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ELECTRON SPIN RELAXATION STUDIES OF SPIN–PHONON INTERACTIONS IN SODIUM AND POTASSIUM METALS

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CONTENTS

ABSTRACT

Conduction electron spin resonance (CESR) spectra are reported for colloidal alkali metal particles in frozen solutions of sodium and potassium in hexamethylphosphoramide (HMPA). Characteristic CESR spectra were not obtained from a study of frozen solutions of potassium in ammonia.

Electron spin–lattice relaxation rates are governed primarily by spin–orbit coupling during spin–phonon scattering of high velocity electrons, and the relaxation rates are shown to correlate extremely well at all temperatures with electrical resistivity as predicted by Yafet. The temperature dependence is adequately described by a Bloch–Grüneisen function above 35 K whilst deviations from this function at lower temperatures are attributed to co-operative spin–phonon Umklapp processes. The deviations are used to calculate effective Debye temperatures for each of the metals which agree closely with values calculated from resistivity.

A novel method of isolating the spin–orbit contribution to spin relaxation at 1.3 K is described: there is no evidence for freezing in of Umklapp processes in potassium at this temperature.

I. INTRODUCTION

Electronic wave functions in the conduction bands of metals are modified considerably from free atom functions, and for metals with a spherical Fermi surface, much information about the structure of the conduction band can be obtained from magnetic resonance studies.

Knight [1] shifts of metal nuclear magnetic resonance spectra monitor the Fermi contact interactions between conduction electrons and metal nuclei (i.e. *s*-electron contributions) whilst shifts of electron spin resonance spectra, coupled with spin relaxation rates, give information concerning the mixing of higher angular momentum states in the band (e.g. *p*-electron contributions). Temperature dependent changes in both types of magnetic resonance spectra highlight the role of spin–phonon interactions in the lattice. This paper is concerned primarily with the analysis of electron spin relaxation rates (and *g*-factor shifts) for sodium and potassium metals.

A. The duality of spin and resistivity scattering processes

The motion of conduction electrons through a metal is modulated by collisions of the electrons with lattice phonon waves, the time between collisions being of the order 10^{-14} seconds. Assuming a Debye model for the spectrum of lattice modes with a characteristic temperature parameter Θ, the total resistance of a metal is given [2] by

$$\rho_{\mathrm{L}} = \frac{3\pi\hbar\tilde{a}^{6}\mathscr{C}^{2}(0)}{4e^{2}mNk\Theta R^{4}v_{\mathrm{F}}^{2}}\left(\frac{T}{\Theta}\right)^{5}\mathscr{J}_{5}\left(\frac{\Theta}{T}\right) \tag{1}$$

where $\tilde{a}$ is the radius of the "Debye zone" for phonons and R is the radius of the Fermi sphere. The quantity $\mathscr{C}(0)$ is the electron–phonon interaction energy, usually taken [7] as the Fermi energy of the electrons, and v_F is the corresponding Fermi velocity.

In this expression e represents the charge on the electron, m is the mass of the ion, N is the number of unit cells/unit volume and k is Boltzmann's constant. $\mathcal{J}_5(x)$ is one of the class of Debye integrals defined [2, 3] by

$$\mathcal{J}_n(z) \equiv \int_0^z \frac{x^n}{(e^x-1)(1-e^{-x})}\,dx$$

The temperature dependence of the resistivity may be expressed [2] by

$$\rho_L = 4\left(\frac{T}{\Theta}\right)^5 \mathcal{J}_5\left(\frac{\Theta}{T}\right)\rho_\Theta \tag{2}$$

where the constant ρ_Θ is definable from (1). This is essentially the Bloch formula [4] for the lattice resistance of a pure metal. It is well established [5–7] that a formula of type (2) with appropriate values of the Debye temperature, Θ, represents the temperature variation of the electrical resistivity of many metals over a wide temperature range.

At high temperatures ($T \gg \Theta$) $\mathcal{J}_5$ behaves like

$$\int_0^{\Theta/T} z^3 dz = \frac{1}{4}\left(\frac{\Theta}{T}\right)^4 \quad \text{and} \quad \rho_L \sim \left(\frac{T}{\Theta}\right)\rho_\Theta$$

At low temperatures, the upper limit on the integral becomes very large and $\mathcal{J}_5$ approaches the limit 124.4 so that $\rho_L \sim 497.6(T/\Theta)^5\rho_\Theta$.

