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Abstract

Full Text

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PARAMAGNETIC RESONANCE ON CONDUCTION ELECTRONS IN LIQUID SODIUM

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The influence of impurities on paramagnetic resonance on conduction electrons (c.e.p.r.) in alkali metals in the solid phase has been studied in a number of works ([1–6]). However, no investigations of liquid metallic systems by the c.e.p.r. method have been carried out, although they can provide information on the dynamics of thermal motion of particles in a liquid metal.

In the present work, the temperature dependence of the c.e.p.r. linewidth in metallic Na in the Na + K system has been studied for the first time in the temperature interval from −200 to +300°. Sodium of 99.8% purity was used as the starting material. Measurements were carried out at a frequency of 9320 MHz on a standard RE-1301 spectrometer. The samples were prepared by ultrasonic dispersion in an inert medium to an average metal-particle size on the order of the skin-layer depth δ.

Fig. 1. Temperature dependence of the peak linewidth for initial Na

Figure 1 shows a typical dependence of the peak linewidth δH on temperature for one of the Na samples. The entire investigated temperature interval is clearly divided into three regions: $-200 \div 0^\circ$ (I), $0 \div 100^\circ$ (II), $100 \div 300^\circ$ (III). In regions I and III the dependence $\delta H(T)$ is linear, although the slope coefficients $\alpha = \partial(\delta H)/\partial T$ are not equal to one another; in the intermediate region (II), between $\sim 0^\circ$ and the melting temperature of Na, δH grows exponentially with T. The qualitatively observed dependence of δH on temperature is explained as follows. In the first temperature region the linear behavior of $\delta H(T)$, with slope coefficient $\alpha = (0.025 \pm 0.005)$ Oe/deg, is in good quantitative agreement with the data of a number of authors ([7–10]) for pure Na. The relatively large linewidth δH of our samples (δH at room temperature for our samples is $\sim (22 \pm 3)$ Oe, whereas in work ([5]) it is 6 Oe) indicates that the sodium used by

Figure 2

Figure 2: Figure 2

us contains impurities, the paramagnetic relaxation of conduction electrons on which gives a comparatively large (but temperature-independent) contribution of ~ 15 Oe to the width.

Thus, by analogy with Matthiessen' s rule for the electrical resistance of metals, the c.e.p.r. linewidth in the solid phase may be represented in the form

$$\delta H\ (T) = \delta H\ \ (T) + \delta H\ \ . \tag{1}$$

The observed scatter of δH for different samples of the initial sodium (within ~ 3 Oe) indicates that some of the impurities are in the pe-

dissolved state and is nonuniformly distributed over the volume of the metal. This is manifested still more clearly in the following temperature region II. Levy ([9]) observed for sodium of high purity a linear dependence $\delta H(T)$ up to the melting temperature T_{m} of sodium. At the melting point δH apparently increased discontinuously. A change in the width at the moment of transition to the liquid state may also be expected by analogy with the corresponding jump in the electrical resistance. The broadening we observe of the region of the discontinuous increase in the line width over a temperature interval of $\sim 100^{\circ}$ can be explained by the change in the solubility of impurities in sodium with temperature. At $T \geq T_{\text{m}}$, when all impurities are already dissolved, the dependence is again linear, but $\alpha_{\text{tv}} \neq \alpha_{\text{l}}$.

Fig. 2. Dependence of the peak line width at 100°, $\delta H_{100^{\circ}}$ (1), and of the angular coefficients $\alpha_{\text{l}} = [\partial(\delta H)/\partial T]_{\text{l}}$ (2), for Na + K samples on the atomic concentration of potassium.

Thus, the change in the character of the thermal motion of impurity atoms upon the transition of the metal to the liquid state leads to the appearance of a temperature dependence of the impurity contribution to the EPR line width. The validity of Matthiessen' s rule (1) in the liquid phase is violated.

In order to study the concentration and temperature dependence of the impurity contribution to the total line width δH_{l}, we investigated liquid solutions of potassium in sodium for concentrations 3; 5; 8; 10.7 at.%. The temperature behavior of δH for these samples in region II–III coincides qualitatively with the corresponding dependence for the initial sodium. Figure 2 gives the dependences of the peak line width at 100° and of the angular coefficients α_{l} on the potassium concentration c_1, expressed in atomic fractions. The observed curves $\delta H_{\text{l}}(T, c_1)$ are described by the expression

$$\delta H_{\text{l}} = AT + BTc_1 + Dc_1 + E, \tag{2}$$

where $A = (0.045 \pm 0.005)$ Oe/deg, $B = (0.70 \pm 0.15)$ Oe/deg, $D = (1250 \pm 30)$ Oe, $E = (15 \pm 3)$ Oe.

