Spin-Lattice Relaxation Time of Conduction Electrons in Alkali Metals: Sodium (*) (**).

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Summary. — A theory of the spin-lattice relaxation time T_1 of conduction electrons in liquid and solid alkali metals has been calculated here. The T_1 is expressed in terms of the dynamical structure factor which includes a Debye phonon spectrum. The normal and umklapp processes are calculated separately. We find that the transverse phonons contribute greatly to the umklapp process. We also have measured the temperature dependence of T_1 in sodium metal from 100 °K to 600 °K. The experimental data are in fair agreement with our theory from 13 °K to 600 °K.

1. – Introduction.

The most comprehensive treatise on the theory of spin-lattice relaxation time T_1 of conduction electrons in solid metals is that given by YAFET ([1]). He derived a spin-flip transition matrix elements of the spin-orbit interaction, with assumptions of an isotropic Debye spectrum for the phonons and two different Debye temperatures, and was able to show that the temperature dependence of T_1 is analogous to that of the resistivity as given by Gruneisen's law ([2]). For his derivation, the transition matrix must be calculated by treatment of umklapp processes and by introduction of three adjustable parameters.

([1]) Y. YAFET: *Solid State Phys.*, **14**, 1 (1963).
([2]) J. M. ZIMAN: *Proc. Roy. Soc.*, A **226**, 436 (1954).

Recently, HELMAN [3] et al. found that the difficulty in determination of the adjustable parameters and the complex calculation of the umklapp process can be overcome by expressing T_1 in terms of the dynamical structure factor of the metal which includes the actual spectrum of lattice excitations and automatically takes into account the umklapp processes. In their calculations, only the longitudinal phonons are considered. The transverse phonons which have smaller velocities of propagation are expected, however, to have more effect on the relaxation time in the umklapp process. To integrate over all directions of the phonon wave vector q, they used the phonon dispersion curve given by the Born-Von Kármán model [4]. But the Born-Von Kármán model, which is modified by multiplication of the frequencies by the dispersion factor given in the theory of the one-dimensional linear chain, neither represents the spectrum nor predicts the specific heat any better than the simple nondispersive models, i.e. the Debye and Einstein models.

In this study we have calculated the normal process and the umklapp process separately and have extended both the theoretical and experimental work to a temperature of 600 °K. We find that at very low temperatures, $T \ll \Theta_D$, where Θ_D is the Debye temperature of the lattice, the spin-lattice relaxation time T_1 should vary as T^{-5}. At high temperatures, the theory predicts the T_1 is approximately proportional to T^{-1}, however the umklapp processes cause the spin-lattice relaxation time T_1 to vary with temperature at a rate much slower than that by the normal processes. We found, from experiment, that there is a 30% discontinuity in T_1 at the melting point. This discontinuity is not compatible with the smooth theoretical curve that is drawn from solid structure factor. A theory including liquid structure factor can satisfactorily fit the experimental values from 371 °K to 600 °K.

2. – Theory of the spin-lattice relaxation time.

A theory of the spin-lattice relaxation time T_1 of conduction electrons in analogy with resistivity calculations performed by GREENE and KOHN [5] was proposed by DEVINE and HELMAN [3]. According to DEVINE and HELMAN, the spin-lattice relaxation time is given by

$$(1) \qquad \frac{1}{T_1} = \frac{mk_F}{(2\pi)^3} \int |\Gamma_{k_F\uparrow,k_F'\downarrow}|^2 S(K)\,\mathrm{d}S_k\,\mathrm{d}S_k',$$

where $\Gamma_{k_F\uparrow,k_F'\downarrow}$ is the matrix element of the spin-orbit Hamiltonian, which does not depend on the ionic co-ordinates, and where $S(q)$ is the dynamical struc-

[3] J. S. HELMAN and R. A. B. DEVINE: Phys. Rev., **4**, 1153, 1156, 4384 (1971).
[4] M. BORN and T. VON KÁRMÁN: Phys. Zeits., **13**, 297 (1912).
[5] M. P. GREENE and W. KOHN: Phys. Rev., **137**, A 513 (1965).

ture factor defined by VAN HOVE ([6]), and $\mathrm{d}S_k$, $\mathrm{d}S_k'$ is the surface integral over the Fermi surface. Here