In a related effect, interaction of the orbital motion of electrons with phonon modes produces electron spin flips via the coupling of spin and orbital angular momenta. Spin–lattice relaxation of conduction electrons was first considered by Overhauser [8], but Elliott [9] first suggested that the spin–orbit interaction was likely to be the dominant relaxation process. Elliott's theory received some support from studies of lithium and sodium metals [10] which had electron spin relaxation times (T_1) and electronic g-factors approximately dependent upon the spin–orbit coupling constant of the metal core. Elliott [9] obtained (for $T \gg \Theta$)

$$T_1^{-1} = \Delta g^2/\beta\tau_R \tag{3}$$

where τ_R is the resistivity relaxation time and β a constant of order 0.03 for a Debye spectrum of lattice modes.

The g-shift, Δg, is a measure of the shift of the electron spin resonance frequency from the free electron value. If spin–orbit coupling is the only contribution to the shift then [9]

$$\frac{h(v_0 - v_E)}{\mu_B H} = \Delta g \approx \lambda/\Delta E \tag{4}$$

where h is Planck's constant, μ_B is the Bohr magneton, H is the applied magnetic field, and ν_0 and ν_E are the experimental and free electron resonance frequencies respectively. In (4) λ is the appropriate spin–orbit coupling constant and ΔE the energy gap to the nearest band with the same transformation properties.

Whilst forward scattering makes only a negligible contribution to resistivity [4], Elliott [9] showed that all scattering processes can contribute to electron spin relaxation and predicted that the spin–lattice relaxation rate, T_1^{-1}, should not parallel the resistivity but should vary as T^3 in the low temperature limit ($T \ll \Theta$),

$$T_1^{-1} = (\Delta g^2/\tau_R)(\Theta/T)^2 \tag{5}$$

Yafet [11, 12] questioned Elliott's one parameter (Θ) model suggesting a three parameter model with separate Debye temperatures for normal (Θ_N) and co-operative Umklapp (Θ_U) processes and an adjustable term expressing the strength of the spin–lattice interaction, and he concluded [12] that T_1^{-1} should parallel resistivity with a T^5 variation at very low temperatures. Yafet [12] found

$$(T_1^{-1})_{T \gg \Theta} = \frac{1}{2\pi\hbar}\,\frac{kT}{du^2}\left\langle \int_0^{q_0} \frac{|M_{K,\,K+q}|^2}{|\nabla_K E|_\xi}\,\frac{dq}{q} \right\rangle_K \tag{6}$$

where q_0 is the maximum phonon wave number, u the velocity of sound in the metal and d the density of the metal. The incident and scattered wave vectors are represented by K and $K+q$, $|\nabla_K E|_\xi$ is the modulus of the gradient in K space of the energy at the Fermi surface. Here $M_{K,\,K+q}$ is the troublesome matrix element for spin reversal. Although (6) is written explicitly for $T > \Theta$, it can also be used [12] to find the temperature dependence of T_1^{-1} at low temperatures ($T < \Theta$). The corresponding expression is obtained by replacement of the upper limit, q_0, in the integral by $q_{\max} = kT/\hbar u$, representing the most energetic phonons excited at a particular temperature. This modification reflects the increasing importance of quantization of phonon modes at low temperatures.

In the high temperature limit ($T > \Theta$) the theories of Elliott [9] and Yafet [12] both predict $T_1^{-1} \propto T$, whilst the Bloch–Grüneisen relation (2) also predicts $\rho_L \propto T$.

Recently Helman's theory [13] of spin relaxation of conduction electrons in liquid metals has been generalized [14] to interpret CESR in solid and liquid pure metals and liquid metal alloys [18, 19].

II. ELECTRON SPIN RELAXATION STUDIES ON ALKALI METALS

A. Sodium metal

Feher and Kip [10] found $T_1 T \sim 3 \times 10^{-6}$ s K over the range 4–300 K in direct conflict with all theoretical treatments of conduction electron spin relaxation. Vescial et al. [20] redetermined T_1^{-1} and using results of Levy [21] and of Feher and Kip [10] concluded that the data supported Yafet's prediction [11] that T_1^{-1} should deviate from a linear dependence on T for $T < \Theta$, but the data did not attain a T^5 dependence even at 4 K. However, Vescial et al. [20] found good absolute agreement with relaxation rates predicted by Yafet [12] over the range 35–50 K for $\Theta_N = 250$ K and $\Theta_U = 150$ K. Devine and Dupree [15] have corrected an error in the method used by Vescial et al. [20] to extract relaxation times from observed spectra.

