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ABSTRACT

A satellite line shifted in the direction of lower internal fields as compared with the main line has been observed in the NMR spectrum of ^{63}Cu in Cu-Mn alloys diluted to 0.5 or 2.5 at% Mn. The shift of the satellite is independent of the Mn concentration but varies with the applied field and the temperature as H_o/T. This indicates that the satellite is due to the spin density perturbation around the localized magnetic moment. The experimental data suggest that the satellite originates most probably from the ^{63}Cu nuclei on the first coordination shell of the Mn atoms. The NMR spectrum of the same nuclei shows no second order quadrupole effect appreciable within the experimental error.

РЕЗЮМЕ

В спектре ЯМР ^{63}Cu в разбавленных сплавах Cu-Mn, содержащих 0,5 и 2,5 ат%Mn , кроме основной линии наблюдалась побочная линия, сдвинутая в сторону более слабого внутреннего поля. Сдвиг побочной линии независит от концентрации Mn. Зависимость сдвига от магнитного поля и температуры имеет вид, подобной зависимости H_o/T. Из этого следует, что побочная линия является следствием возмущения спиновой плотности вокруг локализованного магнитного момента. На основе полученных результатов можно предположить, что побочная линия вызвана ядрами ^{63}Cu, находящимися в первой координационной сфере ядра Mn. Квадрупольный эффект второго рода в спектре ЯМР этих же ядер, в пределах погрешности измерения не наблюдается.

KIVONAT

A 0,5 és 2,5 at% Mn-t tartalmazó Cu-Mn hig ötvözetek ^{63}Cu NMR spektrumában a fő vonal mellett egy, a kisebb belső tér irányában eltolt szatellitet figyeltünk meg. A szatellit eltolódása független a Mn koncentrációtól, mágneses tértől és hőmérséklettől való függése H_o/T alaku. Tehát a szatellit a lokalizált mágneses momentum körüli spinsürüség-perturbáció következménye. Az eredmények alapján nagyon valószinü, hogy a szatellit a Mn atom körüli első koordinációs héjon lévő ^{63}Cu magoktól származik. Ugyanezen magok NMR spektrumában másodrendü kvadrupól effektus - a hibahatáron belül - nem figyelhető meg.

INTRODUCTION

The behaviour and anomalies observed in non-transition metal based alloys with 3d transition metal impurities have been studied and interpreted in numerous reports /see e.g. review papers [1, 2, 3]/. Nevertheless, there are still open problems. Experimentally, new information is expected from the investigation of the microscopic /local/ properties in addition to the study of the transport, thermal and magnetic data. Localized behaviour can be most conveniently observed by NMR spectroscopy.

The asymptotical and preasymptotical behaviour of spin and charge density perturbations in the environment of impurity atoms have been extensively studied both theoretically and experimentally /[1-3] and also [4] [5]/. Lately, an important progress was achieved by the measurement of the local field gradient /charge density/ at a given distance from the impurity atom [6]. Few reports are available on the measurement of the local magnetic /spin density perturbation/ in the environment of impurity atoms. Alloul et al. [7] report such measurement on Al-Mn dilute alloys. For Cu-based alloys only the results of Lang et al. [8] obtained on Cu-Co dilute alloys are known. This group determined the local magnetic field at the sites of the first three neighbours of the Co impurity and measured the vibrations of the local field with the applied field and the temperature in the range of low temperatures, i.e. in the "non-magnetic" state.

In this paper the results of local magnetic field measurements on Cu-Mn dilute alloys are reported. A satellite line with a concentration independent shift as compared with the main line was observed in the ^{63}Cu NMR spectrum measured on the alloys with 0,5 or 2,5 at%. Mn content. The measurements were made with a conventional c.w. NMR spectrometer [9]. The variations of the satellite shift with the applied magnetic field and the temperature unequivocally indicate that the satellite is due to the spin density perturbation caused by the localized magnetic moment. The measurements were performed at temperatures associated with "magnetic" state. As far as we know, no local field measurement in the "magnetic" state has been reported as yet.

RESULTS AND EVALUATION

The measurements were performed at temperatures from 100^{o} to $400^{o}K$ using magnetic fields from 3 to 9 kOe and the equipment described in an earlier paper [9].