(2)
$$\int_{\mathrm{F.S.}} \mathrm{d}S_k\,\mathrm{d}S_k' = \int \mathrm{d}^3k \int \mathrm{d}^3k'\,\delta(k-k_F)\,\delta(k'-k_F) =$$
$$= \int \mathrm{d}^3K \int \mathrm{d}^3q\,\delta(k-k_F)\,\delta(|k+q|-k_F) = \int_{q<2k_F} \mathrm{d}^3q \oint \mathrm{d}k\,,$$

where

$$\oint \mathrm{d}k = \int \mathrm{d}^3k\,\delta(k-k_F)\,\delta(|k+q|-k_F)\,.$$

The above two delta-functions each define a sphere of radius k_F with their centres displaced by a distance q. The integral $\oint \mathrm{d}k$ is a line integral over the circle of the interaction of the above two spheres. Then

(3)
$$\frac{1}{T_1} = \frac{mk_F}{(2\pi)^2}\frac{\beta}{MN} \int_{q<2k_F} |\Gamma_{k_F\uparrow,k_F'\downarrow}|^2 \sum_p \frac{(\xi_p\cdot q)^2\,\mathrm{d}^3k}{(\exp[\beta\omega_{qp}]-1)(1-\exp[-\beta\omega_{qp}])} \oint \mathrm{d}k\,,$$

where M is the ionic mass, N is the ionic density, and ξ_p is the polarization vector with their components $p = 1, 2, 3$.

The transition matrix element $M_{k',k}$ defined by YAFET ([1]) can be expanded in power series of q in the limit of small q. YAFET has shown the term that is of zeroth order in q is the matrix element of the commutator of the momentum p and the Hamiltonian H between the Kramer conjugate states, which is zero according to the time-reversal symmetry. And the term that is of first order in q is proportional to the strain. Since a uniform strain does not affect the time and space inversion properties of the periodic potential, it cannot split the two conjugate states, and its matrix element for spin reversal must vanish too. The lowest-order term of $M_{k,k'}$ is therefore proportional to q^2. The matrix element $|M_{k\uparrow,k'\downarrow}|^2$ relates to the $\Gamma_{k\uparrow,k'\downarrow}$ by

(4)
$$|M_{k\uparrow,k'\downarrow}|^2 \propto |\Gamma_{k\uparrow,k'\downarrow}|^2\,S(q)\,.$$

Since $S(q)$ is proportional to q^2 from the above argument, $\Gamma_{k\uparrow,k'\downarrow}$ is evidently proportional to the electronic scattering vector K. If the proportional constant is taken as A, eq. (3) is then reduced to

(5)
$$\frac{1}{T_1} = \frac{A^2 mk_F\beta}{(2\pi)^3 MN} \int_{q<2k_F} \sum_p \frac{(\xi_p\cdot q)^2 K^2\,\mathrm{d}^3q}{(\exp[\beta\omega_{qp}]-1)(1-\exp[-\beta\omega_{qp}])} \oint \mathrm{d}k\,.$$

For the normal process we have the electronic scattering vector K equal to the phonon wave vector q, so that only the longitudinal process can cause

([6]) L. VAN HOVE: *Phys. Rev.*, **95**, 249 (1954).

the scattering and then $(\xi \cdot q)^2 = q^2 = K^2$. Equation (5) now reduces to

$$(6) \qquad \left(\frac{1}{T_1}\right)_N = \frac{A^2 m k_F^3 \beta}{(2\pi) M N} \int_0^{2k_F} \frac{q^5 \, dq}{\cosh(\beta \omega_{qp}) - 1} \cdot$$

The phonon dispersion curve is given by the Debye model [7]. From this model we have

$$q_p = \frac{\omega_p}{v_p} \qquad \text{and} \qquad q^2 \, dq = \frac{1}{3} \sum_p \frac{\omega_p^2}{v_p^3} \, d\omega_p \,,$$

where v_p is the velocity of sound in the p-branch. Changing the integration of variable, we have

$$(7) \qquad \left(\frac{1}{T_1}\right)_N = \frac{A^2 m k_F^3}{3 \cdot 2\pi M N} \frac{\beta}{v_l^6} \int_0^{\omega_D} \frac{\omega^5 \, d\omega}{\cosh \beta \omega - 1} = \frac{A^2 m k_F^3}{3\pi M N} \frac{\beta^{-5}}{v_l^3} \mathscr{J}_5\left(\frac{\Theta_D}{T}\right),$$

where $\mathscr{J}_5(\Theta_D/T)$ is a Debye integral defined as [8]

$$(8) \qquad \mathscr{J}_n(x) = \int_0^x \frac{\exp[z] z^n \, dz}{(\exp[z] - 1)^2} \cdot$$

At low temperatures, Θ_D/T approaches infinity, and $\mathscr{J}_5$ tends to have a definite numerical value

$$(9) \qquad \mathscr{J}_5(\infty) = 3! \sum_{s=1}^{\infty} \frac{1}{s^5} \cdot$$

The relaxation is then inversely proportional to the fifth power of the temperature.