Kolbe [22] has remeasured T_1^{-1} in high purity bulk sodium from 4 to 77 K, finding good agreement with results of Vescial et al. [20]. A comparison of the two sets of data is shown in Fig. 1. Spin relaxation rates tend to a constant residual value $(T_1^{-1})_{\text{res}}$ at low temperatures; the data obeying a "Matthiessen" type relationship,

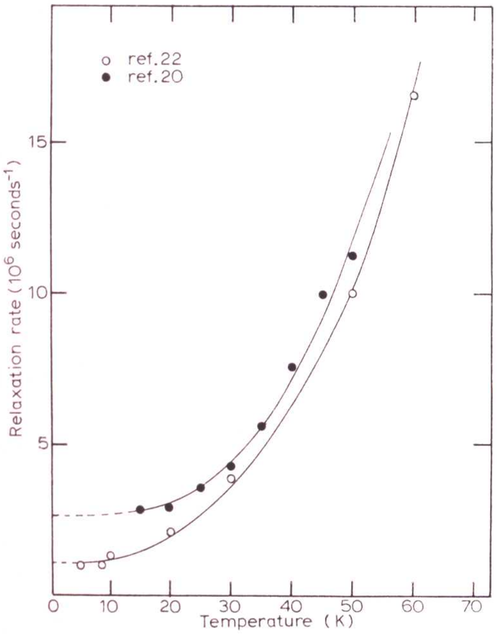

Fig. 1. Temperature dependence of the observed electron spin–lattice relaxation rate in bulk and particulate sodium metal at low temperatures.

$$(T_1^{-1})_{\text{obs}} = (T_1^{-1})_{\text{so}} + (T_1^{-1})_{\text{res}} \tag{7}$$

similar to that found in electrical resistivity measurements [6, 7]. The residual relaxation rate, which must be subtracted from $(T_1^{-1})_{\text{obs}}$, is a major source of uncertainty at low temperatures in the spin–lattice contribution $(T_1^{-1})_{\text{so}}$.

Devine and Dupree [15, 17] have measured spin relaxation rates in liquid and solid sodium and have explained their results in terms of Helman's expression [13] for the electron spin relaxation rate.

B. Potassium metal

Feher and Kip [10] reported $T_1 = 5 \times 10^{-9}$ s for potassium at 4 K, whilst Levy [21] reported a pronounced minimum in T_1 at $\sim$ 100 K. This last result, which is in direct conflict with all theoretical investigations [8, 9, 12, 14] has generally been discounted without any attempt at either explanation or presentation of new data.

Walsh et al. [23] obtained CESR from sheets of vacuum distilled potassium at 1.3 K giving $T_1 = T_2 \sim 8 \times 10^{-7}$ s. McMillan [24] produced colloidal potassium by irradiating and heat treating potassium azide and found linewidths proportional to resistivity in the range 100 to 450 K.

Devine and Helman [14] have recently calculated the spin relaxation rate of conduction electrons in solid potassium as a function of temperature. They found good agreement with the experimental data of Walsh et al. [23] down to about 40 K.

C. Lithium, rubidium and caesium metals

Conduction electron spin relaxation in bulk lithium metal is unlikely to proceed via a spin–orbit interaction and is dominated by surface and impurity effects [10].

CESR in bulk rubidium and caesium metals (< 2 K) has been reported by Walsh et al. [25] and by Schultz and Shanabarger [26].

III. EXPERIMENTAL

A. Purification of materials

1. Alkali metals

Both electron spin relaxation [10] and resistivity studies [6, 30] of bulk alkali metals have emphasized the need for high purity metals. Alkali metals (Koch-Light 99.99 %) were melted under vacuum ($\sim 10^{-2}$ torr) and forced into small diameter Pyrex tubing under dried argon. When not in use these tubes of alkali metal were stored in evacuated vessels. Final metal purification in the preparation cell involved four consecutive metal distillations under high vacuum ($\sim 10^{-5}$ torr) through 2–3 mm constrictions.

2. Solvent

HMPA (Koch-Light) was refluxed over calcium hydride under an argon atmosphere. This was followed by two vacuum distillations from sodium–potassium alloy (NaK), the first under low ($\sim 10^{-2}$ torr) vacuum, the second under high ($\sim 10^{-5}$ torr) vacuum in the sample preparation cell.

B. Sample preparation

Samples were prepared using standard high vacuum techniques, described in detail elsewhere [36].

C. ESR measurements

Electron spin resonance spectra were recorded at 9.3 GHz on a Varian V4502-E spectrometer. Magnetic field, microwave frequency and temperature were controlled and measured using standard accessories. Direct *g*-factor measurements were made consecutively on metal samples and on standard free radical samples.

IV. RESULTS

A. Sodium–HMPA solutions

ESR signals from frozen sodium–HMPA samples had line shapes approximating closely to Lorentzian. The temperature dependence of the electron resonance signal was found to agree closely with other results for bulk and particulate samples (Fig. 2).

