NMR AND THE ANTIFERROMAGNETIC CRYSTAL PHASE REGIONS IN RAPIDLY QUENCHED RIBBONS AND IN ALLOYS OF THE TYPE $Cu - Mn - Al$.

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$NMR AND AFM REGIONS IN RAPIDLY QUENCHED RIBBONS AND ALLOYS Cu - Mn - Al$.  

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Abstract

It was shown that anomalous resistivity behavior of the $\text{Cu} - \text{Mn} - \text{Al}$ ribbons is explained by the s-d interaction between conduction electrons and the clustered Mn atoms. While nuclear magnetic resonance measurements show the antiferromagnetic and ferromagnetic clusters of Mn atom coexisting without long-range order, it is an interesting problem to study magnetic resonance properties also for the antiferromagnetic crystal phase regions (which have long-range order for larger regions) and which may also occur in these ribbons. The Heusler Type $\text{Cu} - \text{Mn} - \text{Al}$ Alloy has a composition half way between $\text{Cu}_2\text{MnAl}$ and $\text{Cu}_3\text{Al}$. Electron microscopy of the premartensitic $\beta\text{Cu} - \text{Zn} - \text{Al}$ alloy has shown that the $\beta\text{Cu} - \text{Zn} - \text{Al}$ alloy quenched from high temperature has the electron diffraction patterns of this alloy well explained by the model with the existence of small particles with an orthorhombic structure. It was noted that an important aspect of improvement in the material properties is to create a nanostructured state in matrix, which has significant advantages in magnetic and mechanical characteristics in contrast to the bulk materials in crystalline or amorphous state. It is an interesting problem to study magnetic resonance properties not only for the Mn atoms and clusters without long-range order but also for the antiferromagnetic crystal phase regions (which have long-range order for larger regions) which may also occur in ribbons. This is the aim of our paper.
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1 INTRODUCTION.

Metallic glasses are a class of metallic materials that do not display long-range atomic order. Their amorphous character and the lack of dislocations, these materials exhibit mechanical properties that are quite different from those of other solid materials. They have also interesting physical and chemical properties. Some metallic glasses exhibit superior soft magnetic properties, good magnetocaloric effects, and outstanding catalytic performance, thus having potential for a widespread range of technological applications.

Metallic glasses when heated in the supercooled liquid region allow molding and shaping with microscale precision by means of thermoplastic processing. This has lead to the development of diverse products based on these alloys (sporting goods, medical and electronic devices and advanced aerospace applications). In spite of their large elasticity, metallic glasses exhibit poor room-temperature macroscopic plasticity compared to polycrystalline metals. This low plastic deformation, particularly evidenced when testing metallic glasses under tension, is related to the formation and rapid propagation of shear bands.

Therefore routes to enhance plasticity of metallic glasses include procedures to hinder shear band propagation. This can be achieved, by designing composite materials consisting of particles which act as second-phase reinforcements embedded in the amorphous matrix. Other approaches towards toughening of metallic glasses have also been developed, such as the preparation of the so-called dual-phase amorphous metals, some specific surface treatments (e.g., laser or shot pinning).

In his PhD. work V. Ocelik, supervised by one of the authors (O.H.), formation and rapid propagation of phase change from amorphous to crystalline was studied, and described were nonhomogeneous plastic deformation and defects in metallic glasses. These defects contribute to the macroscopic rapid propagation of shear bands. Ocelik (et al.), also in studied influence of laser treatment. Based on a recently published recursive model describing the geometry of laser clad coatings and on experimental track characteristics the authors propose specific functions to describe the geometry of laser clad coatings formed by overlap of individual tracks depending on the processing parameters. This work was extended in, where the failure of amorphous metallic materials under uniaxial tensile stress at temperatures much lower than the glass transition temperature was studied. It is known that it is preceded by an intense shear deformation localized into narrow bands. These bands lie near the planes of maximum shear stresses. Significant changes in the original structure, taking place during the process of a local shear deformation inside the bands, leads to a considerable decrease in the viscosity. Because of this, the sample will fail under the influence of tensile stress in one of these shear bands. The crack propagates alternatively in two equal-stress planes of maximum shear stresses, which are perpendicular to each other. In, where there were done statistical investigations of fracture demonstrations on Ni-Si-B metallic glass ribbons failed in tension at 4.2 to 300K, two alternative quantitative mathematical descriptions of the yield stress anisotropy in the plane of amorphous alloys ribbons are proposed in this paper, that are based on two models: model of the plane stress state and model of the oriented anisotropic polyatomic clusters. These descriptions give adequate approximations of the experimental angular depen-
dences of the yield stress for some amorphous alloys. This models were used
to explain phenomena in ribbons of the type Ni$_{80}$Si$_{10}$B$_{10}$ and Ni$_{80}$Si$_{5}$B$_{15}$ for
determination of temperature dependence of propagation of defects.

In [17] the metallic ribbons Fe$_{40}$Ni$_{40}$B$_{20}$ and Cu$_{47}$Ti$_{35}$Zr$_{11}$Ni$_{6}$Si$_{1}$ and
Zr$_{65}$Cu$_{17.5}$Ni$_{10}$Al$_{7.5}$ with different microhardness and glass forming ability
were studied at different loading rates from 0.05 to 100 mN/s. Authors describe
in details the differences in elemental discontinuities on the loading curves for
the studied alloys. They have found that the discontinuities began at a certain
local deformation independently on the macroscopic mechanical properties of a
ribbon.

A review how the presence of interstitially defects and the change in their
concentration can induce structural relaxation when metallic glasses are heat
treated to temperatures below or around the glass transition is in [18]. Struc-
tural relaxation is important, it can induce changes in many physical properties
of the glasses, particularly in the mechanical behavior (elasticity, anelasticity,
viscoelasticity, etc. [19]), but also in the electrical, corrosion and even magnetic
performances.