At high temperatures $\mathscr{J}_5$ behaves like

$$(10) \qquad \int_0^{\Theta_D/T} z^3 \, dz = \frac{1}{4} (\Theta_D/T)^4 \cdot$$

Then $T_1^{-1} \sim T$; this means that the scattering amplitude is proportional to the mean square thermal fluctuation of the lattice, which is proportional to the absolute temperature.

[7] C. KITTEL: Introduction to Solid State Physics, II ed. (New York, N. Y., 1956).
[8] A. H. WILSON: The Theory of Metals, II ed. (Cambridge, Mass., 1953), p. 336.

At high temperatures, because of the increase of the electronic scattering angle, the umklapp process becomes more important. A phonon of wave vector q and frequency ω could be combined by longitudinal and transverse waves such that their polarization vector ξ_p is parallel to K. The calculation of the U-process is more complicated. To obtain a simple analytical formula, let us assume that the reciprocal lattice points are distributed in spherical symmetry as proposed by ZIMAN [9]. As shown in Fig. 1, a typical geometrical configuration
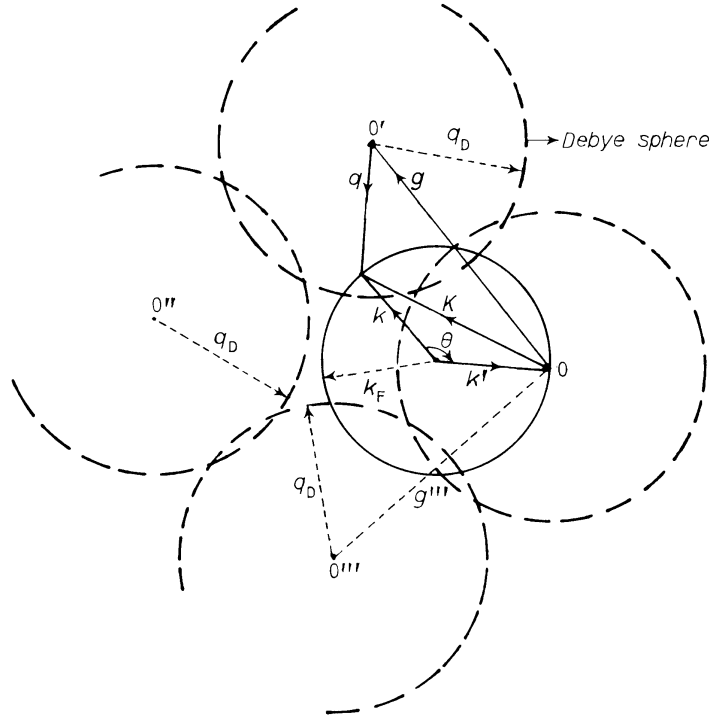

Fig. 1. – Reciprocal lattice points for representing the Debye approximation of electron-phonon U-process.

of an U-process, the surface integral $\mathrm{d}S_k \, \mathrm{d}S_{k'}$ is taken over all orientations of k and k' with assumed g to be fixed. We can obtain the same integral by averaging over all directions of g with k and k' first assumed to be fixed and then with k' allowed to vary relative to k. However, averaging over the directions of g turns into an integration over allowed values of the length of q. And, similarly, since $K^2 = 2k_F^2(1 - \cos\theta)$, $K\,\mathrm{d}K = k_F^2 \sin\theta \, \mathrm{d}\theta$, the average over the relative orientations of k and k' can be replaced if K is taken as the variable of integration. To find the limits of integration, suppose we integrate over K first. This may take any value between $g - q$ and $2k_F$. The only natural limitation of q is that the wave vector should lie inside the Debye sphere in respect to Debye model. Obviously, it may not be less than $g - 2k_F$, since