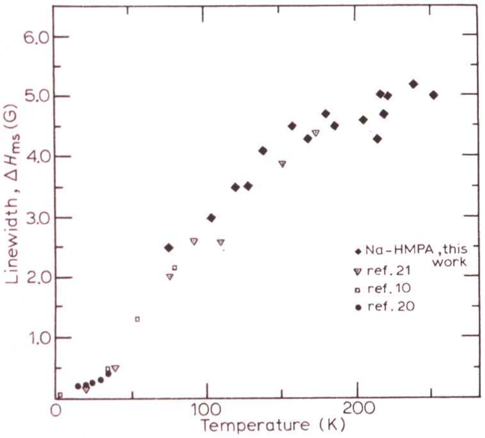

Fig. 2. Electron resonance linewidth between points of maximum slope (ΔH_{ms}) for sodium metal. Experimental data is shown for investigations which explicitly tabulate ΔH_{ms}.

We conclude that colloidal sodium particles were precipitated on freezing sodium–HMPA solutions.

B. Potassium solutions

1. Potassium–ammonia

Our results for two samples of frozen potassium–ammonia solutions are given in Fig. 3. The results were in fair agreement with those of Levy [21] and confirm the existence of a maximum linewidth at ~ 100 to 120 K.

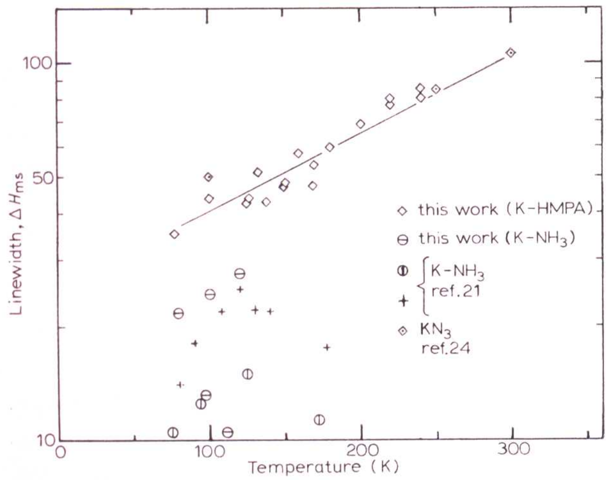

Fig. 3. Electron resonance linewidth (ΔH_{ms}) for frozen potassium–HMPA and potassium–ammonia solutions. Three points from the work of McMillan [24] on potassium azide are also included.

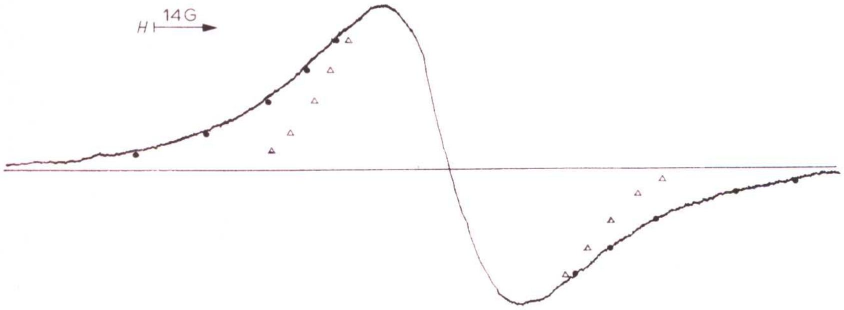

Fig. 4. A typical electron spin resonance spectrum of colloidal potassium in a frozen potassium–HMPA solution (77 K). Theoretical Gaussian (△) and Lorentzian (●) lineshapes for a resonance of this linewidth are included.

2. Potassium–HMPA

A typical electron spin resonance spectrum (Fig. 4) had a line shape approx-

TABLE 1

g-FACTORS OF CONDUCTION ELECTRONS IN POTASSIUM METAL

g-factor	Temperature (K)	Reference
1.9997 ± 0.0001	4.2	23
1.9995 ± 0.0006	< 7	26
1.9984 ± 0.0004	77	[a]
1.9982 ± 0.0006	170	[a]
1.9976 ± 0.0026	293	37
1.9982 ± 0.0005	373–723	24

[a] This work – precipitated from HMPA solutions.

imating closely to Lorentzian. The temperature dependence of the linewidth (ΔH_{ms}) is shown in Fig. 3. The results showed marked differences from those obtained from potassium–ammonia solutions; in particular there was no evidence for a maximum linewidth at $\sim$ 120 K whilst linewidths at all temperatures were generally greater than those from the corresponding ammonia system. Our g-factors (Table 1) for potassium–HMPA resonances line close to values interpolated from earlier sources at < 7 K [23, 26] and > 293 K [24] and we conclude that, although colloidal potassium particles can be precipitated from potassium–HMPA solutions, they cannot easily be precipitated from potassium–ammonia solutions. Some discussion of the species responsible for the electron spin resonance signal from frozen potassium–ammonia solutions has been presented elsewhere [27] and the subject will not be discussed further in this paper.