The samples were prepared by vacuum melting from 99,999 at% Cu and 99,9 at% Mn. The Mn concentration of the samples was 0.5 ± 0.02 and 2.5 ± 0.03 at%. Sandwich-type samples consisting of 15μ thick foils prepared by cold-rolling [10] were used in the measurements which were carried out both after cold--rolling and after annealing at 10^{-5} mmHg vacuum pressure and $400^{o}C$ for 1 hour. The amplitude and integral intensity of the NMR spectrum showed no appreciable change within the experimental error in the two types of measurement, while the separation of the satellite from the main line appears more clearly in the spectra taken after cold-rolling. For this reason the spectra measured on the cold-rolled foils are reproduced here.

Fig. 1 shows the ^{63}Cu NMR spectra measured at 6 MHz frequency and at room temperature. The amplitude and integral intensity of the NMR spectrum of the sample with 0.5 at% Mn, as normalized to these values in pure copper, were found to be 0.14 ± 0.01 and 0.39 ± 0.02, respectively. As marker signal the ^{27}Al NMR spectrum of Al foils was measured along with alloy specimen.

Assuming that the inhomogeneously broadened satellite has the same width as the main line, the shift of the satellite is easy to evaluate. Since the shift is the same in both types of alloys within experimental error, it must be independent of the Mn concentration. Fig. 2 shows the magnetic field /i.e. frequency/ dependence of the shift and the high external field peak of the satellite along with that of the main line width as measured from peak--to-peak which is proportional to the average hyperfine broadening. Fig. 3 shows the temperature curves for the satellite shift and for the peak-to-peak distance of the main line. Numerically, these data give for the shift of the satellite, as normalized to the Knight shift of pure copper at room temperature,

$$\frac{K_1}{K_{Knight}} = -2.1 \pm 0.1$$

and for the variation of the shift with temperature

$$\frac{K_1(100^{o}K) - K_1(300^{o}K)}{K_1\ 300^{o}K} = 2.0 \pm 0.15$$

The shape and the characteristic features of the satellite can be determined from the decomposition of the NMR spectrum. The thus obtainable shift of the satellite is less accurate than that evaluated with our earlier assumption of equal width for satellite and main lines. On the other hand the amplitude of the satellite can be determined, and the integral intensity of that one can be estimated in this way. In the NMR spectrum of the Cu - 0.5 at% Mn alloy the integral intensity of the satellite is 6 $\pm$ 2 % that of the total spectrum and the amplitude measured at the satellite peak is also 6 $\pm$ 1 % that of the main line normalized to the same side if the spectrum of the alloy taken as reference for both values.

CONCLUSIONS

Following inferences can be made from the experimental data.

The ^{63}Cu NMR spectra of alloys with 0.5 at% Mn are contributed only by the central component /+1/2 $\leftrightarrow$ -1/2 transition/ and quadrupole satellites /[3/2] $\leftrightarrow$ [1/2] transitions/ do not contribute to this spectrum because of first order quadrupole perturbation [11]. The spectrum of the 0.5 at% Mn sample shows the total contribution from the central component /40 % integral intensity/.

It follows from the measured amplitude and integral intensity of the satellite that it is contributed by atomic nuclei on a coordination shell with coordination number 12. This number holds for near neighbours on the first and fourth coordination shells. The integral intensity normalized in the same way would 3 % for the second, 12 % for both the third and the fifth neighbours. Now, if the absolute value of the local magnetic field is higher at the first three than at the fourth neighbour sites, the satellite must be a contribution from the first neighbours of the Mn impurity. This assumption was confirmed by the measured integral intensity of 0.39 $\pm$ 0.02 which would have been 0.32 /i.e. reduced by 21 %/ without the contribution from the first three neighbours. This inference is qualitatively supported also by the dipole-dipole interaction generated asymmetry of the satellite spectrum. This asymmetry could be only approximately evaluated because of the low signal-to--noise ratio.

The temperature and applied field dependence of the shift of the satellite line definitely shows that it is a contribution from local magnetic perturbation. The shift occurs in the direction of lower internal fields /that is why it appears at the same frequency at higher applied field/, thus the shift is negative.