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[9] J. M. ZIMAN: *Electrons and Phonons* (Oxford, 1960), p. 362.

the value of K would then exceed its upper limit $2k_F$. With the above considerations, we have for U-process

(11) $$\left(\frac{1}{T_1}\right)_U = \frac{A^2 m k_F^3}{12\pi} \frac{\beta}{MN} \int\limits_{g-2k_F}^{q_D} q \sum_p \frac{(\xi_p \cdot q)^2}{\cosh \beta \omega_{qp} - 1} \left\{ \frac{z'}{2g} \int\limits_{g-q}^{2k_F} K^2 \, dK \right\} dq \,,$$

where z' is the number of equivalent nearest neighbors. The integration over dq has contributions from both the longitudinal and transverse phonons.

Liquid phase – Above the melting point, the dynamical structure factor can be written as

(12) $$S(q) = \int\limits_{-\infty}^{\infty} d\omega \, S(Q, \omega) \frac{\beta \omega}{\exp[\beta \omega] - 1} =$$

$$= \int d\omega \, S(q, \omega) \left(1 + \frac{\beta \omega}{2} + \ldots\right) = S^{(0)}(q) + \frac{\beta}{2} S^{(1)}(q) + \ldots \,.$$

In the long-wavelength limit, $\langle S(q) \rangle_{av}$, the average of $S(q)$ over all solid directions, is determined by average thermal dynamic properties [10]; the zeroth-order term can be written as

(13) $$S^{(0)}(0) = N \beta_c k_B T \,,$$

where β_c is the isothermal compressibility. Using a sum rule and assuming the potential being a function of particle co-ordinate only, RAHMAN *et al.* [11]
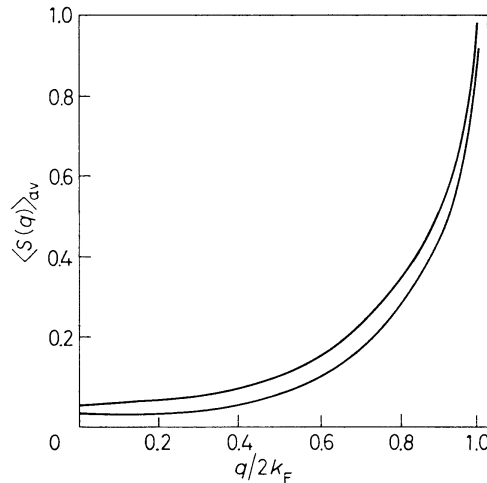

Fig. 2. – The structure factor $\langle S(q) \rangle_{av}$ for liquid sodium.

[10] A. GUINIER and G. FOUNET: *Small Angle Scattering of X-Rays* (New York, N. Y., 1955).

[11] A. RAHMAN, K. S. SINGWI and A. SJØLANDER: *Phys. Rev.*, **126**, 986 (1962).

found

(14) $$S^{(1)}(q) = \hbar q^2 / 2M \,.$$

RANDOLPH [12] had measured $S(q, \omega)$ and its moment for liquid sodium by neutron diffraction. He found that $S^{(0)}(q)$ agree with eq. (12), but found $S^{(1)}(q)$ to be two to three times greater than predicted theoretically by eq. (14). The structure factor $\langle S(q) \rangle_{\text{av}}$ for liquid sodium is plotted in Fig. 2. The spin-lattice relaxation time for normal and umklapp processes are

(15) $$\left(\frac{1}{T_1}\right)_N = \frac{A^2 m k_F^3}{3(2\pi)^2} \int\limits_0^{\omega_D} \frac{\omega^3}{v_l^4} \langle S(q) \rangle_{\text{av}} \, d\omega$$

and

(16) $$\left(\frac{1}{T_1}\right)_U = \frac{A^2 m k_F^3 z'}{36\pi g} \int\limits_{g-2k_F}^{\omega_D} \langle S(q) \rangle_{\text{av}} \, q \, [(2k_F)^3 - (g-q)^3] \, dq \,,$$

respectively. It is conceivable that the electronic and phonon states would undergo a significant change in going from a solid state to liquid state. This would show up a discontinuity in the spin-lattice relaxation time which has been checked experimentally.

3. – Experimental details.