C. Electron spin relaxation rates

If metal particles are large compared with the skin depth then microwave penetration is incomplete, resulting in poor signal to noise ratios, whilst spin diffusion effects result in distorted resonance line shapes with only approximate (and largely untested) methods [10, 28] of extracting relaxation rates.

All spectra attributed to colloidal metal in frozen M–HMPA solutions had symmetrical Lorentzian line shapes, characteristic of metal particles small compared with the skin depth and signal/noise ratios > 15. Thus extraction of relaxation parameters was particularly simple and unambiguous. The high velocity of conduction electrons ensures motional narrowing [12] and [29]

$$T_2^{-1} = T_1^{-1} = \frac{\sqrt{3}}{2} \frac{g_{\text{e}} \mu_{\text{B}} \Delta H_{\text{ms}}}{\hbar} \tag{8}$$

where ΔH_{ms} is the width (in gauss) between points of maximum slope of the Lorentzian line and g_{e} is the electronic g-factor.

V. DISCUSSION

A. Conduction electron spin resonance in frozen potassium–HMPA solutions

In the high and intermediate temperature ranges the theories of both Yafet [12] and Elliott [9] predict that the temperature dependence of the electrical resistivity and spin relaxation rate $(T_1^{-1})_{so}$ are identical. Electron spin relaxation rates obtained from potassium–HMPA spectra are compared with resistivity data [6] for potassium in Fig. 5. The generally excellent agreement between the temperature dependence of the two processes in the range $\sim \Theta/2$ to $\sim 2\Theta$ confirm our identification of potassium CESR in frozen potassium–HMPA solutions.

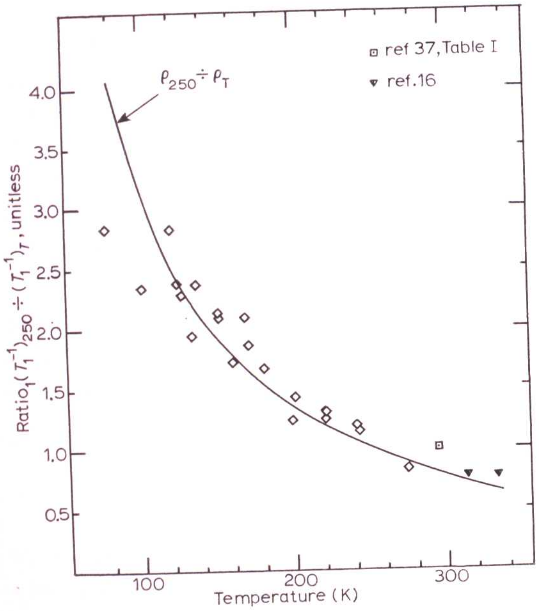

Fig. 5. Potassium CESR, a correlation of ideal resistivity (ρ_{250}/ρ_T, solid line) and spin relaxation times ($(T_1^{-1})_{250}/(T_1^{-1})_T$, points) normalized at 250 K.

B. Temperature dependence of the electron spin–lattice relaxation time

1. A Bloch–Grüneisen model for spin–phonon interactions

Spin relaxation and resistivity data for sodium metal are compared in Fig. 6. Both properties yield

$$T_1^{-1} \propto T^n \tag{9}$$

with $n = 1$ at high temperature but increasing to ~ 3 at lower temperature. A T^5