In [20] and [21] Al nuclear-quadrupole-resonance studies of CeAl$_2$ in the
temperature range between 0.09 and 4.2K were done. We started from [22] -
[26]. Below $T_N = 3.45K$ (the Nel temperature) CeAl$_2$ orders antiferromag-
etically. The spin-lattice relaxation rate $\frac{1}{T_1}$ shows a sharp peak at $T_N$, and the
NQR linewidth increases from 273kHz in the paramagnetic state to 27015kHz
at 2K. Below 1.5K, in the low-temperature regime of the magnetically ordered
state, the temperature dependence of the spin-lattice relaxation rate follows a
Korringa law with $\frac{1}{T_1} = 7.90.8 \frac{1}{Ksec}$. This relaxation rate is much larger than
those found in normal metals. Above 1.5 K deviations from the Korringa law
are observed. These deviations are consistent with a relaxation produced by
magnonlike excitations with an energy gap of 113K, in agreement with results
of previous neutron scattering and $T_1$ measurements. The NQR is here a method
which enables to study properties of antiferromagnetic phase and a transition
to it from the paramagnetic phase. The NMR method is usually used with mea-
suring other properties of the material. For example thermodynamics of CeAl$_2$
at low temperatures was studied measuring specific heat and spin-lattice relax-
ation rate [20]. Thermodynamic calculations show that a considerable fraction of
the observed low-temperature nuclear spin-lattice relaxation rate and spec-
ific heat of CeAl$_2$-both varying linearly with temperature-may be due to the
existence of new low-frequency features in the spin-excitation spectrum of in-
commensurate magnetic structures. In [27] we studied magnetic nanoparticles
with core shell structure. We formulated the macroscopic model and calcu-
lated the coercive field in these nanoparticles with nonhomogeneous structure.
They were mechantosynthesized and consisting of an ordered core surrounded
by the shell. The shell may be structurally and magnetically disordered, or it
may be ordered. These nanoparticles are found to be roughly spherical. We
formulate the macroscopic model for the description of magnetic properties of
nanoparticles with core-shell structure. The case of spheroids oriented in the
same direction of polar axes is considered. There exits two coercive fields. Thus
we see that for above mentioned nanoparticles it is not possible to use the NMR
theory as for crystalline particles, which are from the type of microparticles to
larger particles. We will use in our paper the description of these later particles
as those which may describe small crystals in ribbons and alloys.

Let us also note [28] that an induced magnetic anisotropy in amorphous ribbons may occur, we studied the case of negative magnetoelastic constant. The case of positive constant was studied elsewhere, see [28]. One of the most important mechanisms for the appearance of the induced magnetic anisotropy in amorphous ferromagnetic materials is due to internal stresses in the case of nonzero magnetoelastic coupling. It has been proposed that according to different ways of solidification in different regions, the amorphous ribbon may have four types of these solidification regions. The distribution of internal stresses may be specified for each of these regions. Then the orientations of the magnetization of the ribbon may be specified from the magnetoelastic energy. We have found that [29] for amorphous materials the spins are in disordered state also in nonzero magnetic field, besides some isolated spins. Local internal fields in vector spin glasses with random uniaxial local anisotropy are shown to be positive on all non-isolated spins whenever the spin state corresponds to any minimum of configurational energy within the classical theory. Moreover it is shown that there exists a lower positive bound on the values of the local internal fields. This bound depends on the exchange interaction constants and on the strength of the local anisotropy. Thus in amorphous ribbons with regions of crystalline phase the AFM state should be studied using theory of NMR for the AFM phase to distinguish it from the disordered regions of amorphous ribbons.

However as second-phase reinforcements embedded in the amorphous matrix may be present antiferromagnetic phase, which may be hard to detect by macroscopic magnetic measurements. Multicomponent bulk metallic glasses (BMG) have attracted great attention [30] because of their unusual physical, chemical and mechanical properties [31]. Mechanical relaxation of metallic glasses was overviewed (experimental data and theoretical models) in [32]. In the paper [33] the authors refer about anomalous electrical resistivity and nuclear magnetic resonance in rapidly quenched Cu-Mn-Al ribbons. In the Cu$_{32}$Mn$_{35}$Al$_{33}$ ribbon, it is found [33] by nuclear magnetic resonance measurements that the antiferromagnetic and ferromagnetic clusters of Mn atom coexist without long-range order. Authors show that anomalous resistivity behavior of the Cu – Mn – Al ribbons is explained by the s-d interaction between conduction electrons and the clustered Mn atoms. While [33] found by nuclear magnetic resonance measurements the antiferromagnetic and ferromagnetic clusters of Mn atom coexist without long-range order it is an interesting problem to study magnetic resonance properties not only for the Mn atoms and clusters without long-range order but also for the antiferromagnetic crystal phase regions (which have long-range order for larger regions) which may also occur in these ribbons. This is the aim of our paper.

2 RAPIDLY QUENCHED Cu-Mn-Al RIBBONS, AND ALLOYS.

In the paper [33] the authors refer about anomalous electrical resistivity and nuclear magnetic resonance in rapidly quenched Cu-Mn-Al ribbons. As they write the rapidly quenched Cu$_{67-x}$Mn$_{x}$Al$_{33}$ (at. percent) ribbons show high electrical resistivities and low temperature coefficients of resistivity. The resistivities de-
crease monotonically with increasing temperature for the ribbons of more than 30(at.percent) Mn concentration. In the \( \text{Cu}_{33}\text{Mn}_{35}\text{Al}_{33} \) ribbon, the author found by nuclear magnetic resonance measurements that the antiferromagnetic and ferromagnetic clusters of Mn atom coexist without long-range order. The anomalous resistivity behaviour of the Cu-Mn-Al ribbons is explained by the s-d interaction between conduction electrons and the clustered Mn atoms. Let us note that in [34] for the \( \text{Cu} - \text{Mn} - \text{Al} \) detailed electron metallographic studies were made of interfacial dislocations which are formed to relieve the elastic coherency strains developed upon long aging of spinodal alloys in the system. Interfacial dislocations in the Heusler type alloy \( \text{Cu} - \text{Mn} - \text{Al} \) which also appears to undergo spinodal decomposition [35], and in recent paper [36]. As authors [34] have found for the Heusler Type \( \text{Cu} - \text{Mn} - \text{Al} \) alloy the alloy studied has a composition half way between \( \text{Cu}_{2}\text{MnAl} \) and \( \text{Cu}_{3}\text{Al} \). Upon quench-aging possesses all the metallographic characteristics of a spinodal decomposition. The ternary constituent has the \( L2_1 \) structure and the binary constituent has the closely related \( D0_3 \). Their lattice parameters differ by 2 percent. The \( \text{Cu} - \text{Mn} - \text{Al} \) alloy develops interface dislocations lying in pure edge orientation in the 001 interface planes and with (100) Burgers vectors. In rapidly quenched Cu-Mn-Al ribbons with larger regions of antiferromagnetic or ferromagnetic phase the interface may exists with interfacial defects (Oceliks study of defects in amorphous ribbons). This is due to the fact that a restriction in the \( \text{Cu} - \text{Mn} - \text{Al} \) spinodal alloys is that both phases are ordered. In ribbons amorphous phase and ordered phase may exist. As noted by [37] and [38] - [40] in the market of new materials, the functional materials having unusual properties are in great demand, among which the ferromagnetic shape memory alloys are predominant. The control over such properties is exercised using force, thermal, and magnetic fields. As electron microscopy of the pre-martensitic \( \beta\text{Cu} - \text{Zn} - \text{Al} \) alloy has shown that [41] the \( \beta\text{Cu} - \text{Zn} - \text{Al} \) alloy quenched from high temperature studied by electron microscopy has the electron diffraction patterns of this alloy well explained by the model proposed by [42], i.e. by the existence of small particles with an orthorhombic structure, see also [39]. This structure is, however, closely related to the -structure. Thus it was noted in [37] an important aspect of improvement in the material properties is to create a nanostructured state, which has significant advantages in magnetic and mechanical characteristics in contrast to the bulk materials in crystalline or amorphous state. Magnetization and magnetic anisotropy in case of nanoparticles can be significantly greater than that of a bulk sample, and a difference between the Curie temperature \( T_c \) reaches hundreds of degrees [38] - [40].