3˙1. *Microwave apparatus.* – At temperatures above 100 °K, the measurements were performed by use of a Varian X-band homodyne reflection spectrometer. The sodium samples surrounded by a quartz Dewar were mounted in a multipurpose rectangular cavity of mode TE_{102}. A 100 kHz modulation field is used for improvement of the signal-to-noise ratio. Use of highly attenuated microwave power prevents the saturation effect. In our measurements the microwave power is attenuated 25 db down from a 400 MW klystron. Since the relaxation time is short enough above 100 °K, there is no saturation problem when this power level is used with a homodyne detector. Increasing the modulation field greatly distorts the line shape. In our system, we took the 100 kHz modulation field at a.c. 13 G so that there was no sacrifice of the signal-to-noise ratio to avoid the line broadening. The temperature variation arrangement was similar to that of WALSH, JEENER and BLOEMBERGEN [13].

[12] P. D. RANDOLPH: *Phys. Rev.*, **134**, A 1238 (1964).

[13] W. M. WALSH jr., J. JEENER and N. BLOEMBERGEN: *Phys. Rev.*, **139**, A 1338 (1965).

Either a change of the size of the resonant cavity or condensation of moisture on the cavity wall will cause drift of the base line of the recorded spectrum. This trouble can be overcome by blowing dry hot air and cold air into the cavity since the quartz Dewar temperature is below and above the room temperature, respectively. Signals proportional to the derivative of the real part of the surface impedance of the sample were obtained by the locking of the microwave klystron to the cavity resonance frequency.

3´2. *Sample preparation.* – The alkali metals, obtained commercially, are submerged under kerosene. Our sodium samples were first washed in dried petroleum ether or benzene to free them from kerosene. The petroleum ether or benzene is dried by shaking it in contact with calcium chloride. The sodium is then sealed in a pyrex glass chamber which is further connected to a high-vacuum system. The sodium purified by vacuum distillation (14) is finally driven into a receiving ampoule. This ampoule (final receiver) is connected to a capillary tube with outside diameter of 3 mm. After distillation, the liquid sodium is forced into the capillary tube by dry inert gas, and the capillary tube is then sealed off for the conduction electron spin resonance (CESR) measurement.

4. – The experimental and theoretical results and discussions.

The determination of the spin-lattice relaxation is performed by taking advantage of the fact that the transverse and longitudinal relaxation times are equal for isotropic metals. Physically, the high speed of the motion of the conduction electrons and the screening of the electron-electron interaction reduce the spin-spin interaction which tends to broaden the line. It is the absence of spin-spin interaction that is responsible for the equality of longitudinal and transverse relaxation in the isotropic metals.

The relaxation times of sodium which we measured were in the range from $1 \cdot 10^{-9}$ to $2 \cdot 10^{-8}$ s. In most of the temperature region over which we measured, the conductivity of the sample is in the region of anomalous skin effect; *i.e.* the electronic mean free path Λ is larger than the classical skin depth δ, and the sample thickness is larger than Λ. Above the melting temperatures, conduction would naturally reduce skin effect to the normal region because of decrease in the mean free path. The resonance absorption line shape for these cases has been calculated by FEHER and KIP (15) basing on the theory of DYSON (16),

(14) J. STRONG, H. V. NEHER, A. E. WHITBORD, C. H. CARTWRIGHT and R. HAYWARD: *Procedures in Experimental Physics*, Chap. 8 (Englewood Cliffs, N. J., 1938).
(15) G. FEHER and A. F. KIP: *Phys. Rev.*, **98**, 337 (1955).
(16) F. J. DYSON: *Phys. Rev.*, **98**, 349 (1955).