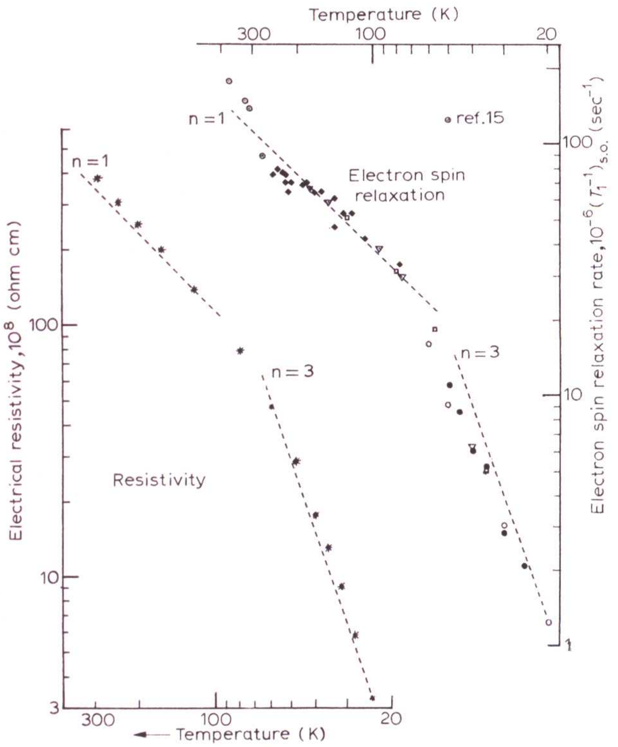

Fig. 6. Temperature dependence of the ideal electrical resistivity [32] and electron spin relaxation rates in sodium metal. Symbols defined in Figs. 1 and 2. The lines correspond to the value of the index in eqn. (9).

dependence of resistivity is found only at very low temperatures [6, 30, 31] ($<$ 15 K for sodium, $\approx$ 10 K for potassium). To date, reliable spin relaxation data in sodium and potassium extends down to about 20 K; below this temperature the dominant relaxation mechanism for conduction electrons is via spin-flip scattering by impurities in the lattice $(T_1{}^{-1})_{\text{res}}$.

The obvious similarity between electron phonon and spin–phonon scattering processes over a wide range of temperature (Fig. 6) suggests a novel method of applying the Bloch–Grüneisen model to spin relaxation data.

From (2) the reduced resistance ($r = \rho_T/\rho_\Theta$) for any metal should be a universal function of the reduced temperature [7] ($t = T/\Theta$), that is

$$r = 4t^5 \mathcal{J}_5(1/t) \tag{10}$$

Similarly, we may define a "reduced relaxation rate", α

$$\alpha = \frac{(T_1^{-1})_T}{(T_1^{-1})_\Theta} = 4t^5 \mathcal{J}_5(1/t) \tag{11}$$

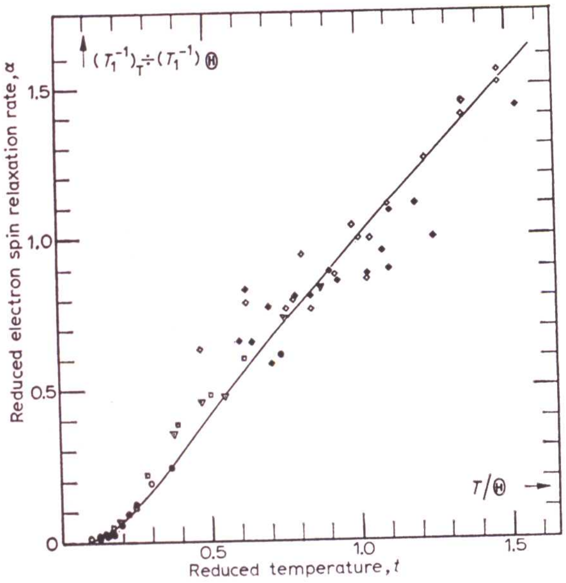

Fig. 7(a). Reduced spin relaxation rate ($\alpha = (T_1{}^{-1})_t/(T_1{}^{-1})_\Theta$) as a function of reduced temperature ($t = T/\Theta$) for sodium and potassium metals. The full curve is the Bloch–Grüneisen function (eqn. (11)). Symbols defined in Figs. 1–3, 5 and 6.

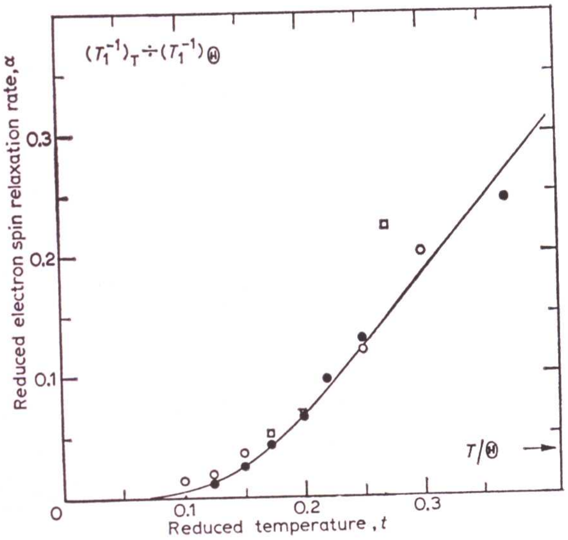

Fig. 7(b). $t \lesssim 0.4$.

for conduction electrons in a metal. Values of α, as a function of t, for both sodium and potassium metals are compared in Fig. 7(a). For these calculations a single

Debye temperature (taken from resistivity studies [6, 32]) is assumed over the entire temperature range ($\Theta_{Na} = 201$ K, $\Theta_K = 110$ K).