To study clusters, and even possibility of existence of regions (nanocrystals) of crystal phase in amorphous ribbons or in a matrix specified by another phase, different measurements of magnetic properties of are used. Measurements of magnetostriction are described in [43]. A survey of different measuring methods suited for soft magnetic materials is given. The methods are subdivided into direct and indirect methods. The SAMR method (Small angle magnetization rotation) is best suited especially for low magnetostrictive ribbons. The author discusses using these methods on example selected results and an analysis of the temperature dependence of the magnetostriction as measured on amorphous \( \text{Fe}_{68-x}\text{Co}_x\text{B}_{15} \). Magnetic nanomaterials have a number of unusual properties, in particular, giant magnetoresistance, abnormally large magnetocaloric effect, and others [44]. \( \text{CuAlMn} \) alloys are one of the most interesting ferro-
magnetics with shape memory (SM). They demonstrate an unusual magnetic behavior in superparamagnetism [45] and giant magnetoresistance [46], and specific mechanical properties such as SM effect, thermoelasticity, superelasticity, and plasticity of transformation [47] and [48]. They exhibit a superelastic strain of about 7 percent, which is comparable to that of TiNi alloys [49] and [50]. To get optimal properties, these alloys undergo an additional thermal, mechanical, or magnetic treatment. Aging of CuAlMn alloys leads to the formation of a system of nanoscale particles of ferromagnetic Cu2MnAl phase in a paramagnetic Cu3Al matrix [45], and annealing in magnetic field increases the $T_c$ of CuAlMn alloys [51]. At the same time, the heat treatment allows to control number and size of particles in the alloy and also the martensitic transformation temperature and hysteresis, which depend on characteristics of precipitated particles [52] and [53]. The clarification of the possibility to control the magnetic and mechanical characteristics of CuAlMn alloys and amorphous ribbons (under annealing in zero- or non-zero magnetic field) is of interest.

3 NUCLEAR RESONANCE IN ANTIFERROMAGNETS - MOTIVATION.

Nuclear resonance as is described in the Jaccarino’s paper [54] has its criteria for its observing nuclear resonance in magnetic solids. They are connected with the nuclear hamiltonian. It is described in general for nonmagnetic solid and magnetic solid via study of internal fields.

In antiferromagnets we have to identify the spin lattice and its symmetry. We will describe macroscopic and microscopic properties by some remarks. It is important to find ground states, excitations, describe phase transitions which may occur. For nuclear relaxation the relaxation and its linewidth is important. Firstly we will describe the relaxation and its linewidth in paramagnetic phase, and then we will study local fields in AFM (lineshape, spin-relaxation rate), with indirect nuclear spin-spin interaction. A possibility of incommensurate antiferromagnetic structure is taken into account. Why are AFM phase regions interesting nowadays for the rapidly quenched ribbons: see above [33]. However in theory the nature of the ground state in quantum AFM $d > 1$ is not understood well. Besides exotic phases (spin liquids, spin nematics, ...) antiferromagnetic periodic and quasiperiodic systems may occur, namely also in metallic glasses. In fact first experiments with nuclear resonance in antiferromagnetic phase observed for water protons of CuCl$_2$.2H$_2$O at $T_LHe$ were done by [55]. However sometimes nature of the ground state in quantum AFM is not understood well for (CeAl$_2$ [20] and [21] and other heavy fermion systems, high-temperature superconductors, quasicrystals, ...). Why NMR measurements are interesting for study of rapidly quenched ribbons? It is well known plus this is weakly interacting probe of internal fields. And why NR in AFM? Static (time-averaged magnetic field) and dynamic properties of ordered phase (some fluctuation components) may be studied.
4 CRITERIA FOR OBSERVING NUCLEAR RESONANCE IN MAGNETIC SOLIDS.

Magnetic solids we call those solids in which magnetically ordered phase (FM, AFM, SDW, ...) occurs. Electronic dipolar fields in mg. solids are \( \approx 10^3 \) times larger than corresponding nuclear dipolar fields, atomic hyperfine fields of magnetic ions are \( \approx 10^6 \) times larger. Does it mean that resonance frequency is \( \approx 10^6 \) larger? No: the integrated spectral density is \( \approx \) constant + distribution of the local field spectra due to exchange over large frequency range \( \approx \) the \( |H_{\text{eff}}| \ll H_{\text{static}} \rightarrow \). Crude necessary condition for observing NR in a magnetic solid for \( T \geq T_N \) is:

\[
\frac{1}{T_{1,2-\text{min}}} \geq \frac{(\gamma H_{\text{int}})^2}{\omega_e},
\]

where \( T_{1,2-\text{min}} \) is the smallest value for which NR is still observable, here \( \omega_e \) is the exchange frequency, \( H_{\text{int}} \) is the static value of the perturbing field at the nucleus.