as is shown in Fig. 3. The line shape in the anomalous region is characterized by extreme asymmetry with A/B-ratio equal to 8.7. The full width at half-maximum of the low-field peak is given by $\Delta H = 1.42/\gamma_e\,T_1$, where γ_e is the electron gyromagnetic ratio, whereas in the normal region we have $A/B \approx$
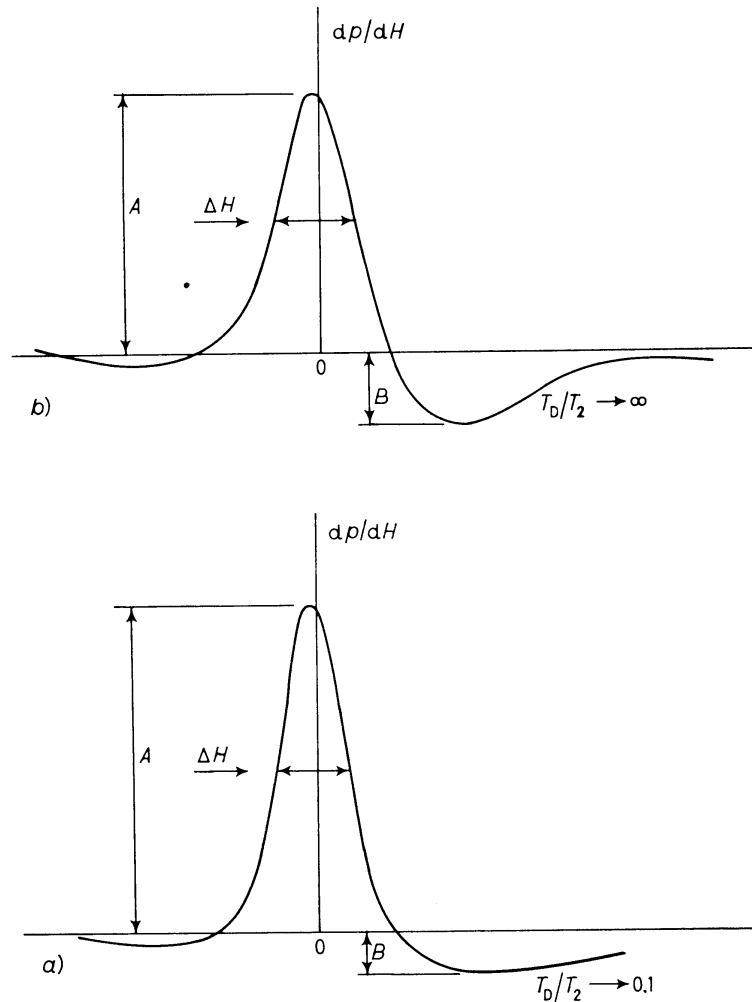

Fig. 3. – The derivative of the resonance absorption line shapes in the region of a) the anomalous skin effect $(A/B = 8.7,\ \Delta H = 1.42/\gamma_e\,T_1)$ and b) the normal classical skin effect $(A/B = 3.6,\ \Delta H = 1.12/\gamma_e\,T_1)$.

≈ 3.6 and $\Delta H = 1.12/\gamma_e\,T_1$. The relation between ΔH and T_1 for any given value of A/B-ratio is shown in Fig. 4. Our measured results are compatible with those found by VESCIAL $et\ al.$ ([17]). We have extended the measurements from the temperature of 100 °K to 600 °K. For comparison of the experimental values with the theoretical predictions, the quantity $|\Gamma_{k_F\uparrow,k'_F\downarrow}|^2$ was chosen to

([17]) F. VESCIAL, N. S. VANDER VEN and R. T. SCHUMACHER: $Phys.\ Rev.$, **134**, A 1286 (1964).

make the calculated value of $1/T_1$ at 100 °K coincide with the experimental value. A table containing parameters for calculating the spin-lattice relaxation time of sodium is shown in Table I. The sound velocities are calculated from

$$v_l = \left(\frac{C_{11} + C_{12} + 2C_{44}}{\varrho}\right)^{\frac{1}{2}} \quad \text{and} \quad v_{t_1} = \left(\frac{C_{44}}{\varrho}\right)^{\frac{1}{2}}, \quad v_{t_2} = \left(\frac{C_{11} - C_{12}}{\varrho}\right)^{\frac{1}{2}}$$
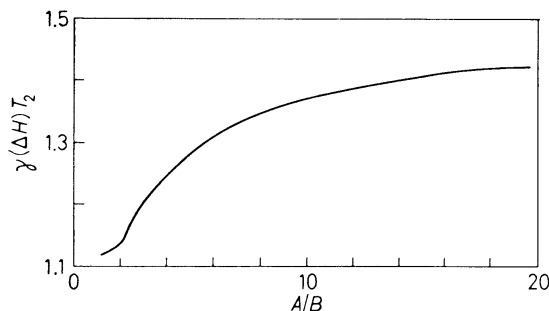

Fig. 4. – The relations between ΔH and T_1 for any given balue of A/B-ratio.

for longitudinal and transverse phonons, respectively. The temperature-dependent elastic constants were taken from the data of DIEDERICH et al. [18]. From Fig. 5 we see the theoretical curves fit the experimental data closely.