No second order quadrupole effect can be observed in the satellite spectrum, the high external field peak position and the shift of the satellite show the same applied field dependence /Fig. 2 and [7]/.

The average hyperfine field /main line width/ shows the same temperature dependence as that of the local field measurable at first neighbour sites. This fact differs from the observation made by Lamb et al. on Cu-Co of "non-magnetic" state.

The temperature and applied field dependence of the field measured at first neighbours can be described by a Curie-Weiss formula.

An attempt was made at the quantitative determination of the measured field by use of the RKKY formula /see e.g. [3]/. For the physical quantities involved the values taken from the following references were used: A_{jk} [12] and [13], the constant J [14] and the phase shift δ_2 in the spin density oscillation [11]. The measured local field gives the best fit with the value calculated for the field at third neighbours which, however, is excluded by measured integral intensity. The RKKY formula does not describe the local field at first neighbour sites.

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FIGURE CAPTIONS

Fig. 1 Recorded NMR spectra of ^{63}Cu in Cu-Mn dilute alloys of 0.5 at% /———/ and 2.5 at% /----/ Mn content.

Fig. 2 Peak-to-peak distance of the main line, the satellite shift, and the high external field peak shift of the satellite in the ^{63}Cu NMR spectrum of Cu - 0.5 at% Mn dilute alloys vs. magnetic field.

Fig. 3 Inverse peak-to-peak distance and inverse satellite shift of ^{63}Cu NMR spectrum vs. temperature in Cu - 0.5 at% Mn dilute alloys.