In the ordered phase \( T \leq T_N \) there is more complex criterium which holds for \( T_2 \). Difference from the paramagnetic case is that in AFM the electron spins do not reorient themselves rapidly, thus the constant in time field \( \approx \) the instantaneous value of the electron field. Difference from the paramagnetic case is that two nuclear spins which have equivalent positions in the crystal do not have necessarily the same magnetic characteristics in AFM.

5 NUCLEAR HAMILTONIAN.

In nonmagnetic solid:

\[
H = \gamma h I \cdot H_0,
\]

where \( I \) is the nuclear moment, \( H_0 \) is the external field, there are small corrections due to dipolar fields of other nuclei, atomic diamagnetism, and chemical shift. In magnetic solids electronic spins rapidly fluctuate due to exchange, dipolar interactions, spin-lattice interactions and spin-quasiparticle interactions. The nuclei in a static field \( \approx < S > \) are related to the uniform magnetization per unit volume \( M_0 \):

\[
M_0 = Ng\beta < S >_{T,H,p,...},
\]

where \( N \) is the volume density of spins, \( g \) is the electronic gyromagnetic ratio (tensor), \( \beta \) is the Bohr magneton. Internal fields of nuclei of nonmagnetic atoms are ( \( H^1 \) in CuCl2.2H2O):

\[
H_k = -\gamma h I_k \cdot (H_0 - g\beta \sum_n r_n^{-3} (\langle S_n \rangle > - \frac{3r_n \langle r_n \cdot S_n \rangle}{r_n^2})).
\]

Here we have (2-nd term) the dipolar field \( H_D \), which is in general not parallel to \( H_0 \) for \( n \neq k \). Note that crystallographically inequivalent sites have different dipolar fields (low symmetry crystals, 2 and more inequivalent sites/unit cell), so there is a number of different transitions \( \omega_i \langle gH_0(a, b, c) \rangle \), here \( g \) is a tensor with an orientation, temperature and field dependence.
For nuclei of magnetic atoms (Co$^{59}$ in CoF$_2$) we have:

$$H_k = -\gamma \hbar I_k (H_0 - g\beta \sum_n r_n^{-3} (<S_n> - \frac{3r_n(<S_n><S_n>)}{r_n^2})) + I_k A_n <S_n>,$$

where $A_n$ is the electron-nuclear hyperfine interaction due to spin and orbital moments of electrons of a given (paramagnetic) atom, and $H_{HF} = -\frac{A_n <S_n>}{\gamma \hbar}$, where resonance frequency is:

$$\omega = \gamma \left( \sum_i (H_{0i} + H_{Di} + H_{HF})^2 \right)^{1/2},$$

and where $g$ and $A$ tensor axis coincide. Here:

$$\omega (I_z \leftrightarrow I_z - 1) = \frac{1}{\hbar} A_z. <S_z > - \gamma (H_D \pm H_0) + \frac{3e^2 qQ (2I_z - 1)}{4\hbar I (2I - 1)}.$$

For nuclei of partially magnetic atoms (F$^{19}$ in MnF$_2$) there is overlap between the wave functions of electrons of nominally nonmagnetic ions and those of electrons of the paramagnetic ions, from this it follows redistribution of the spin magnetization. An example is MnF$_2$ where:

$$< (2s)^-, up | (3d)_{Mn^{2+}}, down >= 0,$$

$$< (2s)^-, up | (3d)_{Mn^{2+}}, up >= \neq 0,$$

orthogonalization leads to net 2s spin. Transfer of electrons of a given spin orientation from the spin-paired orbitals at the F$^-$ to unpaired 3d orbitals on the Mn$^{2+}$ leads to the nuclear Hamiltonian:

$$H_k = -\gamma \hbar I_k (H_0 + H_{kD}) + \sum_n I_k A_n. <S_n >,$$

here we have transferred hyperfine interactions (last sum) and resonance frequencies are:

$$\omega_{\pm} = \frac{1}{\hbar} (2A_I^2 - A_I^2) <S_z > - \gamma (H_D^2 \pm H_0).$$

Numerical values of internal fields magnitudes of three kinds of internal fields are:

- nonmagnetic ions .......... (dipolar fields $0.5 - 7.10^3$ Oe
- magnetic ions ............(mg. hfs fields $0.5 - 7.10^5$ Oe
- partially magnetic ions .....(transfer hfs f $0.5 - 7.10^4$ Oe

6 **ANTIFEROMAGNETS.**

We have a spin lattice in a crystal lattice in which the relevant degrees of freedom are individual atomic spins:

$$S_j, ...... R_j,$$
where:

\[ [S_{j\alpha}, S_{j\beta}] = \delta_{j\mu} i\hbar \epsilon_{\alpha\beta\gamma} S_{j\gamma}. \]

From symmetry considerations for the crystal we can determine structural symmetry where we take into account crystal and spins, e.i. we use the magnetic symmetry. Macroscopic description of this system is based on the free energy \( F \):

\[ F(M, \epsilon_{\alpha\beta}, \ldots, H, \sigma_{\alpha\beta}, T), \]

where order parameter is magnetisation \( M(Q) \), here \( Q \) is wave vector, there exists a coupling to other degrees of freedom in the crystal. We are looking for the free energy minimum which gives a ground state, then we study small oscillations of order parameters and from these spin waves, etc.

Microscopic description has similar principles. Heisenberg Hamiltonian is the simplest hamiltonian introduced by Dirac (1929):

\[ H = \sum_{<i,j>} J_{ij} S_i S_j, \]

where:

\[ J_{ij} \equiv J(|R_i - R_j|). \]

Then we study CEF (crystal electric field) from the Coulomb interactions between each electron and all the charges lying around the ion, we obtain the electrostatic potential which gives splitting of energy levels. Also other interactions like dipole-dipole interaction, are taken into account.