At high temperatures, the theory predicts that T_1 is approximately proportional to T^{-1}, whereas the unklapp processes cause the spin-lattice relaxation time T_1 to vary with temperature at a rate much slower than that by the normal processes. We found, from experiment, that there is a 30% discontinuity of T_1 at the melting point. This discontinuity also had been found by DEVINE and DUPREE [19]. This discontinuity is not compatible with the smooth theo-

TABLE I. – *Parameters for calculating the spin-lattice relaxation time of sodium.*

Description	Symbol	Data (sodium)
Ionic mass	M	$38.1 \cdot 10^{-24}$ g [7]
Ionic density	N	$2.5 \cdot 10^{22}$ cm^{-3}
Free-electron wave vector	k_F	$1.45 \cdot 10^7$ cm^{-1}
Radius of Debye sphere	q_D	$2.14 \cdot 10^7$ cm^{-1}
Longitudinal phonon velocity	v_l	$(14.47 - 1.04 \cdot 10^{-2} T)^{\frac{1}{2}} \cdot 10^5$ cm/s [18]
Transverse phonon velocity	v_5	$(6.6 - 8.75 \cdot 10^{-3} T)^{\frac{1}{2}} \cdot 10^5$ cm/s
	v_4	$(0.725 - 4.75 \cdot 10^{-4} T)^{\frac{1}{2}} \cdot 10^5$ cm/s
Number of equivalent nearest neighbors in the reciprocal lattice	z'	12
Reciprocal lattice constant	$g = 2\sqrt{2}\,\pi/a$	$2.08 \cdot 10^8$ cm^{-1}

[18] M. E. DIEDERICH and J. TRIVISINO: *Journ. Phys. Chem. Sol.*, **27**, 637 (1966).
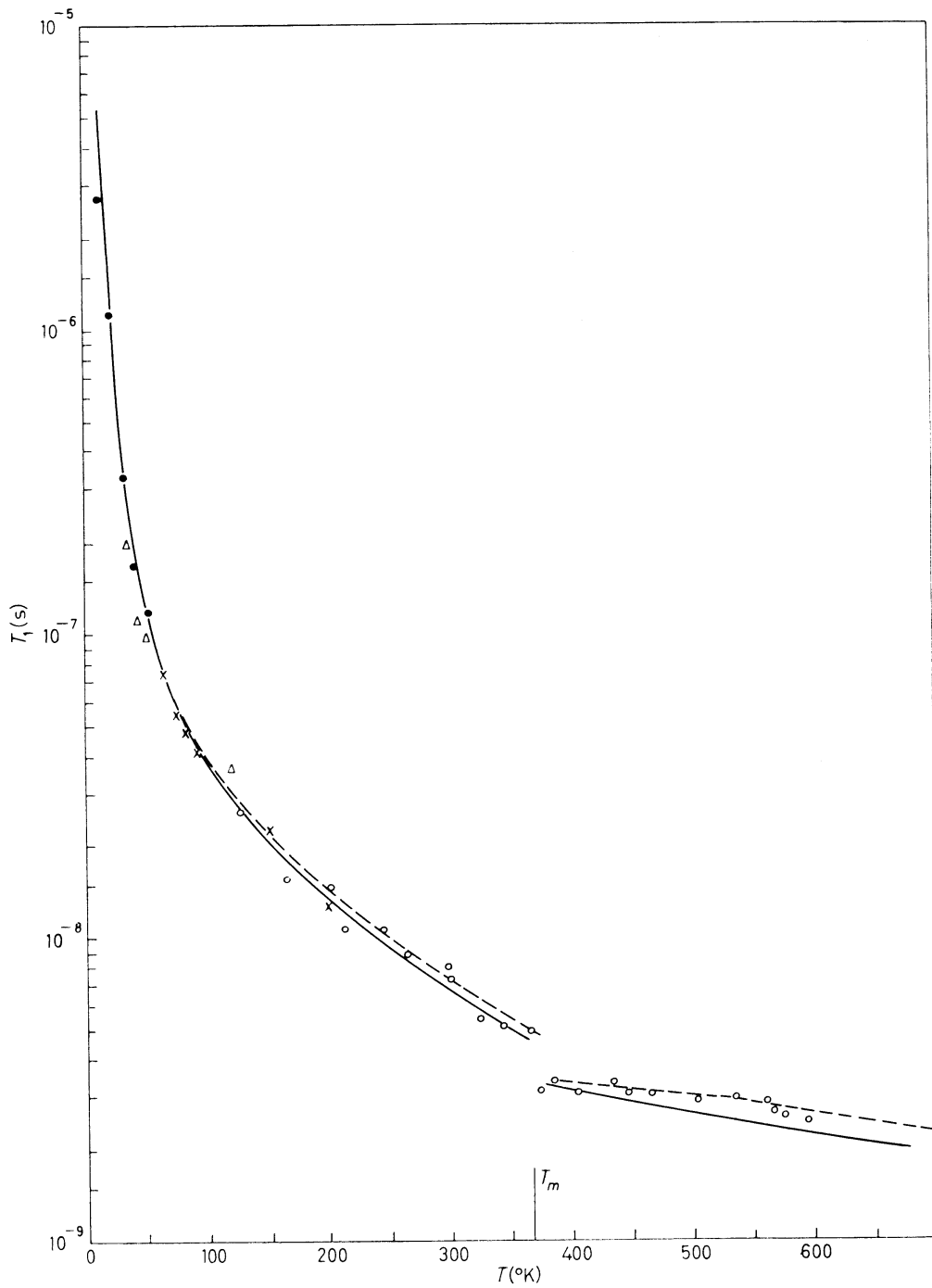[19] R. A. B. DEVINE and R. DUPREE: *Phil. Mag.*, **21**, 787 (1970).