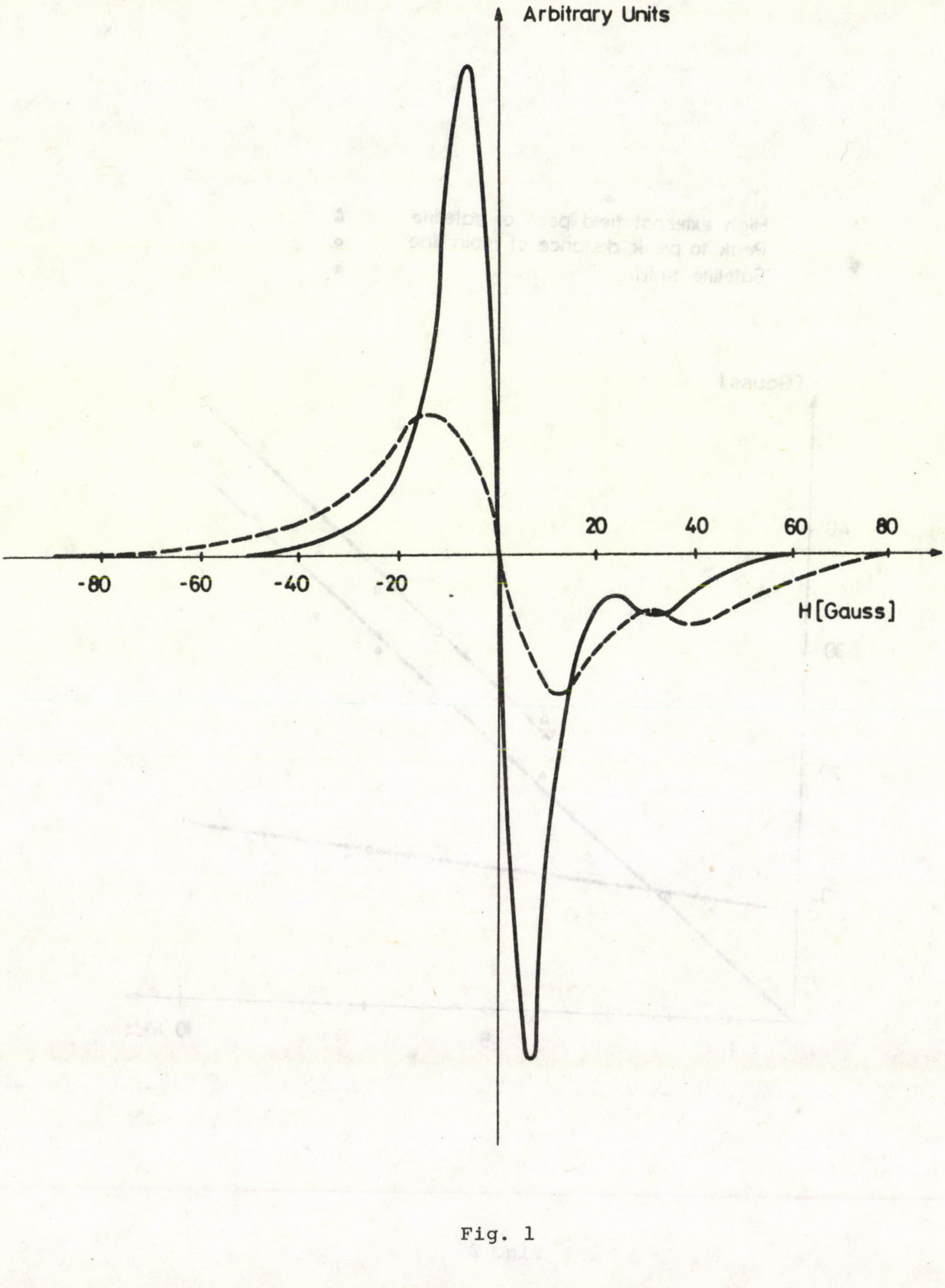

Fig. 1

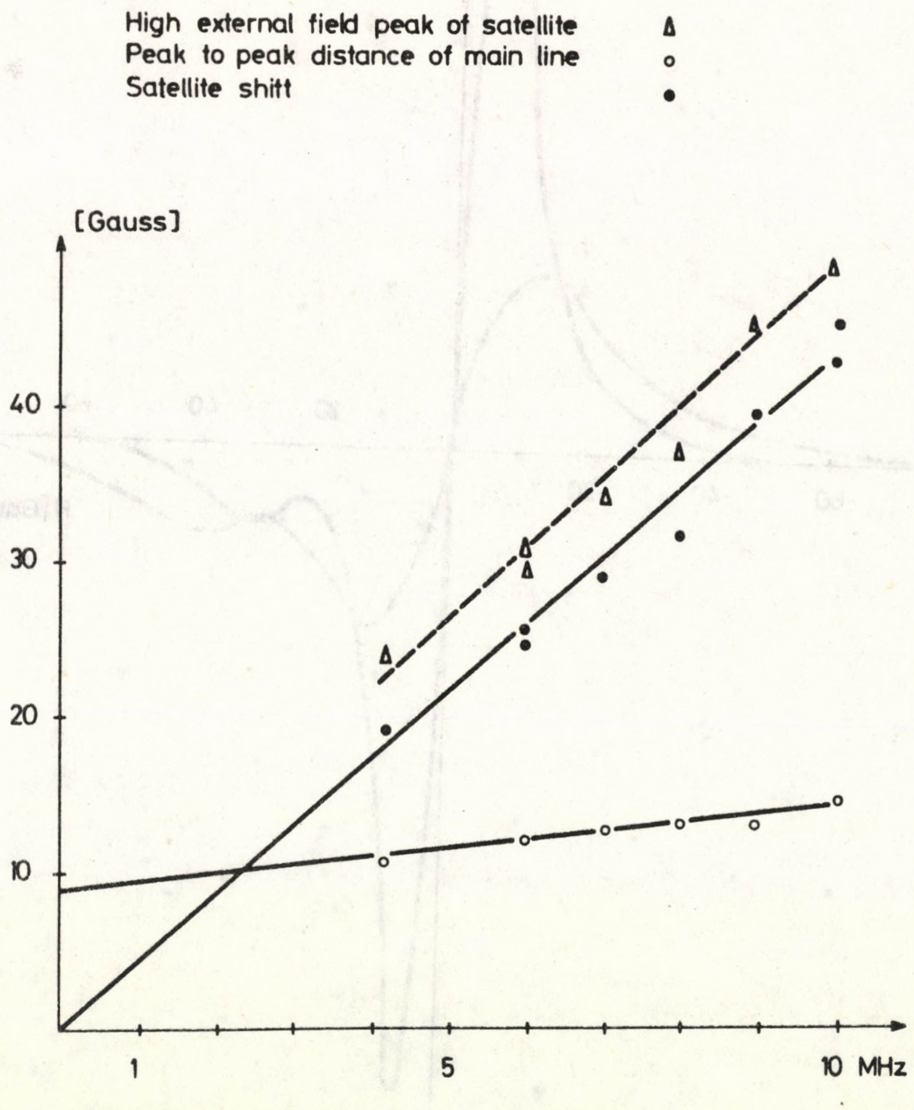
High external field peak of satellite Δ
Peak to peak distance of main line ○
Satellite shift ●
[Gauss]
40
30
20
10
1
5
10 MHz