There are several ground states: the Neel state (simple, complicated) (i.e. in superconductors(AB), in \( CeAl_2 \), in a commensurate state:

\[ M = M_0 \cos(k \cdot r + \phi) \]

with the modulation wavevector \( k \). This later phase may be 1, single-k structure 2, double-k structure 3, triple-k structure. The condition for commensurability (sc lattice with a - lattice const. ) is:

\[ k = \frac{2\pi}{a} \left( \frac{M_1}{N_1}, \frac{M_2}{N_2}, \frac{M_3}{N_3} \right), \]

there exists at least one \( R \) such that:

\[ k \cdot R = 2\pi x INTEGER, \]

and where \( M \)'s and \( N \)'s are integers, minimum of \( |R| \) gives new periodicity. Polarization of this structure may be longitudinal \( M \parallel k \) or transversal \( M \perp k \). This structure may be determined by diffraction from Bragg peaks, it is pinned to the lattice and has an energy gap.

The incommensurate state is characterized by a modulation wavevector \( k \) which may be again 1, single-k structure 2, double-k structure and 3, triple-k structure. Conditions of incommensurability of the structure (for sc lattice with a - lattice const. ) are:

\[ k \neq \frac{2\pi}{a} \left( \frac{M_1}{N_1}, \frac{M_2}{N_2}, \frac{M_3}{N_3} \right), \]
there is no $R$ such that:

$$k \cdot R = 2\pi x \text{INTEGER},$$

where $M$'s and $N$'s are integers. The translational symmetry is lost, however the polarization exists and is longitudinal or transversal, diffraction gives Bragg peaks which still exist, and the structure is not pinned to the lattice, there is continuous degeneracy of the ground state with $\phi$ arbitrary. There may exist domain walls: the ground state degeneracy (discrete, continuous) lead to the configuration of spins connecting different ground states, this is called a domain wall. We speak about solitons for some 1d walls. Note that the spin orientation changes in domain walls.

Antiferromagnetic excitations were studied in [22], [23], [24], [25], and [26]. Let us first discuss linear spin waves (LSW). We have a bipartite lattice:

$$A...S^+ | 0 \rangle = 0,$$
$$B...S^- | 0 \rangle = 0.$$

Diagonalization of the Hamiltonian (Heisenberg with anisotropy):

$$H = E_{GS} + \sum_k \epsilon(k)(a_k^\dagger a_k + b_k^\dagger b_k),$$

where the spin wave excitation energy $\epsilon(k)$ is:

$$\epsilon(k) = ((g\beta H_A + 2 | J | S^z)^2 - 4J^2 S^2 \gamma^2(k))^{1/2},$$

and where:

$$\gamma^2(k) \equiv \sum_{<nm>} \exp(ik\Delta)$$

leads to two modes - degenerated modes. The anisotropy energy:

$$\epsilon_A \equiv g\beta H_A$$

and the exchange energy:

$$\epsilon_x \equiv 2JSz,$$

give the gap energy:

$$\epsilon(0) = (\epsilon_A(\epsilon_A + 2\epsilon_x))^{1/2}.$$

In the longwavelengths $k \approx 0$ with no anisotropy we obtain:

$$\epsilon(k) \approx (8z)^{1/2}JSka.$$

In the longwavelengths $k \approx 0$ with the anisotropy we obtain:

$$\epsilon(k) \approx (\epsilon_A^2 + 2\epsilon_A\epsilon_x + 8J^2 S^2 z^2 k^2 a^2)^{1/2}.$$

We can obtain the commensurate structure and the incommensurate structure via nonlinearities. The spin fluctuations - correlations are:

$$[< \{\delta S^z(\tau)\delta S^z(0)\}>],$$
$$[< \{\delta S^+(\tau)\delta S^-(0)\}>].$$
The phase transitions depend on the phase boundaries. In antiferromagnetic regions in the amorphous matrix these boundaries may substantially depart behavior of spin waves from those which are obtained in very large (physically) infinite regions as concerning its characteristic length. Using the mean field we can describe behaviour of spin waves including the critical behavior. This (later) behavior was studied for itinerant electrons in the antiferromagnet for Cr by [56].

7 RELAXATION AND LINEWIDTH.

Relaxation and linewidth here are studied following [57]. Local fields for time dependent perturbation are given by:

\[ H' = A \hbar \delta S, \]
\[ \delta S \equiv S(t) - \langle S \rangle. \]

The NMR line profile [58] is:

\[ I(\omega) = \int_{-\infty}^{+\infty} \exp(i\omega t - \Psi(t)) dt, \]

Let us note that this is a theoretical lineshape:

\[ \Psi(t) = \left( \frac{A}{\hbar} \right)^2 \int_0^t (t-\tau) \langle \{ \delta S^z(\tau) \delta S^z(0) \} \rangle + \frac{1}{2} \exp(-i\omega_0 \tau) \langle \{ \delta S^+(\tau) \delta S^-(0) \} \rangle d\tau. \]

The spin-relaxation rate is:

\[ \frac{1}{T_1} = \frac{1}{2} \left( \frac{A}{\hbar} \right)^2 \int_0^{+\infty} \cos(\omega_0 t) \langle \{ \delta S^+(\tau) \delta S^-(0) \} \rangle dt. \]

In the limit of short electron spin time correlations \( \omega_0 \tau_e \ll 1 \) we obtain for lineshape:

\[ \psi(t) = \left( \frac{A}{\hbar} \right)^2 \int_0^{+\infty} \langle \{ \delta S^z(\tau) \delta S^z(0) \} \rangle + \frac{1}{2} \langle \{ \delta S^+(\tau) \delta S^-(0) \} \rangle d\tau. \]

It is the Lorentzian lineshape with the halfwidth \( \Delta \omega_1 = \)

\[ = \frac{1}{T_2} = \frac{1}{T_2} + \frac{1}{T_1}, \]

where:

\[ \frac{1}{T_2} = \left( \frac{A}{\hbar} \right)^2 \int_0^{+\infty} \langle \{ \delta S^z(\tau) \delta S^z(0) \} \rangle d\tau, \]
\[ \frac{1}{T_1} = \left( \frac{A}{\hbar} \right)^2 \int_0^{+\infty} \frac{1}{2} \langle \{ \delta S^+(\tau) \delta S^-(0) \} \rangle d\tau. \]

The spin-relaxation time is given as:

\[ \frac{1}{T_1} = \frac{1}{2} \left( \frac{A}{\hbar} \right)^2 \int_0^{+\infty} \langle \{ \delta S^+(\tau) \delta S^-(0) \} \rangle d\tau, \]
\[ \frac{1}{T_1} = 2\left(\frac{1}{T_1}\right). \]