Fig. 5. – The theoretical and experimental T_1's on a semi-logarithmic plot. ● KOLBE [20],
▲ DAW [21],   × VESCIAL et al. [17],   o our data, —— —— $N+U$ processes, ———— N-process.

[20] W. KOLBE: Phys. Rev. B, **3**, 320 (1971).
[21] G. P. DAW: Ph. D. Thesis, University of Exeter (1968) (unpublished).

retical curve that is drawn from solid structure factor. The spin-lattice relaxation time is roughly proportional to $\varkappa = \varrho v_s^4/\beta_c$, where ϱ is the density of the metal and v_s is the velocity of sound. The ratio $\varkappa$ for liquid to solid phases is 0.74, when the data given by EGELSTAFF ([22]) are used. This ratio is approximately equal to the ratio of the spin-lattice relaxation time of liquid to solid at the melting point. For liquid phase, the theoretical curve with umklapp process is drawn by first fitting both the theoretical values of normal and umklapp processes to the experimental value at the melting point, and then the spin-lattice relaxation time is calculated by use of the following formula:

$$(17) \qquad \frac{2}{T_1} = \left(\frac{1}{T_1}\right)_N + \left(\frac{1}{T_1}\right)_U .$$

We see from Fig. 5 that the theory including the liquid structure factor can satisfactorily fit the experimental values from 371 °K to 600 °K.

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([22]) P. A. EGELSTAFF: An Introduction to the Liquid State (New York, N. Y., 1967).

● RIASSUNTO (*)

Si è sviluppata una teoria relativa al tempo di rilassamento T_1 spin-reticolo degli elettroni di conduzione dei metalli alcalini liquidi e solidi. Si è espresso T_1 per mezzo del fattore dinamico di struttura che comprende uno spettro di fononi di Debye. Si calcolano separatamente i processi normali e di umklapp. Si trova che ai processi di quest'ultimo tipo contribuiscono grandemente i fononi trasversali. Si è anche misurata la dipendenza dalla temperatura, fra 100 e 600 °K, di T_1 per il sodio metallico. I dati sperimentali si accordano bene con i calcoli teorici fra 13 e 600 °K.

(*) Traduzione a cura della Redazione.

Время спин-решеточной релаксации для электронов проводимости в щелочных металлах: натрий.

Резюме (*). — Предлагается теория для времени спин-решеточной релаксации T_1 для электронов проводимости в жидких и твердых щелочных металлах. T_1 выражается через динамический структурный фактор, который включает дебаевский фононный спектр. Нормальные процессы и процессы переброса вычисляются отдельно. Мы получаем, что поперечные фононы дают существенный вклад в процессы переброса. Мы также измеряем температурную зависимость T_1 в металлическом натрии в области 100 °К до 600 °К. Экспериментальные данные хорошо согласуются с теорией в области от 13 °К до 600 °К.

(*) Переведено редакцией.