{aligned} \tag{4}$$

where $\epsilon = -3g^2\beta^2/2d^6$, d is the lattice constant, A is the exchange coefficient for neighboring particles and $\lambda = S(S+1)$.

2. COMPARISON WITH EXPERIMENT AND DISCUSSION OF RESULTS

For the demonstration of the adequacy of the exchange narrowing let us determine the exchange coefficients from a comparison of the calculated 4th and 6th order moments with experimental values. Insofar as the numerical value of the 4th moment determined by Van Vleck is approximate, its value was calculated under the same assumptions as used for the 6th order moment. The 4th and 2nd moments come out equal to:

$$\begin{aligned}\overline{\Delta\nu_4} = h^{-4}[&\varepsilon^2A^2(24.22\lambda^2 - 3.6\lambda)\\ &+ 3h^4(\overline{\Delta\nu_2})^2(0.74 - 0.021\lambda^{-1})],\end{aligned} \tag{5}$$

$$\overline{\Delta\nu_2} = 4.44\lambda\varepsilon^2h^{-2}.$$

It is more convenient to compare the ratios

$$X = \overline{\Delta\nu_4}/(\overline{\Delta\nu_2})^3$$

and

$$Y = \overline{\Delta\nu_6}/(\overline{\Delta\nu_2})^2.$$

rather than the moments. In our case, these ratios are equal to:

$$\begin{aligned}X = &(A/\varepsilon)^2(1{,}228 - 0{,}183\lambda^{-1})\\ &+ 2{,}22 - 0{,}6\lambda^{-1},\\ Y = &(A/\varepsilon)^4(5.94 - 2{,}63\lambda^{-1} + 0.16\lambda^{-2})\\ &+(A/\varepsilon)^2(12.34 - 3.65\lambda^{-1} + 0.05\lambda^{-2})\\ &+ 7.60 - 2{,}07^{-1} + 0.02\lambda^{-2}\end{aligned} \tag{6}$$

if the odd powers of A/ϵ with small coefficients are thrown away.

Most often we have to deal with experimental absorption curves in substances for which the spin of the particles $S = 1/2, 3/2, 5/2$. We give the ratios X and Y for these values of S:

$$\begin{aligned}&S = {}^1/_2:\\ &X = (A/\varepsilon)^2 + 2{,}13;\\ &Y = 2{,}72(A/\varepsilon)^4 + 7{,}67(A/\varepsilon)^2 + 4{,}88,\\ &S = {}^3/_2:\\ &X = 1{,}18(A/\varepsilon)^2 + 2{,}21;\ Y = 5{,}25(A/\varepsilon)^4\\ &\qquad + 11{,}39(A/\varepsilon)^2 + 7.05,\\ &S = {}^5/_2:\\ &X = 1{,}21(A/\varepsilon)^2 + 2{,}21;\ Y = 5.66(A/\varepsilon)^4\\ &\qquad + 11.94(A/\varepsilon)^2 + 7{,}36.\end{aligned} \tag{7}$$

It should be kept in mind that experiment gives the curves $\chi''(H)$, measured with a contant frequency ν of the high frequency field by means of the variation of the static intensity H. However, if one takes into account the smallness of the zero absorption at high frequencies, the weak thermal dependence $\chi''(T)$, and the invariance of the structure of the bands of the energy spectrum of the spin system in a large static field H under its variation, one can regard that $\chi''(H)$ (especially its side to the right of the peak) is a good approximation of the course of the curve $f(\nu)$. The ratios X and Y were determined from the experimental absorption curves for the various substances.

TABLE

Substance	S	$(A/\varepsilon)_4$	$(A/\varepsilon)_6$	ΔA, %
$Cu(NH_3)_4SO_4 \cdot H_2O$	$^1/_2$	1.490	1.481	0,6
$Cu(NH_3)_4SO_4 \cdot H_2O$	$^1/_2$	2,486	2.218	10,8
$CuCl_2 \cdot 2H_2O$	$^1/_2$	1,166	1.103	5,4
$CuBr_2$	$^1/_2$	0.900	0.935	4,4
CuF_2	$^1/_2$	0.990	0.980	1
$CuCl_2 \cdot 2(NH_4Cl) \cdot 2H_2O$	$^1/_2$	2,445	2,280	6.8
$Cu(C_5H_7O_2)_2$	$^1/_2$	1,300	1.265	2,7
$Cu(CHO_2)_2 \cdot 4H_2O$	$^1/_2$	1.386	1.301	6.1
$VOCl_2$	$^1/_2$	1.221	1.155	5,4
$VO_3(C_6H_4)_3N_2(CH)_2$	$^1/_2$	1,506	1.422	5.6
$VOSO_4$	$^1/_2$	1.900	1.830	3.7
$CrCl_3$	$^3/_2$	1.236	0.981	20.6
$CrCl_3$	$^3/_2$	1.603	1.276	20,4
$CrK(SO_4)_2 \cdot 12H_2O$	$^3/_2$	1.488	1.349	9,4
$CrK(SO_4)_2 \cdot 12H_2O$	$^3/_2$	1.438	1.283	10.8
$CrK(SO_4)_2 \cdot 12H_2O$	$^3/_2$	1.363	1.142	16.7
$Cr(C_7H_5O_3) \cdot H_2O$	$^3/_2$	0.911	0,731	19.8
$Cr(NH_3)_6Cl_3 \cdot H_2O$	$^3/_2$	1.062	0,890	16.2
$CH_2(NH_3)_2 \cdot Cr[N(CS)(CO)SCN_2]$	$^3/_2$	0.503	0,336	33.5
$MnCO_3$	$^5/_2$	1.030	0.816	14
$MnCO_3$	$^5/_2$	1.290	1.11	20.2
$MnSO_4$	$^5/_2$	1.61	1.36	15.5
$MnSO_4 \cdot 4H_2O$	$^5/_2$	1.648	1.431	13.2
$MnSO_4 \cdot 4H_2O$	$^5/_2$	1.739	1.468	15.6
$MnSO_4 \cdot 4H_2O$	$^5/_2$	1.009	0.813	19.6
$(FeF_3)_2 \cdot 9H_2O$	$^5/_2$	1.613	1.290	20
$Fe(C_5H_7O_2)_3$	$^5/_2$	1.126	0.910	19.2