At high temperatures ($t \gtrapprox 0.4$) errors for electron relaxation rates are relatively large, but data from various investigations lie equally on both sides of the predicted curve (eqn. (11)). In the temperature range $t \lessapprox 0.3$ electron relaxation rates can be measured with considerably higher precision and the majority of experimental data lie close to, but above, the Bloch–Grüneisen function (Fig. 7(b)).

Kolbe's measurements [22] on bulk sodium have the lowest residual spin–lattice relaxation time and must be considered the most reliable in the low temperature ($t \lessapprox 0.3$) range. His data [22] below 40 K consistently lie above the Bloch–Grüneisen function (Fig. 7(b)).

Similarly resistivity measurements have shown that the observed resistivity falls off considerably more slowly at low temperatures than is predicted by the model [6, 8, 30, 32].

Our treatment of the reduced relaxation rate clearly highlights the similarities between the spin– and electron–phonon scattering phenomena; whilst the spin relaxation data complements the resistivity studies and allows one to investigate the origins of the deviations from the Bloch–Grüneisen model.

2. *Debye temperatures from electron spin relaxation measurements*

When discussing the temperature dependence of the resistivity, it is customary to express results in terms of a temperature dependence of the parameter Θ in (2). Applying a similar analysis to the temperature dependence of the electron spin relaxation rate, we compare Θ calculated from both relaxation and resistivity measurements for sodium (Fig. 8) and potassium (Fig. 9).

Values of Θ for sodium and potassium derived from both measurements are comparable within the limits of experimental error.

At high temperatures ($T > \Theta/4$) a single Debye temperature within the Bloch–Grüneisen model is adequate to describe the temperature dependence of $(T_1^{-1})_{so}$ and ρ_L for both metals. At low temperatures departures from the model result in a decrease in Θ.*

Bloch's [4] treatment of electronic resistance is based upon the premise of quasi-free conduction electrons interacting with the phonon modes of a Debye lattice; agreement with (10) and (11) is expected only in an ideal monovalent metal.

Ziman [3] has outlined in detail the objections to the Bloch theory; in particular deviations from the theory arise from two sources [3, 7]:

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* In sodium a martensitic transition [33] occurs below 36 K and this somewhat clouds any quantitative interpretation of data. Hasegawa [34] has suggested that such a transition may give rise to a change in the phonon spectrum of the metal lattice. However, the generality of a decreasing Θ at low temperatures cannot be in doubt (see, for example, refs. 6, 30, 32). No martensitic transformation has yet been observed in potassium.

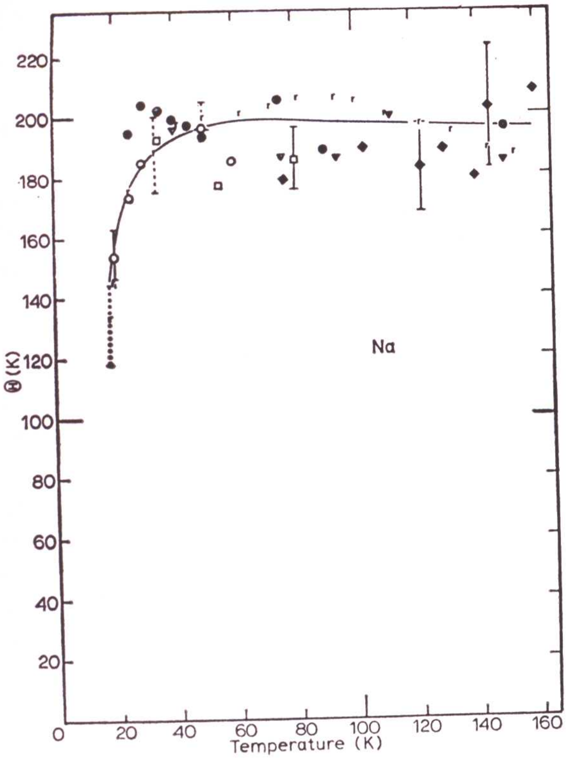

Fig. 8. Debye temperature for sodium metal obtained from resistivity [32] (r in the figure) and spin relaxation (points) measurements. The solid vertical lines represent estimated error bounds associated with the measurement of $(T_1{}^{-1})_{so}$ and the corresponding calculation of Θ. The dotted vertical error bars are taken directly from Dugdale and Gugan [32]. Symbols defined in Figs. 1, 2 and 6.