For \( T \gg T_N \), the paramagnetic region, the local field spectra \( \sim \) Gaussian distribution centered about zero frequency:

\[ < \{ \delta S^i(t)\delta S^i(0) \} > = \frac{S(S + 1)}{3} \exp\left(-\frac{1}{2}\omega_e^2 t^2\right), \]

here:

\[ \omega_e^2 \equiv \left(\frac{J}{\hbar}\right)^2 zS(S + 1) \]

and:

\[ \frac{1}{T_1} = \frac{1}{T_2} = \frac{(2\pi)^2}{3} \frac{S(S + 1)}{\omega_e} \frac{1}{\omega^2}. \]

Note that the anisotropy of A tensor leads to \( \frac{1}{T_2} \neq \frac{1}{T_1} \) in general. Also note that without exchange we obtain:

\[ \frac{1}{T_2} \approx \left(\frac{AS}{\hbar}\right)^2. \]

Relaxation time \( T \ll T_N \) and low temperature region at those temperatures \( T \) at which the spin wave description is adequate: there is strong angular dependence of \( T_1 \) but not \( T_2 \) due to preferential direction of ordered spins. We find \( T^3 \) dependence of both \( T_{1,2} \) for \( T_{AE} \ll T \ll T_N \), and exponential decrease of both \( T_{1,2} \) for \( T_{AE} \geq T \).

Types of processes contributing to nuclear relaxation are direct: \( E_{SW} = E_{Zeeman-nuclear} \), however \( \hbar\omega_0 \approx 0.01K \rightarrow \) is usually negligible, and Raman: \( |\omega_k - \omega_{k'}| = \omega_0 \). Let us discuss the Raman scattering: The Hamiltonian:

\[ H = A\sin(\theta)(I^+ + I^-) \sum_{k, k'} \exp(i(k - k')r_j)(u_k u_{k'}^* \alpha_k \alpha_{k'}^* + u_k^* u_{k'} \beta_k \beta_{k'}^*), \]

in small-k limit for \( \omega_k \) gives:

\[ \frac{1}{T_1} = \sin^2(\theta)(const)\frac{T}{T_N}^3 \int_{-\infty}^{+\infty} \frac{xdx}{\exp(x) - 1}, \]

here \( \theta \) is an angle between the direction of spin antiferromagnetic alignment and the direction of nuclear quantization:

\[ const \equiv \frac{(A\Omega)^2 \eta^4 (S + 1)^4}{81\pi^4 \hbar^4 k T_N}. \]

Here \( \Omega \) is an atomic volume,

\[ \eta \equiv \frac{3kJ}{2JzS(S + 1)} \approx 1, \]

\[ b \equiv \frac{\eta^2}{3} \ldots s.c. \]

Note that for \( \theta = 0 \) the second order is needed [59] to take into account:

\[ \frac{1}{T_1} \sim (const'')(\frac{T_A}{T_N}). \]
as the Fig. 1. in [57] van Kranendonk shows T-dependence.

For \( T \gg T_N \) we obtain:

\[
\frac{1}{T_1} = \sin^2(\theta)(\text{const})(\frac{T}{T_N})^3
\]

and for \( T \ll T_N \):

\[
\frac{1}{T_1} = \sin^2(\theta)(\text{const}')(\frac{T}{T_N})^2 \cdot \exp(-\frac{T_{AE}}{T})
\]

where (const' ) ≡ ( const ).

In small-k limit for \( \omega_k \), spectral density of the fluctuating field extends to \( \omega \gg \omega_0 \) and we obtain:

\[
\frac{1}{T_2} = (1 + \cos^2(\theta)2)(\text{const}) (\frac{T}{T_N})^3 \int_{+\infty}^{T} x dx \exp(-\frac{T_{AE}}{T})
\]

Note here slight angle dependence only.

For \( T = T_N \) transition region \(| T - T_N | \ll T_N \) the wave-dependent susceptibility \( \chi(k) \) for \( k + Q \approx Q \equiv \frac{\pi}{a}(1, 1, 1) \) in s.c. is given by:

\[
< \{ \delta S_i^k(t)\delta S^k_0(0) \} > = \frac{KT}{g \beta} \chi^i(k) \exp(-\frac{t}{\tau_k})
\]

where \( \tau_k \) is the characteristic decay time in the electronic spin system, \( i = x, y, z \).

Let us discuss several examples.

For a cubic crystal with no magnetic field and no anisotropy:

\[
\frac{1}{T_1} = \frac{1}{T_2} = \text{const}.(2\pi)^{\frac{3}{2}}(\frac{A}{\hbar})^2 S(S+1) \frac{1}{\omega_e} (\frac{T_N}{T - T_N})^\frac{3}{2},
\]

\[
C \approx 10^{-1}
\]

which is valid for:

\[
\frac{\omega_0}{\omega_e} < \frac{T - T_N}{T_N} < 10^{-2}.
\]

For cubic crystal in the magnetic field:

\[
H > 0... \rightarrow \chi_\perp(K_0), \chi_\parallel(K_0) \rightarrow T_\perp, T_\parallel,
\]

\[
T_N - T_\parallel = 3(T_N - T_\perp),
\]

\[
\frac{T_N - T_\parallel}{T_N} \approx (\frac{H}{H_E})^2,
\]

\[
\frac{1}{T_1} = \text{const}.(2\pi)^{\frac{3}{2}}(\frac{A}{\hbar})^2 S(S+1) \frac{1}{\omega_e} (\frac{T_\perp}{T - T_\perp})^\frac{3}{2},
\]

\[
\frac{1}{T_2} = \text{const}.(2\pi)^{\frac{3}{2}}(\frac{A}{\hbar})^2 S(S+1) \frac{1}{\omega_e} ((\frac{T_\parallel}{T - T_\parallel})^\frac{3}{2} + (\frac{T_\perp}{T - T_\perp})^\frac{3}{2}).
\]