In what follows it is convenient to represent δH_1 in a more symmetric form

$$\delta H_1 = c_0 \delta H_0 + c_1 \delta H_1, \qquad c_0 = 1 - c_1. \tag{2'}$$

By analogy with the theory of the electrical conductivity of liquid metals ([11]), let us introduce effective potentials for spin scattering of an electron on solvent ions $U_0(r)$ and impurity ions $U_1(r)$. The probability of inelastic spin scattering w, related to the peak width δH for a Lorentzian line by the relation

$$\delta H = \frac{2}{\sqrt{3}} \frac{\hbar w}{\mu_e},$$

where μ_e is the magnetic moment of the conduction electron, is calculated from the formula

$$w = \frac{2\pi}{\hbar} \rho(\varepsilon_F) \int_{-\infty}^{\infty} e^{i\omega t}\, dt \int_0^{2k_F} \langle U^*(K) U(K,t) \rangle\, d \left(\frac{K}{2K_F} \right)^2. \tag{3}$$

$U(K)$ is the Fourier component of $U(r)$; $\rho(\varepsilon_F)$ is the electron density at the Fermi surface; $K = |\mathbf{k} - \mathbf{k}'|$; $\mathbf{k}, \mathbf{k}'$ are the wave vectors of the electron.

respectively before and after scattering; $\langle ... \rangle$ denotes averaging over the Gibbs ensemble; ω is the resonance frequency. The integrand in (3) for a two-component alloy is represented in the form

$$\sum U_\alpha(K) U_\beta(K) N \{ c_\alpha f_\alpha(t) \delta_{\alpha\beta} + c_\alpha c_\beta f_{\alpha\beta}(t) (a_{\alpha\beta}(K) - 1) \},$$

where

$$a_{\alpha\beta}(K) = 1 + \frac{N}{V} \int_0^{\infty} (P_{\alpha\beta}(r) - 1) \frac{\sin Kr}{Kr}\, dr,$$

$P_{\alpha\beta}(r)$ is the pair-correlation function of the ions [11]; $c_{\alpha,\beta}$ is the atomic fraction of ions of types α, β; N is the total number of ions in a specimen of volume V; $f_\alpha(t)$ and $f_{\alpha\beta}(t)$ are functions characterizing, respectively, the thermal one-particle motion and the motion of a pair of particles of types α, β relative to one another.

According to the measurement results, δH depends linearly on the concentration c_1; hence it follows that terms containing c_1^2 may be neglected.

In view of the absence of data concerning the quantities $U_0(r)$ and $U_1(r)$ for Na and K in the liquid state, we shall make the following assumptions: a) $U_0(r)$

and $U_1(r)$ differ only in the values of the force constants, $U_{0,1}(r) = U_{0,1}F(r)$; b) $U_0/U_1 = \lambda$ is a constant; c) $f_{10}(t)(a_{10}(K) - 1) = f_{00}(t)(a_{00}(K) - 1)$.

Taking these assumptions into account, w can be written in the form

$$w = S_0 U_1^2 \{\lambda^2(a+b)c_0 + [(1-\lambda^2)a + \lambda(1-2\lambda)b]c_1\}. \quad (4)$$

Comparing (4) with (2′), we find an expression describing the temperature dependence of the ratio of the one-particle and interference contributions to the line width:

$$\frac{a}{b} = \frac{(\lambda^2 - \lambda - 1)\delta H_0}{(\lambda \delta H_1 - \delta H_0)} - 1.$$

In conclusion, let us note that the systems investigated up to now are solutions of metals whose atoms have a relatively large spin–orbit coupling and a large mass in comparison with the atoms of the solvent metal. It is of interest to study solutions with the opposite ratio for these quantities. An example of such a system is a liquid solution of lithium in sodium. Our experiments on EPR in liquid solutions of Li in Na (within the range of $\sim$ 5 at.% lithium) gave an unexpected result: a sharp narrowing of the line was observed (by a factor of $2 \div 3$) in both the liquid and solid phases; moreover, $\alpha \simeq \alpha \simeq 0.025$ Oe/deg and, together with the numerical values of δH, did not depend on the Li concentration within the experimental error. This makes it possible to assert that in the process of preparing the alloy an effective purification of sodium occurred due to redistribution of impurities between Na and Li. To detect the intrinsic effect of the influence of Li on δH in liquid Na, owing to the exceptionally small magnitude of the spin–orbit interaction for Li, it is necessary to study solutions with higher Li concentrations, which, however, is limited by the miscibility region of the solution [12].

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Note: Figure translations are in progress. See original paper for figures.