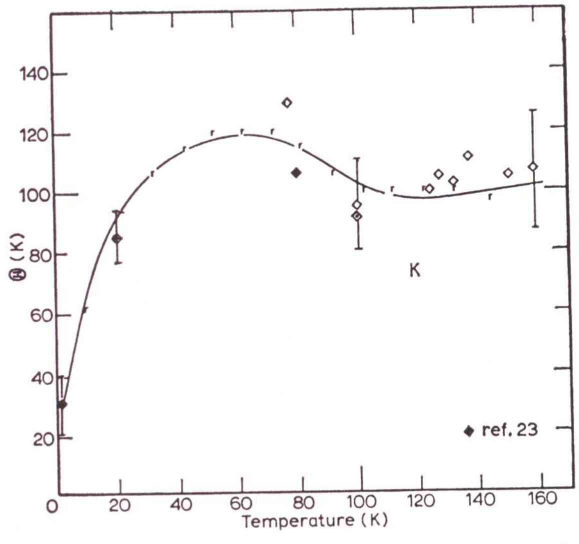

Fig. 9. Values of the Debye characteristic temperature (Θ) for potassium metal obtained from resistivity (r in figure, ref. 32) and spin relaxation (points) measurements. (Error bounds in Θ are defined in Fig. 8, no estimates are available from resistivity data.) Calculation of the Debye temperature at 1.3 K is outlined in Sect. VC. Symbols defined in Figs. 3 and 5.

(a) Lattice vibrations are not accurately described by the Debye model. In particular electron–phonon (and spin–phonon) Umklapp processes are neglected in the Bloch treatment, and these should become increasingly important at low temperatures [3, 30, 32].

(b) Lattice ions are not sufficiently "screened" by conduction electrons [7], this corresponds essentially to a breakdown of the free electron description proposed by Bloch [4].

Consequently, spin-flip scattering and resistivity processes at low temperatures become sensitive to the particular details of the phonon spectrum of the lattice and to the electronic band structure of the metal.

C. Umklapp phonon modes at 1.3 K

In the preceding sections we have shown that conduction electron spin relaxation rates can be used to estimate Debye temperatures at temperatures where

$$(T_1^{-1})_{\text{so}} \gg (T_1^{-1})_{\text{res}}$$

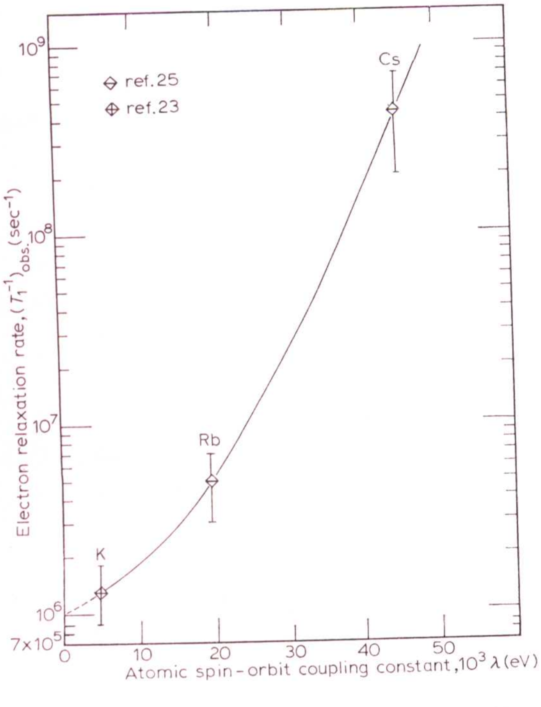

Fig. 10. Conduction electron spin relaxation rate in potassium, rubidium and caesium metals at 1.3 K.

At lower temperatures, however, $(T_1^{-1})_{\text{so}} \sim (T_1^{-1})_{\text{res}}$ and the spin–orbit relaxation makes only a minor contribution to the total spin relaxation. In the absence of an independent estimate of $(T_1^{-1})_{\text{res}}$

$$(T_1^{-1})_{\text{so}} = (T_1^{-1})_{\text{obs}} - (T_1^{-1})_{\text{res}}$$

is subject to large uncertainties. We propose that a realistic estimate of $(T_1^{-1})_{\text{res}}$ can be obtained from a comparison of total electron spin relaxation rates at 1.3 K in the series K, Rb, Cs with an extrapolation to zero spin–orbit coupling constant (Fig. 10). The extrapolation is over a very short range and yields $(T_1^{-1})_{\text{res}} = 10^6\ \text{s}^{-1}$ for potassium giving $\Theta_K = 30 \pm 10$ K. This value is included in Fig. 9 and provides strong evidence that Umklapp processes have not been frozen out in potassium at 1.3 K. Hasegawa [34] has previously shown that these cooperative phonon modes are still operative at 3 K for potassium whilst their importance down to 1 K for sodium was established by Bailyn [35].

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