For tetragonal crystal with strong anisotropy (\( H_A \gg H \)):

\[
\frac{1}{T_2} = \frac{1}{2} (2\pi)^{\frac{3}{2}}(\frac{A}{\hbar})^2 S(S+1) \frac{1}{\omega_e} ((\frac{T_N}{T - T_N})^\frac{3}{2} + (\frac{T_\perp}{T - T_\perp})^\frac{3}{2}).
\]
\[
\frac{1}{T_{2,\perp}} = \text{const.} (2\pi)^{\frac{1}{2}} \left( \frac{A}{\hbar} \right)^2 S(S+1) \frac{1}{3} \frac{1}{\omega_e} \left( (\frac{T_N}{T-T_N})^{\frac{1}{2}} + 3(\frac{T_{\perp}}{T-T_{\perp}})^{\frac{1}{2}} \right),
\]

\[
\frac{1}{T_{1,\parallel}} = \text{const.} (2\pi)^{\frac{1}{2}} \left( \frac{A}{\hbar} \right)^2 S(S+1) \frac{1}{3} \frac{1}{\omega_e} \left( (\frac{T_N}{T-T_N})^{\frac{1}{2}} \right),
\]

\[
\frac{1}{T_{1,\parallel}} = \text{const.} (2\pi)^{\frac{1}{2}} \left( \frac{A}{\hbar} \right)^2 S(S+1) \frac{1}{3} \frac{1}{\omega_e} \left( (\frac{T_N}{T-T_N})^{\frac{1}{2}} + (\frac{T_{\perp}}{T-T_{\perp}})^{\frac{1}{2}} \right).
\]

Let us discuss indirect nuclear spin-spin interaction. It is an important source of linewidth below \( T_N \). A nucleus \( \rightarrow \mathrm{SW} \rightarrow \) another nucleus, there is no contribution to \( T_1 \) and no transfer of energy from nuclear to the electronic spin system. The Hamiltonian in this case is:

\[
H_N = -\frac{A^2 S}{2} \sum_{j,R} F(R)(I_j^+ I_{j+R}^- + I_j^- I_{j+R}^+),
\]

here:

\[
F(R) \approx \frac{a}{R} \exp\left(-\frac{H_A H_E}{16\pi^3} \frac{1}{a R}\right),
\]

\[
\frac{H_A}{H_E} \approx 0.1 - 0.01,
\]

\[
\Delta \omega \approx \Delta \omega_{\text{paramagnet}} \left( \frac{\omega_E}{\omega_A} \right)^{\frac{1}{2}}.
\]

8 NMR and PARAMAGNETIC PHASE.

In van Vleck's paramagnetic phase there are localized spins [60] and [61], nature of the coupling should be known. An atom with a single electron outside closed shells forms such a localized spin, here spin-orbit coupling is negligible, the Hamiltonian for the magnetic interaction of the electron with the nucleus is:

\[
H = 2\beta \gamma \hbar \mathbf{I} \cdot \left( \frac{1}{r^3} - \frac{s}{r^3} + \frac{r(s \cdot r)}{r^5} + \frac{8\pi s \cdot \delta(r)}{3} \right),
\]

here \( \beta \) is the Bohr magneton. Model for an atom with closed shell plus one electron with \( \phi \) the orbital wave-function real \( \rightarrow \phi \):

\[
(\phi \mid 1 \mid \phi) = 0.
\]

There is a tensor coupling:

\[
(\phi \mid H \mid \phi) = \hbar \gamma \mathbf{I} \cdot \mathbf{T} \cdot \mathbf{S},
\]

\[\phi = \sum_{l=s,p,d,\ldots} a_l \phi_l \\text{s-part} \rightarrow \text{a scalar term A:}\]

\[= \hbar A \mathbf{I} \cdot \mathbf{S},\]

\[A = \frac{16\pi}{3} \beta \gamma |a_0|^2 \phi_0(0)|^2.
\]

Note that p,d, ..., -parts contribute:

\[\mathbf{I} \cdot \mathbf{T} \cdot \mathbf{b} \cdot \mathbf{S} = 2\beta \sum_{l,l'} a_l a_{l'} (\phi_{l'} \mid 3 \frac{r_l}{r^{l+1}} (\mathbf{I} \cdot \mathbf{r}) (\mathbf{S} \cdot \mathbf{r}) - \frac{1}{r^3} (\mathbf{I} \cdot \mathbf{S}) \mid \phi_l),\]
where:

\[ |l - l'| = 0, 2. \]

Note also that: if spin-orbit coupling is nonnegligible: Kramers theorem gives \( \rightarrow \) still 2x degeneracy and \( \rightarrow \) fictitious spin 1/2. Atoms with more than one electron outside closed shells have \( S \), it is the total spin, magnetic coupling of an electron with a nuclear spin that does not belong to the same atom is:

\[ \bar{h}A S + 2\gamma h I \text{grad}_R \int \frac{\text{div}(S\rho(r))d^3r}{|r - R|}, \]

where \( \rho \equiv |\phi|^2 \):

\[ A = \frac{16\pi}{3} |a_0|^2 |\phi_0(R)|^2. \]

9 NMR and PARAMAGNETIC CONDUCTORS.

Paramagnetic conducting phase is characterized by the coupling of conduction electrons with the nuclear spins described by the same Hamiltonian as in non-metals, but the conduction electrons are not localized, nuclear spin sees magnetic fields produced by all conduction electrons which form a degenerate Fermi gas. If \( H \) is an applied magnetic field and the gas with density of states on the Fermi level:

\[ g(E_F) = \frac{3NV}{2E_F}, \]

the magnetization is given by:

\[ M = \frac{\beta n}{V} = \frac{\beta^2 H g(E_F)}{V}, \]

and the paramagnetic susceptibility:

\[ \chi_p = \frac{M}{H} = \beta g(E_F) = \frac{3N\beta^2}{2kT_F}. \]

The hyperfine coupling is:

\[ = 2\gamma h bf I \sum_{\text{unfilled orbits}} (\phi_k | (-\frac{s_k}{r_k^3} + \frac{r_k(s_k \cdot r_k)}{r_k^5}) + \frac{8\pi s_k \delta(r_k)}{3}, \]

\[ = \gamma h bf I \sum_{\text{unfilled orbits}} T_k s_k \]

for \( T_k \approx \text{const} \) near the top of the Fermi surface:

\[ = \gamma h bf I. T. \sum_{\text{unfilled orbits}} s_k. \]

Note that:

\[ 2\beta S = -V M = -V \chi_p H_0, \]

thus:

\[ = -V \frac{\gamma h}{2\beta} I \chi_p T. H_0, \]
which is the Knight shift:

\[ K = \Delta H \frac{8\pi}{3} <| \psi_k(0) |^2 >_F \chi_B, MM. \]

Here \( K \) range from \( 2 \times 10^{-4} \ldots Li^7 \) to \( 2 \times 10^{-2} \ldots Hg^{199} \), all known values of \( K \) see in [62].