The exchange coefficients $(A/\epsilon)_4$ and $(A/\epsilon)_6$ were determined from the comparison of their calculated and experimental values. The results are given in the Table. The values of the ratio $(A_4 - A_6)/A_4$ are also given (in percent). The scatter of the values of A/ϵ, determined from various measurements for one and the same substance, on the average can be put within ± 15%.

It follows from the tabulated data that for substances whose atoms have spin $S = 1/2$, the percent deviation of the exchange coefficient A_6 from A_4 does not exceed experimental error, and in the majority of cases is considerably less. Thus, a rather satisfactory agreement of the magnitudes of the exchange coefficients A_4 and A_6 is observed between themselves. For other substances ($S > 1/2$), the difference between these quantities is more substantial and for the most part goes beyond the limits of experimental error. This was to be expected as a consequence of neglecting the effect of the crystalline electric field on the shape of the curve. Thus, the facts show that, within the limits of admissible experimental accuracy, the exchange interaction of the magnetic ions of a crystal explains the observed narrowing of the curves of paramagnetic resonance absorption quite satisfactorily .

Such results attract attention: For substances with a considerable density of magnetic ions, the exchange coefficients A/ϵ are smaller than for substances with a small density of magnetic ions. This can imply that substances with small magnetic density have such crystal structure in which two or more closely spaced magnetic ions are contained per unit cell; however, the same result could arise from another source. Actually in substances with a large magnetic density, the absorption curve is disposed to the edges to a greater extent than in substances with a small density of magnetic ions. Experiment does not permit measurement of the limits of the curves to a sufficient degree, since the curve breaks off early. Therefore, a reduction of the magnitudes of the exchange coefficients can occur, but for the first substances it is strong, and for the second, weak.

The obtained exchange coefficients for paramagnetic substances are not large. They are significantly less than the exchange coefficients determined by Wright[3] from a comparison of the experimental values of the magnetic specific heat and of the Curie temperature Θ with VanVleck's and Opechowski's formulas for them. To what extent should one expect a reduction of the size of the exchange coefficient from a comparison of the moments?. One can point out at least three sources as a reserve for a possible increase of the exchange coefficient: 1) Consideration, in the calculation of the moments, of the correct crystal structure of the substance, 2) Averaging of the moments over the direction of the static magnetic field (for powders) and 3) Use of the exact form of the experimental absorption curve.

Taking account of the actual crystal structure of a substance cannot lead to an essential change of the moments, since the sums which enter in them depend chiefly on the interaction of neighboring magnetic ions.

The use of the averaged 2nd and 4th order moments:

$$\Delta\nu_{2\,\mathrm{av}} = {}^{3}/_{5}\, h^{-2} g^{4} \beta^{4} \lambda \Sigma\, r_{jk}^{-6},$$

$$\overline{\Delta\nu}_{4\,\mathrm{av}} = h^{-4}\,[\varepsilon^{2} A^{2}\,(110.1\lambda^{2}/9 - 4.32\lambda/3)$$

$$+ 3h^{4}\,(\overline{\Delta\nu}_{2\,\mathrm{av}})^{2}\,(0.835 - 0.019\lambda^{-1})]$$

for the determination of the exchange coefficient (4th order moment determined by the authors of the present paper) gives values of the exchange coefficients smaller by 30–40% than those quoted above.

To obtain Wright's exchange coefficients through the consideration of the exact shape of the experimental absorption curve is also difficult. For this, (no longer speaking about the ratio Y), the ratio X determined from the exact shape of the absorption curve must exceed the available experimental values by hundreds of times, which is difficult to expect.

Thus, the exchange coefficients are not large. With such values of the exchange coefficients, the formulas of Van Vleck[4] and Opechowski[5] for the magnetic specific heat and Θ are unable to explain the experimental values of these quantities.

In conclusion, I express my appreciation to S. A. Al'tshuler for his valuable suggestions.

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Translated by R. L. Eisner
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