Fig. 2

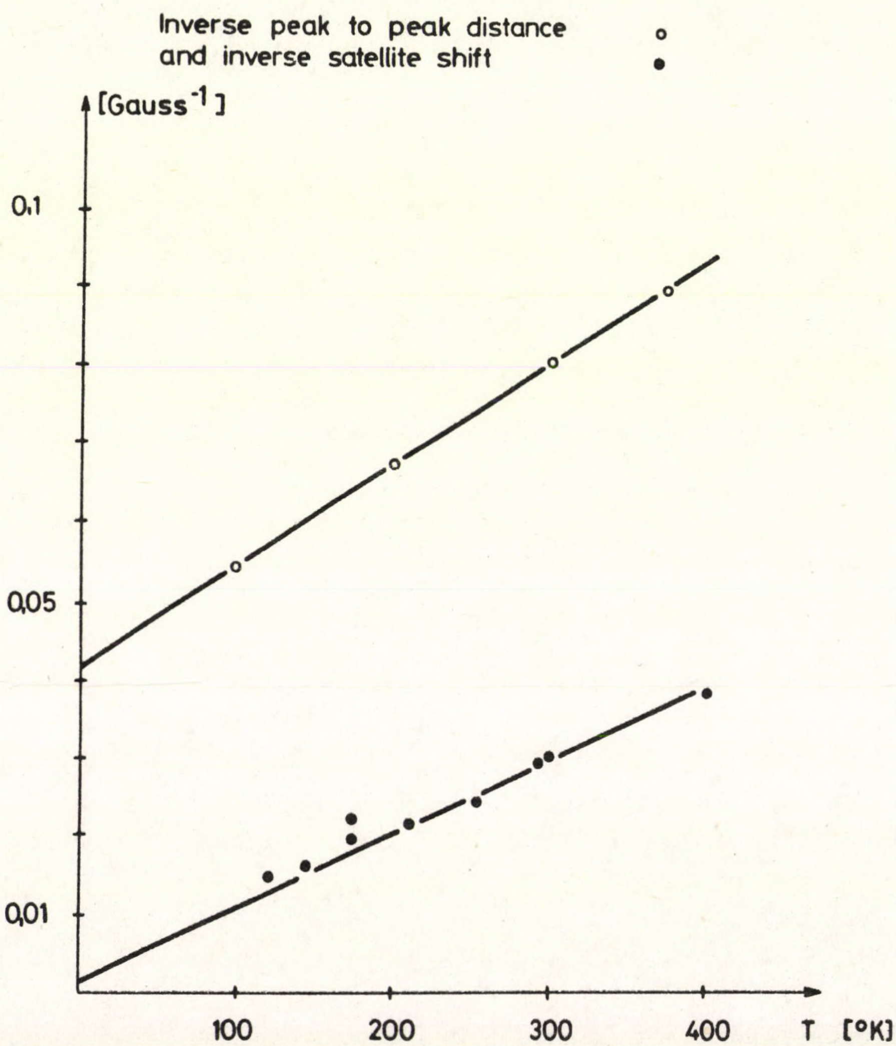
Inverse peak to peak distance
and inverse satellite shift
[Gauss^{-1}]
0,1
0,05
0,01
100
200
300
400
T [°K]

Fig. 3

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Nyelvi lektor: M.Kovács Jenőné
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