The Korringa law - numbers [59] in the approximation of noninteracting conduction electrons the Knight shift \( K \) and the spin lattice relaxation time \( T_1 \) are related via Korringa relation [63] and [26]:

\[ K^2 T_1 = \frac{\hbar}{4\pi k_B} \left( \frac{\gamma_e}{\gamma_n} \right)^2, \]

where \( \gamma_e, \gamma_n \) are the electronic and nuclear gyromagnetic ratios.

The electron-electron interactions within the conduction band modify the Korringa relation to:

\[ K^2 T_1 = \frac{\hbar}{4\pi k_B} \left( \frac{\gamma_e}{\gamma_n} \right)^2 \cdot \frac{1}{K(\alpha)}, \]

where \( K(\alpha) \) is the enhancement factor smaller than \( 1 \), see in [63] - [66]. Let us introduce some numbers for: ( 1 \( \equiv LaAl_2 \), 2 \( \equiv CeAl_3 \) are: for 1:

\[ T_1 T = 14(\pm 1)secK \rightarrow \frac{1}{K(\alpha)} = 1.34, \]

for 2: see fig 10 [67]. More details are described elsewhere on e-e interaction enhancement and on Kondo effects ( short range spin-spin correlations in the paramagnetic phase [68] at sufficiently high temperatures such that critical fluctuation phenomena are unimportant for normal metals.

10 DISCUSSION.

Behavior of the \( Cu - Mn - Al \) ribbons was explained by the s-d interaction between conduction electrons and the clustered Mn atoms. While nuclear magnetic resonance measurements shows the antiferromagnetic and ferromagnetic clusters of Mn atom coexisting without long-range order, we described theory of NMR for AFM phase to study magnetic resonance properties also for the antiferromagnetic crystal phase regions (which have long-range order for larger regions) and which occur in these ribbons. The Heusler Type \( Cu - Mn - Al \) Alloy has a composition between \( Cu_2 MnAl \) and \( Cu_3 Al \). Electron microscopy of the premartensitic \( Cu - Zn - Al \) alloy has shown that the \( Cu - Zn - Al \) alloy quenched from high temperature has the electron diffraction patterns of this alloy well explained by the model with the existence of small particles with an orthorhombic structure. It was noted that an important aspect of improvement in the material properties is to create a nanostructured state in matrix, which has significant advantages in magnetic and mechanical characteristics in contrast to the bulk materials in crystalline or amorphous state. Thus it is an interesting problem to study magnetic resonance properties not only for the Mn atoms and clusters without long-range order but also for the antiferromagnetic crystal phase regions (which have long-range order for larger regions
in microcrystals and larger crystals) which may also occur in ribbons, besides nanocrystal regions. To study nanocrystal regions it is necessary to take into account more complicated magnetic structure of these nanocrystals.

Let us note that NMR tables and basic physical constants, as well as conversion of Gaussian to SI Units are in [63], index of nuclear species is in [61]. Tabular data of NMR in rare-earth intermetallic compounds is in [60] and a survey of applications of NMR and NGR methods in [69].

Domain walls were studied in [60], they may occur in crystal regions of ribbons. In this case the zero-field NMR spectra of ferromagnetically ordered compounds are complicated due to presence of domain walls:

\[ H_{1,\text{eff.}} = H_1(1 + \eta), \]

where enhancement factor for nuclei situated in Bloch walls and domains is \( \approx 100 - 10000 \) but differs depending on the position, there exists broadening. Similar problem may occur in antiferromagnetic phase regions.

Let us note that several other problems are studied for NMR and AFM state. The influence of the crystal electric field (CFE) on NMR spectra in AFM state are described in [70]. Here effect of spin fluctuations on the relaxation of a crystal-field-split rare-earth impurity is studied. In [60] the CFE influence on NMR spectra is studied experimentally and theoretically.

While \( Cu – Mn – Al \) materials are not ferromagnetic let us note that the NMR spectra for the ferromagnetic phase are studied and described in [59] and [60]. There is described the ferromagnetic phase hamiltonians for nuclei and for electrons. The spin waves are studied with spin-relaxation rate experimentally and theoretically.

On NMR and conduction electron polarisation has influence which is studied, together with the Kondo phenomenon, in [71], [72] and in [60]. Usually the uniform polarization model is used. The RKKY-type analysis of the conduction electron polarization leads to description of correlation of magnetic ordering temperatures and transferred hyperfine fields, the distance dependence of the transferred hyperfine interaction, the anisotropy of the transferred magnetic hyperfine interaction wand evidence for magnetically induced nuclear quadrupole interaction.

In some cases the AFM structure is incommensurate, see above. Such a case was studied for example in [73] for NMR proton line shape in \((\text{TMTSF})_2X\) where there is an incommensurability of nesting vector and order parameter, in [21] and [20] for \( CeAl_2 \). The lineshape in this case is described in [73]. Analysis of the lines in the metallic state leads to:

\[ g(\omega, \Delta) = \frac{1}{(2\pi)^{\frac{3}{2}}} \exp(-\frac{\omega^2}{2\Delta^2}). \]

Thus besides SDW in commensurate case also incommensurate case may be determined from the spectra.

In AFM and phonons and structures were studied experimentally and theoretically, and also AFM and phase transitions, critical phenomena (where a critical index is seen by NMR), experimental and theoretical situations are described in [64] - [66].

In [74] authors study noise characteristics of microwire magnetometer. Current trends lead to replacement of amorphous ribbon cores with magnetic microwires. However the miniaturization causes degradation in the parameters of
sensors, so, considering measurement of weak magnetic fields, it is necessary to explore noise parameters, temperature drift and stability of the magnetometer output value. The article deals with analysis of microwire sensor noise characteristics based on the experimental data processing. In these magnetic wires are, however, metallic ribbons used on as the surface layers of wires to minimize degradation. Then it is necessary again to study amorphous metallic ribbons, see also [74]. As it is known an amorphous metallic surface layers improve these characteristics. To obtain optimal influence of the surface amorphous metallic layer (ribbon-like) it is necessary to understand its basic properties.

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