Observation of the Electron Spin Relaxation in Antiferromagnets above the Néel Point by Mössbauer Spectroscopy

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An investigation was made of the electron spin relaxation in several antiferromagnets (high-spin divalent iron compounds) at temperatures well above the Néel point. The broadening of the γ-resonance line indicated that the relaxation frequencies of these compounds did not exceed 10^{11}–10^{12} sec^{-1} in the temperature range 70–600°K and that these frequencies depended weakly on the temperature. It was also found that the relaxation frequency was strongly affected by the structure of the substance.

WHEN the temperature is raised, magnetically ordered materials lose their spontaneous magnetization above the Curie or the Néel point and become paramagnetic. The transitions to the paramagnetic state have been investigated quite thoroughly by various methods including the γ-resonance (Mössbauer) spectroscopy. The magnetic hyperfine structure in the γ-resonance spectra disappears because of a sharp increase in the electron spin relaxation frequency and because of averaging of the effective magnetic field to the zero value. Nevertheless, the results of our experiments show that under some conditions the electron spin relaxation can be investigated by the γ-resonance spectroscopy at temperatures exceeding T_C or T_N.

The present paper describes an experimental study of the influence of the spin relaxation on the γ-resonance spectra of several high-spin iron compounds. We found that the temperature dependence of the relaxation time was very weak. We studied high-spin antiferromagnetic compounds with approximately equal Néel points ($\sim 20°K$)[1] in order to equalize the exchange interactions and to reveal the influence of the magnetic anisotropy.

The relatively low value of T_N was one of the conditions for the observation of the spin relaxation above T_N because the magnetic relaxation effects in substances with high values of T_N should disappear rapidly with increasing temperature because of thermal fluctuations.

The other condition for the observation of spin relaxation was the presence of a strong magnetic anisotropy. The strongest magnetic anisotropy was known to be exhibited by substances with a uniaxial symmetry of the crystal lattice. We investigated $FeSO_4 \cdot 7H_2O$, $FeC_2O_4 \cdot 2H_2O$, $FeCl_2 \cdot 4H_2O$, $Fe_3(PO_4)_2 \cdot 8H_2O$, and $FeCO_3$ and only one of these (siderite $FeCO_3$) had a rhombohedral axially symmetrical lattice. It was known that siderite has a high value of the magnetic anisotropy energy and is a "metamagnet."[1] The structures of $FeCl_2 \cdot 4H_2O$, $FeSO_4 \cdot 7H_2O$, and $Fe_3(PO_4)_2 \cdot 8H_2O$ were not axially symmetrical: their lattices were monoclinic. The structure of $FeC_2O_4 \cdot 2H_2O$ was not known. The experiments were carried out using a γ-resonance spectrometer with a Co^{57} source embedded in Cr. The electron spin relaxa-

tion was deduced from the broadening of the quadrupole lines which was observed when the temperature was lowered. The accuracy in measuring the line widths was improved by carrying out the experiments at low relative velocities of the source and the absorber, so that the width of only one of the two lines could be studied in doublet spectra near zero relative velocity of the source and the absorber. The accuracy of measurements of the line width under these conditions amounted to 2%. The line width of $FeCO_3$ was investigated in the temperature range 90–600°K (Fig. 1). The widths of the lines of all the hydrated crystals were determined at T = 90–300°K because heating above room temperature resulted in thermal decomposition of these crystals. Our data on the broadening of the lines of $FeSO_4 \cdot 7H_2O$ and $FeC_2O_4 \cdot 2H_2O$ were in agreement with the results reported in [2]. In the case of $FeCl_2 \cdot 4H_2O$ the change in the line width with temperature was of opposite sign to that reported in [2]. In the case of vivianite $Fe_3(PO_4)_2 \cdot 8H_2O$ we obtained Γ = 0.470 ±0.01 mm/sec at T = 300°K and Γ = 0.520 ± 0.01 mm/sec at T = 90°K. However, vivianite was characterized by two crystallographically inequivalent positions of iron and by two systems of quadrupole spectra. Therefore, at zero relative velocity of the source and the absorber the spectra consisted effectively of paired left-handed lines of two doublets. When the temperature was lowered from 300 to 90°K the line broadening amounted to 4% for $FeSO_4 \cdot 8H_2O$, 5% for $Fe_2C_2O_4 \cdot 2H_2O$, 10% for $Fe_3(PO_4)_2 \cdot 8H_2O$, and 12% for $FeCO_3$.

Our experiments demonstrated that the line of $FeCl_2 \cdot 4H_2O$ became narrower by 8% whereas Kerler and Neuwirth[2] found that the line broadened by 10%. Evidently this was due to different "stoichiometric" compositions of the samples in the two cases, which could
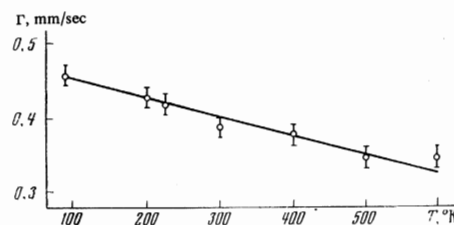
Temperature dependence of the width of the left-hand line in the γ-resonance spectrum of $FeCO_3$.

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[1] The Néel temperatures were $T_N = 24°K$ for $FeCl_2 \cdot 4H_2O$, $T_N = 23°K$ for $FeC_2O_4 \cdot 2H_2O$, $T_N = 35°K$ for $FeCo_3$, $T_N = 21°K$ for $FeSo_4 \cdot 7H_2O$, and $T_N = 9°K$ for $Fe_3(PO_4)_2 \cdot 8H_2O$.

be due to—for example—different degrees of hydration of hygroscopic $FeCl_2$.

Let us now consider in greater detail the causes of line broadening with decreasing temperature. There are three factors which may alter the line width when the temperature is varied:

1) the increase in the probability of the Mössbauer effect (f') with decreasing temperature, which leads to line broadening; [3]

2) the reduction in the scatter of the values of the crystal field gradient with decreasing temperature because of decrease in the amplitudes of atomic vibrations, which results in line narrowing; [4]

3) the increase in the relaxation time of spins with decreasing temperature, which should result in line broadening.

An estimate of the line broadening caused by the first mechanism (for variation of f' from 0.6 to 0.45 for all compounds) gives 6%. On the other hand, calculations [4] show that the line narrowing due to the second mechanism is on the average 5%, i.e., the first two effects almost completely balance each other out. Consequently, the observed line broadening represents the relaxation broadening effect which depends on the structure of the substance in question. The strongest broadening is observed for siderite which has the strongest magnetic anisotropy; the other substances exhibit weaker broadening. The relaxation of electron spins in $FeCO_3$ was also investigated by Dézsi et al. [5] and by Walker et al. [6] on the basis of the ratio of intensities of two lines in the quadrupole spectrum. An asymmetry of the quadrupole spectrum was observed at temperatures up to 35°K in [5] and up to 300°K in [6]. The asymmetry was attributed to the relaxation mechanism, in agreement with our results.

Two conclusions can be drawn from our investigation:

1) the relaxation frequency of electron spins in the investigated magnetically ordered substances is 10^{11}–10^{12} sec^{-1} above the Néel point and, in accordance with theoretical calculations, [7] it depends weakly on the temperature;

2) the relaxation frequency of spins above T_N depends on the structure of the substance in question: the substances possessing axial anisotropy have a lower relaxation frequency.

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